Performance comparison between electrochemical and semiconductors sensors for the monitoring of O₃

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Abstract. As part of the Quality of Life and Urban Mobility (MouVIE) Chair, an individual mobile sensor
designed as an adaptable and scalable "platform" is being developed within the LATMOS (Atmospheres Space
Observations Laboratory). This sensor must contribute to answering problems related to the exposure of
15   individuals to air pollution and their impact on health. In this context, its adaptable and scalable nature will allow
the insertion of new consumer measurement components available ("low cost" micro-sensors).
In this paper we present a laboratory evaluation of commercially sensors for the monitoring of ozone (O₃). Two
type of sensors are tested: electrochemical and semiconductors sensors. Theses sensors are tested at different
temperatures, humidity and at ppb level. The voltage response and their dependence on ambiant temperature and
20   humidity are evaluated. The time drift effect on electrochemical sensors was also evaluated during 4 months of
use.

Keywords. individual mobile sensor, electrochemical sensors, semiconductors sensors, ozone (O₃)

1. Introduction

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For the monitoring of ambient air pollution, the use of low-cost portable gas and particle sensors in addition to
fixed sensors allows greater spatial coverage and is undergoing a recent and wide development. Many papers have
studied the performance of these sensors and make comparisons between different sensors technologies and
commercial sensors.

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An analysis of the performance of various commercial sensors measuring ambient gases (Aleixandre and
Geirboles, 2012) concluded that metal oxide semiconductor sensors generally have high sensitivity but have
reproducibility and stability problems. Electrochemical sensors do not have a very good sensitivity but have a
better stability. Infrared gas absorption spectra sensors are less sensitive and are not available for each target gas.
35   Finally, the Photo-ionization sensors are really sensitive, selective and reproducible, but they are only available
for a few gases.

Recently, the performance of commercial sensors (CairclipO3/NO2 and CairclipNO2) was evaluated (Spinelle et
al., 2013a, 2013b). The authors show that on the measurement range between 0-250 ppb the sensors have a good
40   response linearity, good repeatability of measurements and limited sensitivity to temperature and humidity.
However, the CairClipNO2 long-term drift and the high cross-sensitivity of these sensors for these two gases,
require simultaneous measurements with these 2 sensors. In addition the cost of these sensors (about 600 euros per
sensor) is too expensive for large-scale deployment.

45   Several papers have highlighted the important cross-sensitivity between the ozone and NO₂ electrochemical
sensors (Spinelle et al., 2014, 2015a; Pang et al., 2017; Wei et al., 2018). This lack of selectivity has been shown,
for example, in the article on the comparison of different electrochemical sensors with 3 and 4 electrodes (Spinelle
et al., 2015a): B4 type sensors (O₃-B4 and NO₂-B4) of Alphasense, City Technology model O₃ 3E1F and NO₂

3E50 sensors, and Cairpol O_3/NO_2 and NO_2 sensors. Nevertheless, these studies show that electrochemical sensors give good linear response and high precision in low concentration conditions and only slight temperature influence on voltage response. The humidity effect on electrochemical sensors also studied: an increase in tension response with an increase in humidity was highlighted (Spinelle et al., 2014, 2015a; Pang et al., 2017) and also a significant hysteresis effect (Spinelle et al., 2014, 2015a). Another study also obtained a slight slope of about 5% of the voltage response during a change in humidity of 15% to 48% (Wei et al., 2018). The drift effect on electrochemical sensors studied too (Spinelle et al. 2014, 2015a; Wei et al. 2018). A slight short term drift effect for NO_2 and O_3 sensors obtained but for the long term drift effect the NO_2 sensors seems to suffer more from long term drift than O_3 sensors (Spinelle et al. 2014, 2015a).

The performance of metal oxide sensors, particularly for ozone, evaluated also in different papers (Spinelle et al., 2016; Peterson et al. 2017; Lerner et al. 2015) and showed that the MOS sensors are generally sensitive with the temperature. The study in laboratory on MiCS-4514, MiCS-2614, MiCS-5914 sensors, and SGX sensors from Sensortech for the measurement of NO_2 and O_3 concentrations on 18-month extended tests shows significant drift and loss of accuracy after four months of use (Peterson et al., 2017). The study of wind effect on resistive metal oxide sensors in laboratory permit to conclude that it is important to take this effect into account when measuring NO_2 and O_3 concentrations (Lerner et al., 2015).

