Measure of carbon dioxide using a gas sensor of a semiconductor type based on tin dioxide (SnO_2)

H. Abderrahim [1, 2, *], M. Berrebia [1], A. Hamou [2], H. Kherief [3], Y. Zanoun [2], K. Zenata [2]

[1]*Institut Hydrométéorologique de Formation et de Recherche, Département des Instruments, Oran, Algérie*
[2] *Laboratoire des Sciences des Matériaux et Environnement, Département de Physique, Université d'Oran, Algérie*
[3]*Director, CLIP and ESL Programs, York College, SC-114, NewYork, USA,*
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*Corresponding author. Tel : +213 0 41 42 12 10, E-mail: hamza_or@yahoo.fr

Abstract

To analyse and predict recent and future climate change on a global scale exchange processes of greenhouse gases-primarily carbon dioxide (CO_2)-over various ecosystems are of rising interest [1]. Monitoring the chemical composition of the atmosphere, especially CO_2, which is considered one of the main greenhouse gases, is a continuous in specialized measuring stations scattered in different places over the planet. The system proposed in this work measures carbon dioxide using a gas sensor of a semiconductor type based on tin dioxide (SnO_2) and is mainly a process of understanding the air quality to meet in one hand to a goal of miniaturization, low cost and portability, and it is a portable desktop instrument which measures carbon monoxide concentration in air, within range of 0-1200 ppm and a resolution of 1ppm. The LCD can display outputs concentration immediately in ppm in real time, every one hour, every three hours or every six hours. On the other hand to carry out either punctual measures in different places or to determine the temporal variations of a fixed site the concentration of carbon dioxide. This system offers two options for display: the first on an LCD display and the second via microcomputer via a RS232 link. Considering the importance of temperature, its measurement is therefore incorporated into the measurement entity.

Keywords: air quality, warming, carbon dioxide, measurement, sensor.

1. Introduction

Currently, a major concern of scientists is global warming, largely due to huge emissions of carbon dioxide (CO_2). Considered as one of the main greenhouse gases inducing a warming climate, CO_2 concentration in the atmosphere is under special scrutiny of many weather services in the world [2]. Suburban areas continue to grow rapidly and are potentially an important land-use category for anthropogenic for carbon dioxide emissions [3]. In Algeria, the only continuous measurement of CO_2 concentration made since 1995 is part of a program initiated by the World Meteorological Organization (WMO) in 1989 in collaboration with the

United Nations Environment Program (UNEP). It is the global program for monitoring the chemical composition of the atmosphere and of air quality based in the Hoggar, more specifically in Assekrem (50 kms north-east of Tamanrasset) [4].
The program involves capturing samples of atmospheric air at the Assekrem station twice a week, using 2 special bottles of 1.5 litres. These bottles are then sent to the NOAA laboratory (Boulder-USA) to determine concentrations of major greenhouse gases: CO_2 in ppm, CH_4 and CO in ppb [5]. This is a time-consuming process as it usually takes months to receive the results.
For gas analysis there are many principles of spectrometers that operate by taking a sample of gas to analyse and spectroscopy is then made with a duration which is generally significant [6]. Despite their good performance, these tests use devices that are bulky, fragile and very expensive, hence the alternative we propose. Taking into consideration a goal of miniaturization, low cost and portability, the analysis of various sensors led us to retain only sensors of Taguchi type. In this regard, SnO_2 is widely used as a base marerial for commercial semiconductor gas sensors for detection of toxic or explosive gases such as : H_2, C_2H_5OH, CO, NOx, CH_4, SO_2, H_2S, and CO_2 [7]. The field experience of the research group has shown that the metal oxide-based gas sensors are the best chemical sensors for long term application [8].
Semiconducting metal oxides have been known for decades to be good gas sensing materials [9].We opted for a gas sensor of a tin dioxide- based semiconductor type that is used for the measurement of CO_2, its detection principle being based on the change in electrical resistance depending on the composition of the gaseous atmosphere. In 1982, Williams [10] registered a patent for a gas sensor of potentiometric type developed from a solid electrolyte and two metallic electrodes in the same gaseous phase and different in their nature or their size.
The realized measuring system is performed primarily in an apprehension approach of air quality (we chose to focus on measurement campaigns at a fixed site) and thus follows the possible variations in the concentration of CO_2. The proposed system offers two options of display: the first on an LCD display and the second microcomputer via an RS232 link. Other functions are also integrated: view choice of the concentration of CO_2 (real time, every hour, every three hours or every six hours); recording and / or printing; an autonomous measurement with the addition of a storage battery; measurement of the ambient temperature.
The system developed and produced in the laboratory of the Instruments Department of IHFR, in collaboration with the “Laboratoire d'Etudes des Sciences des Matériaux et Environnement” of the Department of Physics of the Faculty of the University of Oran, had two distinct stages:

A / - A hardware stage which consisted in developing an electronic system capable of :
- acquiring and processing CO_2 and ambient temperature.
- processing the signals from the sensors.
- displaying on an LCD.
- displaying the data on a microcomputer via an RS232 serial link.

B / - A software stage which consisted in developing the acquisition and data processing CO_2 and ambient temperature, and graphic user interface.

2. Experimental details

2.1. The HS135 sensor:
The HS135 is a gas sensor of a semiconductor type based on tin dioxide (SnO_2), designed for the measurement of carbon dioxide CO_2. It features on a substrate of 3 mm, 4 different sensing elements; each sensing element is a thin 500 x 500μm silicon membrane [11].
It includes a ceramic substrate of a pileup of two active layers:
- a resistive metallic layer designated to act as a heating system and temperature control.

- a semi-conductive porous layer with tin oxide possibly doped, sensitive to gases in which the principle of these sensors is based on monitoring changes in electrical resistance of tin dioxide according to the surrounding gas.
- a set of electrodes.

2.1.1. Property of HS-135 air pollution sensor

Table 1. Standard work condition [12]

	Parameter name	Technical condition	Remarks
	Circuit voltage	5V	AC or DC
	Heating voltage	5V	AC orDC
	Load resistance	Can adjust	
 HS135 sensor	Heater resistance	33Ω±5%	Room temp
	Healing consumption	Less than 800 mw	
	Operating Temp	-20℃-50℃	

2.1.2. Electric parameter measurement circuit

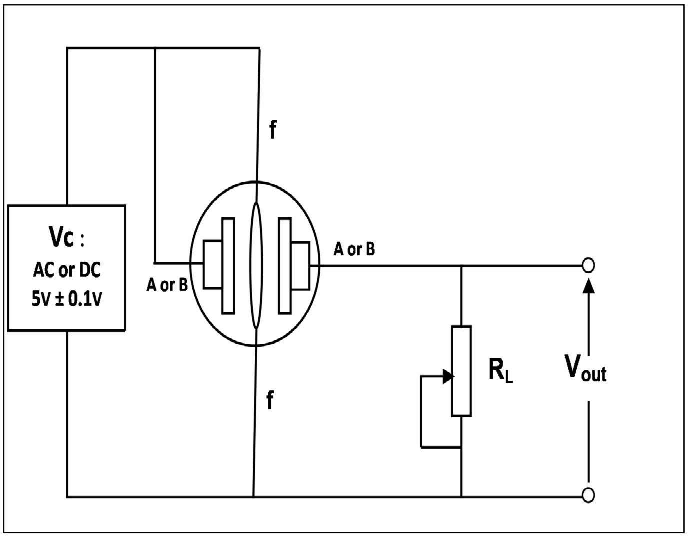

Figure 1. Standard test circuit of HS135 [12]

The gas sensors using oxide semiconductors detect a target gas from a change in electrical resistance [13]

2.1.3. Sensitivity characteristic curve of HS-135 air pollution sensor
Figure 2a given by the manufacturer represents the relation curve of V_{RL} and gas concentration at following conditions:

Temperature: 20°C, humidity: 65%RH, O_2: concentration 21%, R_L=5 kΩ
Figure 2b given by the manufacturer represents the relation between ratio R_S/R_0 and the concentration of gas at the following conditions:
Temperature: 20°C, humidity: 65% RH, R_0 at 20°C, R_S at another temperature.