Many methods are developed to improve the performance of sensor measurements. These aims methods are to correct the effects of drifts, of the irreproducibility of individual sensors and also the effects of cross interference between NO_2 and O_3. The performance of several field calibration methods for low-cost metal oxide and electrochemical sensors are evaluated (Spinelle et al., 2015b, 2017). One study shows that supervised learning techniques can be more effective than linear or multilinear regression methods to estimate the concentration of a gas (Smith et al., 2018).

Many field campaigns using low-cost sensors have been deployed to test their performance in real conditions of use and over time. For example, the use of networks of electrochemical sensor nodes held by pedestrians and cyclists, as well as static and dense networks in the Cambridge area, in the United Kingdom, measured personal exposure to pollution in urban areas (Mead et al., 2013). Other authors have developed a system called "M-Pods" [Piedrahita et al., 2014] designed with Sensortech's commercial SGX metal oxide sensors for CO, O_3, NO_2 and VOC measurements. The laboratory and field study found that a better estimate of the amount of pollutants is achieved if the system is calibrated on the field. A large study of 132 metal oxide sensors (Sensortech MICS-2614) and 11 electrochemical ozone sensors (Alphasense) compared the performance of these two sensor technologies for 5 months (Ripoll et al., 2019). Metal oxide sensors appeared to have an upper concentration limit (about 170 $\mu g/m^3$), incompatible with peak pollution. However, the long-term performance of both types of sensor nodes was comparable to short-term (1-2 months), with no sign of drift over time. An evaluation of 24 identical AQMESH-type systems, based on electrochemical sensors from the manufacturer Alphasense, for the measurement of gaseous pollutants (CO, NO, NO_2, O_3) was carried out in the laboratory and in the field for 6 months (Castell et al., 2017). The authors show that the response of each sensor is unique and that it is not only necessary to evaluate each sensor node individually before deploying it in the field, but field calibration may be required to correct bias and measurement errors between sensor nodes.

A set of integrated ARISense sensors (Cross et al., 2017), containing electrochemical sensors were deployed over a period of about 4 months at an urban neighbourhood site in the state of Massachusetts (USA). The ARISense system uses high-dimensional model representation techniques (which take into account the effects of interference and different climatic conditions) to measure the levels of five gaseous pollutants (CO, NO, NO_2, O_3 and CO_2) and particles.

Another study characterized the performance of a portable personal air quality monitor (PAM) that incorporates electrochemical sensors of nitrogen oxides (NOx), carbon monoxide (CO), ozone (O_3) and particulate matter (PM) (Chatzidiakou et al., 2019). The authors show that with appropriate calibration and post-processing, their performance is comparable with reference instruments under various operating conditions (indoor, outdoor).

A mobile autonomous air quality sensor box (MAAQSbox) has been developed to measure air pollution (Gonzales et al., 2019). MAAQSbox contains gas and particle sensors. Field calibration was performed with MAAQSbox and the stationary air monitoring stations of the Minnesota Pollution Agency. The authors used multivariate linear regressions with temperature and relative humidity data to improve their ability to predict gas concentrations. Due to the evolution of sensor sensitivity over time, the authors concluded that it was necessary to perform periodic field calibration, in the order of 3 months, to obtain reliable results.

Recently an inter-comparison campaign during seven months with low cost air quality monitoring sensors and commercial analyzers was carried out in a High Mountain Station (Li et al., 2020). The performance of three electrochemical sensors for carbon monoxide (CO), ozone (O₃) and particle matter sensor (PM2.5) were evaluated. Using two methods, namely a multiple linear regression model and a random forest model, to minimize the influence of meteorological factors, results show it's possible to use low-cost air quality sensors in high-elevation areas.

A large-scale field deployment in the study of air quality requires low-cost and adaptable sensors. We have developed our own sensor designed as a portable and adaptive platform in order to be able to use the latest commercial micro-sensors, the most efficient and the cheapest. With our first sensor prototype (Fereira et al., 2017) we studied the behavior of several ozone-sensitive micro-sensors during 4 months of use. A cluster of ozone sensors made up of two types of micro-sensors was tested: OX-A431 electochemical ozone sensors (Alphasense Ltd., 2019) and MICS-2614 metal-oxide ozone sensors (SGX Sensortech). The calibration curves of these sensors were carried out with a response in tension (and not directly in concentration). This work aims to highlight the variations in the voltage response obtained from one sensor to another, to study their dependence on temperature and humidity as well as the time drift of the voltage response.

2. Experimental Setup

2.1 Exposure chamber

The prototype sensor, the two personal ozone monitors (POM) and the ozone generator (by corona effect) are placed in an exposure chamber (Figure 1). This exposure chamber has two entrances, one of which allows the evacuation of air, the other allows the injection of particles or gases. There is also a small metal door and two fans. By closing the door, we can create a flow of air that allows the evacuation of gases. The fans allow the gas to be homogenized and it is necessary to wait at least 30 minutes for the gas concentration to be homogeneous in the chamber.

Calibration is performed by comparing the voltage response of the micro-sensors to the measured concentration with two personal ozone monitors (POM) from 2B Technologies, previously calibrated by the manufacturer. The measuring principle is based on UV absorption at 254 nm. These instruments record concentrations over a linear dynamic range of 0 to 10 ppm and have an accuracy better than 1.5 ppb or 2% reading. The POM has been designated by the US EPA as a Federal Equivalent Method (FEM) for ozone (Federal Register, 2015). The ozone concentration with these two analyzers was read every minute (each value is the average of the measurements recorded every 10 seconds) and these measurements were compared to the voltages obtained with the micro-sensors.

Two methods of measurement have been tested to record ozone concentrations: 'continuous' measurements with a constant ozone flow at the exit of the exposure chamber and 'staggered' measurements where the exposure chamber is kept closed for 10 minutes for each concentration. Degassing was observed at each valve opening due to ozone trapped on the metal door. This degassing makes it difficult to accurately measure the concentration using the step-by-step method. So we chose the method of a "continuous" measurement with a slow and constant ozone flow coming out of the tank to have enough measuring points for each experiment. It took about an hour and a half for the concentration to decrease from 400 µg/m³ to 5 µg/m³ with this method. In order to validate our results, we repeated the experiments under the same temperature and humidity conditions several times.

2.2 Individual MouVie sensor prototype

The prototype of the ozone sensor cluster (Figure 2) is an intermediate step in the development of the individual MouVie sensor concept. The device allows the integration of a variety of environmental micro-sensors to measure physical quantities in several fields of study (gas, temperature and humidity sensors). This involves, thanks to a small device, creating an image of the environment in which an individual operates. The system consists of a network of data acquisition and pre-processing cards from micro-sensors. This network of cards is controlled by a microcontroller, at the heart of the system, who manages the different functionalities related to the acquisition and processing of the Data. This prototype made it possible to study performance and time drift in the laboratory of sensors from the same series and put in competition with other products.

The high linearity and time-limited drift of electrochemical sensors (Spinelle et al., 2014, 2015a), led us to test the performance of these sensors for use with our future mobile platform. However, these electrochemical sensors have a high cross-sensitivity with ozone and NO_2 (Spinelle et al., 2013, 2014, 2015a; Smith et al., 2018). So we choice to compare these performances with metal oxide ozone sensors whose linearity is less good but which are not very sensitive to other gases (Spinelle et al., 2016). The recording time for each measure was set at one minute, which is a compromise to meet two objectives: the recording time must make it possible to obtain a sensor response with sufficient precision to associate a given concentration value to each voltage response value obtained but calibration of sensors carried out in the laboratory must too be compatible with future field use of these sensors.