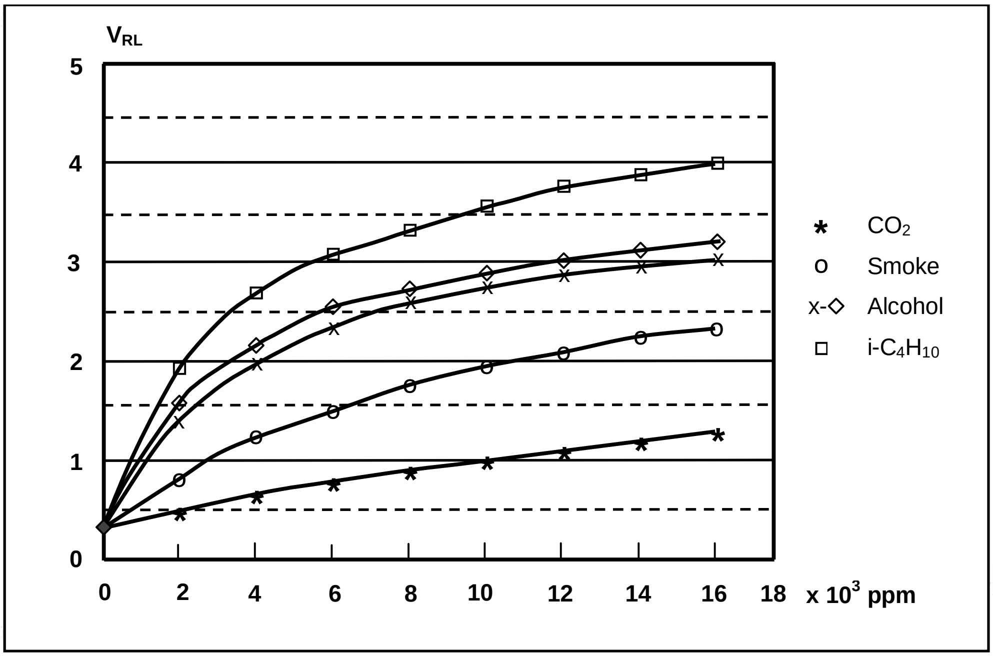

Figure 2a. Relation curve of V_{RL} and gas concentration

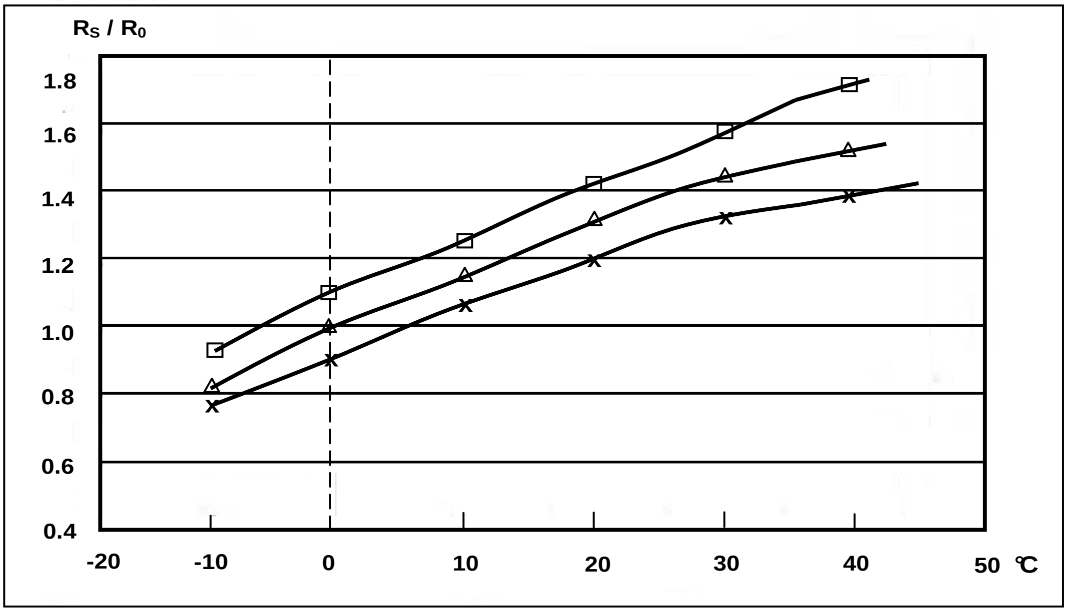

Figure 2b. Relation between surface resistance of HS-135 with environment related temperature

2.2. The operating principle of the acquisition system

Figure 3 represents the electrical diagram of the system achieved. Under the influence of the heat developed by the HS135 internal resistance and because of the choice of materials used to fabricate the electrodes of the sensor, a current is established between points A and B when CO_2 is detected. Analysis of the current allows us to determine CO_2 concentration levels [11].

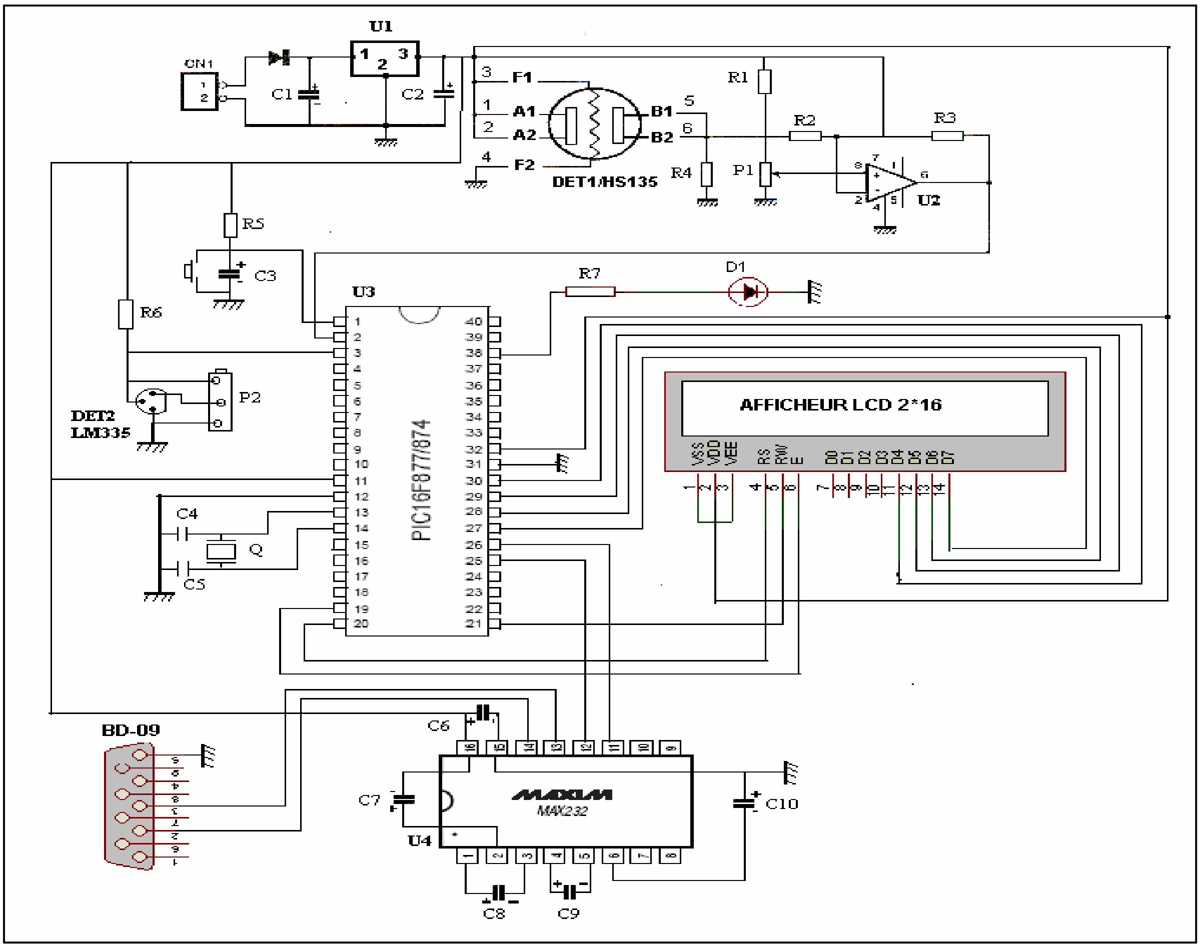

Figure 3. Electrical diagram of the system

2.2.1. CO_2 sensor conditioner

To allow a more sensitive detection of gas in our set-up, we used an adjustable resistance R4 of 10kΩ. This allows adjusting the sensitivity of the sensor according to our needs. For a maximum value of R4, the end of the scale is set at 9000 ppm, corresponding to a level of a very high gas concentration.

The voltage that appears at the terminals of R4 is then slightly amplified by the circuit U1, a “rai to rai “type amplifier which follows exactly the changes in the curve response of the sensor.

2.2.2. Temperature sensor conditioner

At room temperature, the LM335 sensor delivers a non-zero voltage. This temperature is achieved by software using the algorithm defined by: a x T = U - 2.732 where *a* is the coefficient of variation of LM335 (10mV/degree), *T* temperature in degree Kelvin, *U* the voltage output of the sensor in volt and *2732* the output voltage of the sensor at 0 ° C. The R6 Resistance allows us to regulate the operating current of the sensor (I_{max}=500 mA) and the calibration potentiometer P2.

2.2.3. Microcontroller PIC 16F877

The core of the circuit is the microcontroller. The arrangement and synchronization of all operations carried out by the microcontroller are dictated by a program stored in internal flash memory and clocked by quartz connected to pins OSC1 and OSC2 of the internal clock circuit of the PIC. The reset circuit of the microcontroller consists of a single cell RC.

2.2.4. LCD display