2.3 Ozone micro-sensors tested

2.3.1 Electrochemical Micro-sensors (OX-A431 Alphasense)

The electochemical sensors tested (Figure 3) are amperometric sensors (4 electrodes electrochemical sensors). these sensors include at least a measuring and a counter electrode. The gas molecules diffuse into the sensor and the measuring electrode where chemical reactions induce an electron transfer. These reactions produce an electric current proportional to the concentration. The amperometric sensors includes references electrodes, while a 4th auxiliary electrode used for correction of electrode physical changes and sensor drift. In this paper Alphasense sensors are noted "Alpha" sensors.

2.3.2 Metal-oxide sensors (MICS-2614 SGX Sensortech)

The metal oxide (MOS) semiconductors sensors (Figure 4) tested have an exposed surface film on which a target gas adsorbs, a process that causes a change in the conductivity of the film itself. The resulting signal therefore corresponds to a variable resistance according to the evolution of the conductivity. The small change in resistance measured allows to obtain the concentration of the gas at the surface.

2.4 Experimental condition sets

Table 1 gives experiments conditions. A first test period (Series 1-5) was carried out with each type of sensors (metal oxide sensor (MICS 1) and electrochemical sensors (Alpha 1)) together during two weeks in May and one day in July to test new sensors (MICS 2 and Alpha 3).
A second test period (series 6-9) was conducted over a period of three weeks in September/October with MICS 3, Alpha 2, Alpha 3 and Alpha 4 sensors. A third period tests during 2 weeks in December (Series 10-12) and a fourth test period during 3 weeks in January/February (Series 13-15) permitted to study long time drift with these electrochemical sensors.
We select a study range for ozone concentration between 0 and 320 µg/m³ and a range of 40 µg/m³ for each reported value. Thus, all the reported values for each range considered are the average of all the values of the studied range. This choice of 40 µg/m³ allows to obtain values with a good precision and is sufficient for air quality studies with the European regulation. The background gas of NO_2 measured in the laboratory most of the time is less than 2 ppb and represent only 5 % of the 40 µg/m³ range chosen. The humidity and temperature measurements obtained using the ozone sensors were checked using sensor (Testo, 2012) which measures temperature with an accuracy of 0.5 K and relative humidity with an accuracy of 3% at 298 K.

3. Results

3.1. Performance of Metal-oxide sensors (MICS-2614)

3.1.1 Short time drift study with one Metal-oxide sensor

Figure 5 shows the voltage response for the metal oxide sensor MICS 1 with series 1 (11-12 May) and 2 (15-17
May) with the same temperature and humidity conditions. We obtain a drift after a few days of use, about 5%
between the two series. The results obtained at higher temperature for series 3 (24-29-30 May) and 4 (31 May and
1-2 June), are also reported in this figure. A short time drift is too observed between series 3 and 4 and varied
about 2 to 8% on concentration range studied. The short time drift is observed previously (Spinelle et al., 2016;
Peterson et al., 2017; Piedrahita et al., 2014) but our drift is more important of previously studies. One explication
can be the time response of this type of sensors: about 5 min for MICS-2610 (Spinelle et al., 2016).
This short time drift makes it difficult to establish a temperature-induced drift (Spinelle et al., 2016) between series
1-2 and 3-4 even if a decrease in tension response with temperature is observed.

3.1.2 Comparison of the voltage response between different Metal-oxide sensors

Figure 6 shows results obtained for the voltage response with the concentration for 3 metal-oxide sensors. The
voltage response between the different metal oxide sensors studied for a given concentration range varies from 5
to 10%. This is the same order of magnitude as the voltage response variation obtained for one sensor between 0
to 200 $\mu g/m^3$. Moreover the slopes of the curves obtained for the voltage response of each sensor are also very
different and the voltage response obtained for two sensors is non-linear. This non-linear voltage response is
already described by various studies on metal oxide sensors (Spinelle et al., 2016; Ripoll et al., 2019).
We have not done enough experiments for each sensor to get accurate values (especially with MICS 2 and MICS
3) but these experiments are enough to show that the response voltage is very different between the different MICS
sensors. This different voltage response for each metal oxide sensor, highlighted previously (Peterson et al., 2017),
is certainly due to the differences between the sensors during their manufacture.