The transfer of results to the LCD display is realized via the D PORT in parallel access mode on 4 bits (D7-D4). The read / write (R / W) Pin receives a permanently a low level (0 V) signal defining the configuration of the LCD in writing mode. The nature of the information transferred is determined by the value of the signal transmitted to the RS pin. The validation Pin (E), activated on the falling edge receives the necessary pulses to rate and validates the transfer exchange of instruction (RS = 0) and displays a character (RS = 1).

2.2.5. Level of the RS232 serial output

The second output achieved in this assembly results from the circuit of adaptation of signals (U4) that interfaces the communication internal serial unit USART and the computer. PIC sends back numerical data from sensors on the two lines RC7 and RC6 to the computer via a DB9 connector.

2.2.6. Power supply

The power of the assembly, stabilized at 5 volts, is articulated around the LM7805 regulator (U1). The use of a heatsink has proven indispensable as a rate estimated at 800 mA is required for proper operation.

2.3. System programming

The implementation of the digital acquisition chain of data issued from the sensor HS135 and LM335 required use of the JDM program (powered directly by the microcomputer using the DB-09 connector). This was used to reside on the RAM of the PIC16F877 the programs developed.

2.4. Measurement System Calibration and Testing

2.4.1. Sensor Calibration

System calibration has been the subject of special attention. It was performed at the Assekrem (Hoggar) station at an altitude of 2710 m; it is a place free from anthropogenic pollution where the average concentration of CO_2 is around 370 ppm. After the first turning on the sensor, a 24-hour waiting period is recommended by the manufacturer to ensure its internal stability.

The operation was to adjust R4 to set the level of output voltage of the sensor to a value corresponding to a gas concentration equal to 370 ppm. This value of the voltage corresponds to the response curve of the sensor provided by the manufacturer to 0.270Volts.

2.4.2. Attempt and tests of the system at ambient temperature

We conducted two types of operations to test the performance of the system:

1. System response as a function of time: the output voltages of the HS135 to day D, then D +7 and D +15 and finally D +30.
2. System response as a function of temperature: the measurement system, placed in a thermostated chamber, is connected to the computer. At 10°C temperature the concentration of CO_2 was monitored for 1

hour. The same operation was repeated at the following temperatures: 15°C, 25°C and 35°C. 60 minutes time is elapsed between each operation to allow for thermal stabilization of the sensor.

2.4.3. Calibration of the LM335 Sensor

The potentiometer P2 was adjusted to obtain a voltage of 2.982 volts corresponding to a temperature of 25°C (a value given by the manufacturer). This calibration was carried out using a measuring device with a digital display, with a Ni-Cr temperature sensor type, in a thermostatic chamber set at 25°C.

2.5. Development tools

The development and implementation of the entity required the use of several tools:
- the C + + Builder to develop a graphical interface for the acquisition and the return of data in digital form and graph of the temperature and the CO_2 concentration.
- the CCS compiler, C compiler for programming the microcontroller (PCW version is used on Windows).
- the software programming ICPROG for the transfer of programs translated into hexadecimal code to the flash memory of the microcontroller through the selected programmer.
- the publisher of PROTEUS scheme for achieving the typons.

3. Results and discussion

The routines developed, such as the routine of analogical to digital conversion (digitization of tensions), the interpolation routine (correspondence between the digital voltage and the carbon dioxide concentration fitted by a polynomial interpolation of order 5), and the display routine (initialization and transfer of results to the LCD display), have led to the use of the Graphical User Interface (GUI) in figure 2.

The curves in figure 4 are those obtained in real time during the presentation of the system to an audience of about 20 people in a room of about 80 m^3.

In spite of the stability of the room temperature we observe a variable rate of CO_2 which reaches even 600 ppm. That is probably caused by particular conditions: openings and frequent closings of the room's door, people moving, introducing disturbances of the air mass air surrounding the sensor.
Table 1 presents the results of the statistical analysis of the tension output of the sensor HS135 at different time intervals.

Table 2. Statistical analysis of the tension sensor output

Day	T Moy (°C)	Values in millivolts			
		Mean (Y)	Sd (yEr±)	Min (Y)	Max (Y)
D	23.7	320,7	31,7	274	365
D+7	24.2	327,9	27,2	291	367
D+15	27.1	323,7	33,2	265	363
D+30	27.4	331,5	26,5	281	364