3.2 Performance of Electrochemical Micro-sensors (OX-A431)

3.2.1 Short time drift

In Figures 7 and 8, we reported the study of short time drift of Alphasense sensor Alpha 1 at room temperature
and higher temperature. There are no significant effects between series 1 and 2 after a few days of use at room
temperature. For the series 3 and 4 a slight effect can be observed between 0 to 200 $\mu g/m^3$ even if the effect is less
than 1%. Above 200 $\mu g/m^3$, the effect is greater and reaches about 2 % at 300 $\mu g/m^3$. However, the lack of
sufficient values at these concentrations does not lead to the conclusion that an effect is greater when the
concentration is higher. These results are in agreement with previous studies on the performance of electrochemical
sensors which showed that the voltage response only suffers from very small short-term drifts (Spinelle et al.,
2014, 2015a).

3.2.2 Humidity and Hysteresis effect on Voltage response

Humidity effect on electrochemical sensors, highlighted in previous studies (Mead et al., 2013; Spinelle et al.,
2014, 2015a; Pang et al., 2017; Castel et al., 2017; Wei et al., 2018), is studied with Alphasense sensors Alpha 2,
Alpha 3 and Alpha 4 during the second measurement period (September/October). The results are shown in Figure
9 (Alpha 2), Figure 10 (Alpha3) and Figure 11 (Alpha 4).
For the Alpha 2 sensor, we first compared the voltage response on series 6 to 8. The voltage response increases
with humidity, by about 1% between series 6 (H = 36%) and series 7 H = 45%) and about 3% between series 7
(H = 45%) and series 8 (H = 57%) over the entire concentration range studied. The humidity effect can be estimated
at 1% on the voltage response when humidity increases by 5% and it seems to be more important for higher
humidity. The increased in voltage response with higher humidity and non-linearity effects are consistent with the
results of the humidity effect study with the Alphasense B4 O3 model (Spinelle et al. 2014) and the manufacturer's
documentation on the O3-B4 Alphasense (Alphasense Ltd, 2019c.). Further studies will be required to confirm the
non-linearity effect on our type of sensor tested. If we compare now the results of the serie 7 with the serie 9 (about
same temperature and humidity), we obtain a lower voltage response of 1.5 to 4% over the concentration range
studied with serie 9. This result is also consistent with an earlier study (Spinelle et al., 2014), which shows that a
hysteresis effect on response can be more than 10% for the same temperature and humidity.

For the Alpha 3 sensor, the first tests were carried out in July on one day (serie 5) on the range 0-200 μg/ m³. The good agreement with the new measurements made with the serie 7 in September (Figure 10) can be noted even if the values of the serie 5 are slightly higher by 1% than those of the serie 7 on the concentration range 40-200 μg/m³. The difference of 1% of the values and the slope of the curve different between the two series can be explained perhaps by the difference of the temperature between series. The difference between the voltage response of the serie 7 (H = 45%) and the serie 8 (H = 57%) is in agreement with the results of the Alpha 2 sensor: the difference varies from 2 to 3% over the entire concentration range studied. On the other hand, the voltage response with the serie 9 is about 1.5% to 4% lower than that of the serie 7 on the concentration range studied (for the same temperature and humidity).

For the Alpha 4 sensor, we perform measurements only with series 8 (H = 47%) and 9 (H = 57%). We also obtain a difference between the series but less than that obtained with the Alpha 2 and Alpha 3 sensors: the difference due to the humidity effect is about 1% (Figure 11).

3.2.3 Temperature effect on Voltage response

Between the series (1-2) and (3-4), the relative humidity varies between 41 and 33%. But we have seen that the humidity effect is only 1% up to 200 μg/m3 in this humidity range. So we decided to compare in Figure 12 the variations of the voltage response for an electrochemical sensor (Alpha 1) tested with the values obtained at ambient temperature (Series 1-2) and at 309 K (Series 3-4). The deviation of the voltage response between the series (1-2) and (3-4) over all the concentration ranges studied (0 - 320 μg/m3) is very small: The observed deviation reaches a maximum of 3 mV (0.3 mV/°). We therefore conclude that the effect temperature on the voltage response with this sensor is very small, in agreement with the manufacturer's measurements (Alphasense Ltd., 2019a). We can also note that in the study of the sensor response of the Alphasense B4 O3 model (Spinelle et al., 2014), the effects of temperature on the sensor response were much lower than the humidity effects, which is consistent with our results.

3.2.4 Comparison between voltage response of electrochemical sensors

The results obtained for the voltage response for four electrochemical sensors tested are given in Figure 13. We choose to compare the values corresponding to a near temperature and humidity. So for the Alpha 1 sensor, we averaged all the values obtained with series 1 and 2, and for the Alpha 2 and Alpha 3 sensors, the average of all the values obtained with series 7 and 9. The maximum deviation between the voltage response values is in the order of 2 mV over the range 0-40 mV (or 0.7% in relative value). At a higher concentration, the voltage response values vary from 10 to 15 mV (3.5 to 5% in relative terms over the concentration range studied).

In Figure 14 we compare the sensitivity determined from the mean of the voltage response obtained with the four electrochemical sensors tested with that of the manufacturer. We obtained an average sensitivity value of 0.121 mV per μg and per m³ which is lower than the value of 0.179 mV per μg and per m3 derived from the curves given by the manufacturer. The difference between the two curves up to 220 μg/m³ does not exceed 5.7 mV (1.8% of the relative value). But this gap increases to 15.7 mV over the range 280-320 μg/m³ (4.9% of the relative value).

3.3 Study of the long time drift with electrochemical sensors

To evaluate the long-term drift of the voltage response, we perform measurements in two additional periods with two electrochemical sensors (Alpha 2 and Alpha 3 sensors) in December (third period) for 2 weeks (series 10-12) and in January/February (fourth period) for 3 weeks (series 13-15).

Figure 15 shows the results of the Alpha 2 sensor for series 10 to 12. The temperature is the same and the humidity conditions vary between 28 and 34%. The results obtained with these three series are very close. Similar results were obtained with the Alpha 3 sensor, which is consistent given that the tests were performed together.

The voltage response obtained with the last series (13-15) for the Alpha 2 and 3 sensors is shown respectively in Figure 16 (Alpha 2 sensor) and Figure 17 (Alpha 3 sensor). For the Alpha 2 sensor, we get similar results with the third test period with a voltage response obtained with very close for the three series. Nevertheless we obtained a greater dispersion of the measurements. In the case of the Alpha 3 sensor (Figure 17), the dispersion of the measurement is greater too especially for values above 200 μg/m³. The mean values of the voltage response between the series are close up to 200 mg/m³ but for values above 200 μg/m³ the quality of the measurements does not allow to obtain a reliable result.

In the last figure (Figure 18), we compare the average voltage response values obtained for the 4 electrochemical sensors tested during the first month of use (and shown previously in Figure 14) with the average voltage response values obtained for the 2 electrochemical sensors (Alpha2 and Alpha 3) tested for an additional 3 months. (Note:

these last 2 sensors were also used during their second month of use for NO_2 measurements not reported in this paper). The figure shows a strong drift between the values obtained during the first month of use and the 3rd and 4th months of use: the drift varied about 23.5 mV to 10 mV when concentration increase. It can also be noted that the drift increase only about 2 to 2.5 mV between the last two series of measurements. There is also a loss of

5   sensitivity on study range concentration about 50% between the first month and the last months of use: sensitivity is only about 0.082 mV per μg per m³ after the third month study. These results are consistent with the manufacturer's note (Alphasense Ltd., 2013) which specifies that the voltage response has a temporal drift over time, typically 0.5% to 2% per month, depending on the type of sensor, humidity, temperature and gas concentration.

10   The evolution of electrochemical sensor performance over time is frequently observed (Ripoll et al., 2019; WM0 No. 1215, 2018). It may be due to internal drifts during the manufacture of the sensors or the aging of the sensors. Nevertheless one study of the long-term drift of the electrochemical sensor O3-B4 of Alphasense showed it remains weak (Spinelle et al., 2014). There was certainly a premature aging of these 2 sensors for an unknown reason during use because the voltage response is similar for the 2 sensors tested together.