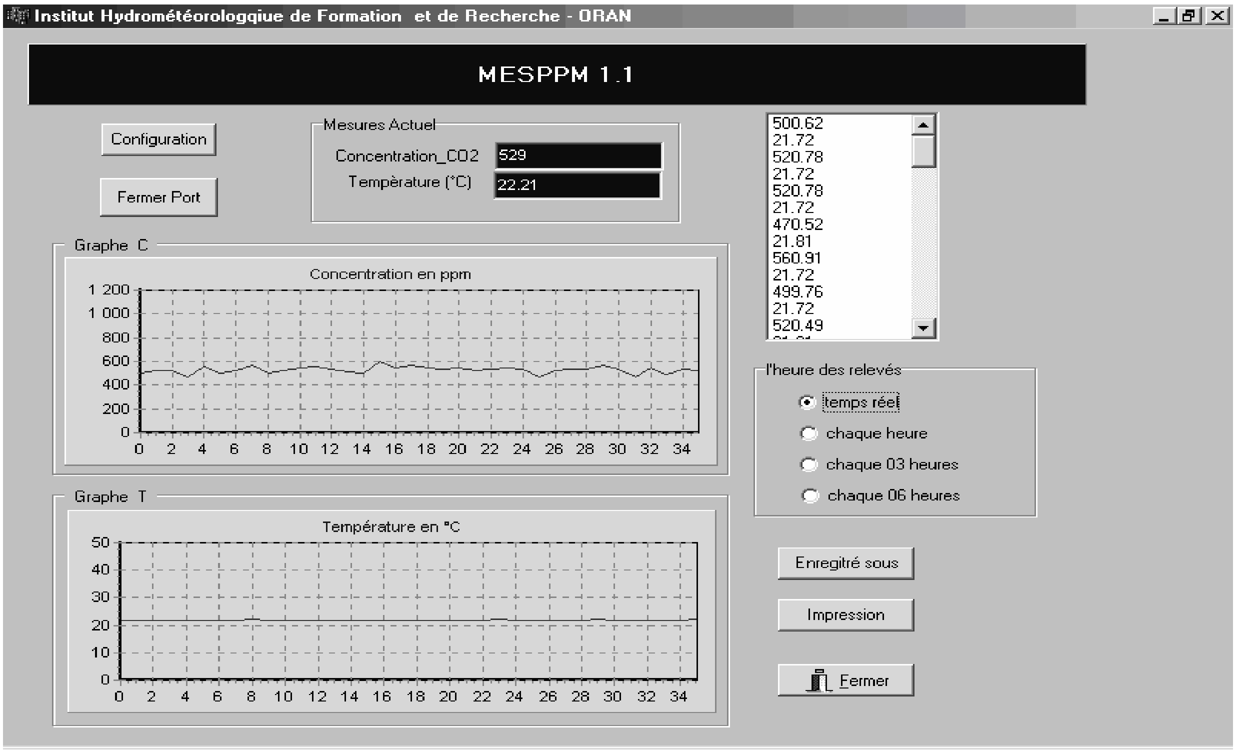

Figure 4. The Graphical User Interface (GUI) of acquisition and restitution of CO_2 data

The data analysis of table 2 shows that the sensor presents a temporal drift. We notice a variation of the output signal according to time.
The curves of the figure 5 show the evolution of the CO_2 rate at various temperatures.
We observe a variation from 418 to 426 ppm for 10,15 and 25°C, and the CO_2 rate reaches to 480 ppm at T=35°C. In both cases we notice instability of the sensor.
At T=35°C the abrupt variations of the CO_2 concentration with two peaks are certainly due to electronic noises which depend mainly on the quality of the semiconductor of the sensor.
We also notice the abrupt variations of the CO2 concentration at T = 35 ° C with two peaks which are certainly due to electronic noises which depend mainly on the quality of the semiconductor of the sensor.
Table 3 summarizes the descriptive statistics of the levels of CO_2 concentration at different temperatures.

Table 3. Statistical results

	Values in ppm				
	Mean(Y)	Sd(yEr±)	Se(yEr±)	Min(Y)	Max(Y)
10°C	421,7	1,3	0,2	419	425
15°C	421,5	2,0	0,3	418	426
25°C	422,8	1,5	0,2	420	426
35°C	432,5	7,9	1,0	423	480

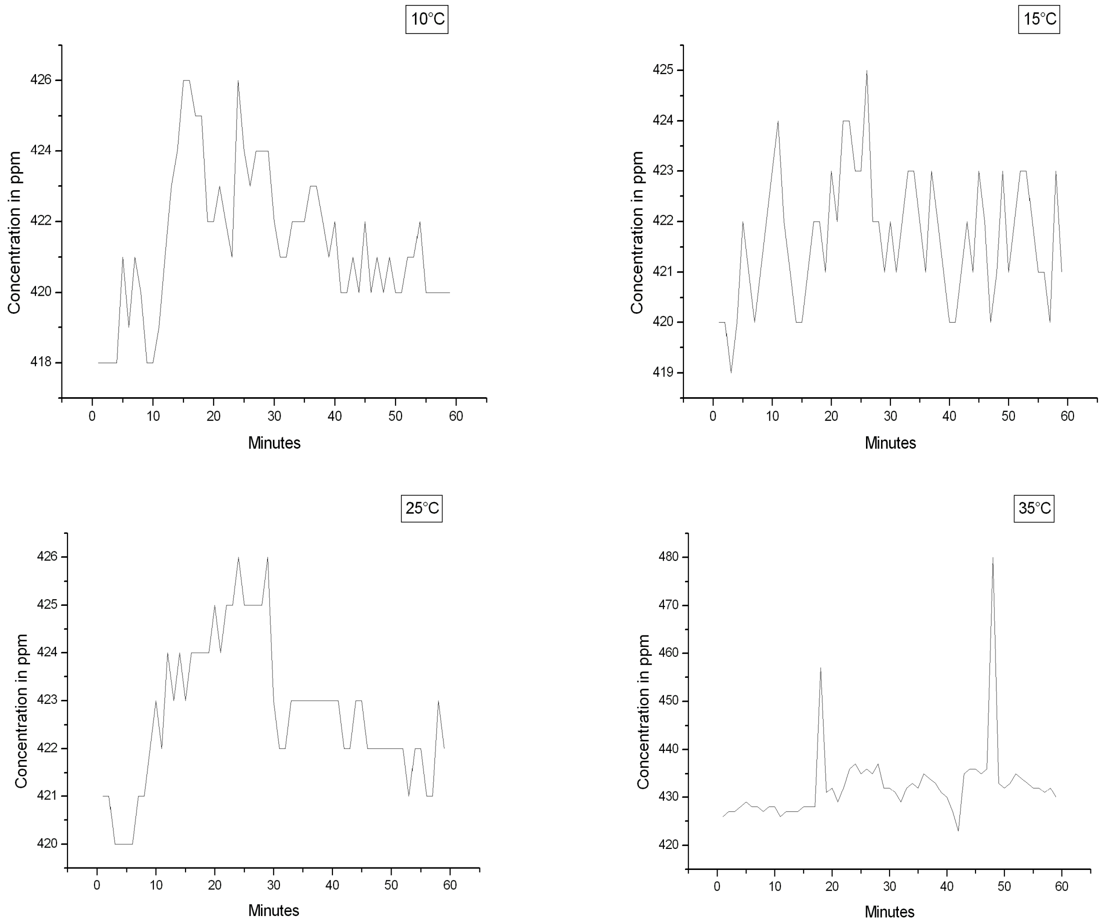

Figure 5. Variations in the rate of CO_2 as a function of temperature

The data analysis of table 3 shows the influence of the temperature on the CO_2 rate. This influence is especially marked at T=35°C where we observe a median value, reaching 480 ppm, largely higher than the cases where T=10, 15 or 25 °C. That is probably related to the intrinsic quality of the sensor with semiconductor. We notice that above 25 °C the sensor shows high deviations, reaching a value of 480 ppm at an ambient temperature of 35°C.

4. Conclusion

Intended for monitoring air quality, the digital chain for the acquisition and restitution of carbon dioxide data shows a satisfactory overall technical performance for continuous measurement by microcomputer. Its efficiency for internal use would be interesting to assess at the 0.1 % (1000 ppm) concentration level, the minimum value of measurement for indoors air. The differences observed for temperatures above 25°C for this type of sensor of semiconductor could be greatly reduced by adding a system of temperature compensation.

The gas sensor of the semiconductor type technology has significantly evolved over the last decade and progress in nanotechnology is such that we have developed this technique on a silicon substrate.

Nanoscience and Nanotechnology are, in fact, devoting great efforts to the development of novel materials for gas sensor applications [14]. Market microsensors integrated on a single substrate of a few centimeters long, a set of 256 microsensors based on the same principle are currently available on the market. Moreover, the prospect of using this type of technology and the implementation of an interactive acquisition of more developed software incorporating more processing functions (statistical calculations, drawing curves, etc...) would certainly add to its performance. This would allow measurements of the order of ppm and could be used for monitoring the evolution of CO_2.

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