15   Despite the loss of sensitivity, these sensors can continue to be used under these conditions to measure air quality, but with a new calibration to associate a voltage response value with a higher concentration range (for example 80 μg/m³ and not 40 μg/m³).

4. Conclusions

20   This study shows the observed variations of the voltage response between the electrochemical sensors are lower than for metal oxide sensors. Moreover, unlike the metal-oxide semiconductors sensors studied, the results obtained with electrochemical sensors are not very sensitive to temperature variations and to short-term drift.

The study of the effect of humidity on the response of electrochemical sensors shows a shift with humidity and especially an effect of hysteresis which requires recalibration in case of significant variation of humidity.

The long-term drift study with 2 electrochemical sensors tested shows a significant drift between 3 to 8% over the
25   concentration range after 3 months of use which is certainly due to premature aging of the sensors. However, a new calibration of these sensors is sufficient to study air quality with a concentration range of approximately 60-80 μg/m³.

Finally even with a low sensitivity (response of the voltage per μg and per m³) obtained for this type of sensor (ie 0.121 mV per μg/m³), the measurements precision is enough for air quality studies with European regulation
30   (European directive on air quality 2008/50/EC for Ozone: 120 μg/m³ on average period of 8 hours and during 25 days over 3 years).

So for ozone air quality studies, given the linearity properties, the reproducibility of the measurements between the different sensors and the low dependence on temperature variations, we recommend the use of electrochemical sensors. However the high cross-sensitivity between ozone and NO_2 for these sensors (Spinelle et al., 2013, 2014,
35   2015a), (Smith et al., 2018) requires simultaneous measurements of ozone and NO_2 in the field using O_3/NO_2 sensors (Alphasense Ltd., 2019a) and NO_2 (Alphasense Ltd., 2019b). This NO_2 sensor uses an ozone filter to measure only NO_2 gas. We recommend too a new calibration of the electrochemical micro-sensors individually after approximately one or two months of continuous use to avoid erroneous measurements due to possible problems of premature aging of the sensors.

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Competing interests. The authors declare that they have no conflict of interest.

Data availability. All data can be provided by the corresponding author upon request

Number of Series	Number of days	Number Experimental tests	Number values on range 0-40 μg/m³ to 280-320 μg/m³	T (K)	H (%)
Serie1 (MICS1-Alpha1)	2	4	140 to 10	301K(1)	41(2)
Serie2 (MICS1-Alpha1)	3	4	120 to 10	302K(1)	38(2)
Serie3 (MICS1-Alpha1)	3	3	95 to 8	309K(1)	34(2)
Serie4 (MICS1-Alpha1)	3	3	100 to 10	309K(1)	33(2)
Serie5(MICS2-Alpha3)	1	2	85 to 8	303K(1)	38(2)
Serie6 (MICS3-Alpha2)	2	3	70 to 8	300K(1)	36(2)
Serie7 (Alpha2-Alpha3)	2	5	120 to 18	297K(1)	45(5)
Serie8 (Alpha2-Alpha3-Alpha4)	1	2	50 to 8	297,5K(0,5)	57(2)
Serie9 (Alpha2-Alpha3-Alpha4)	2	3	60 to 14	296,5K(0,5)	47(2)
Serie10 (Alpha2-Alpha3)	2	4	170 To 15	297,0K(0,5)	28(2)
Serie11 (Alpha2-Alpha3)	2	3	140 to 14	297,0K(0,5)	30(1)
Serie12 (Alpha2-Alpha3)	3	6	250 to 20	296,5K(0,5)	34(3)
Serie13 (Alpha2-Alpha3)	2	2	70 to 8	294K(1)	40(2)
Serie14 (Alpha2-Alpha3)	6	6	250 to 20	296,0K(0,5)	39(2)
Serie15 (Alpha2-Alpha3)	3	3	85 to 18	296K(1)	28(2)

Table 1: Experimental conditions

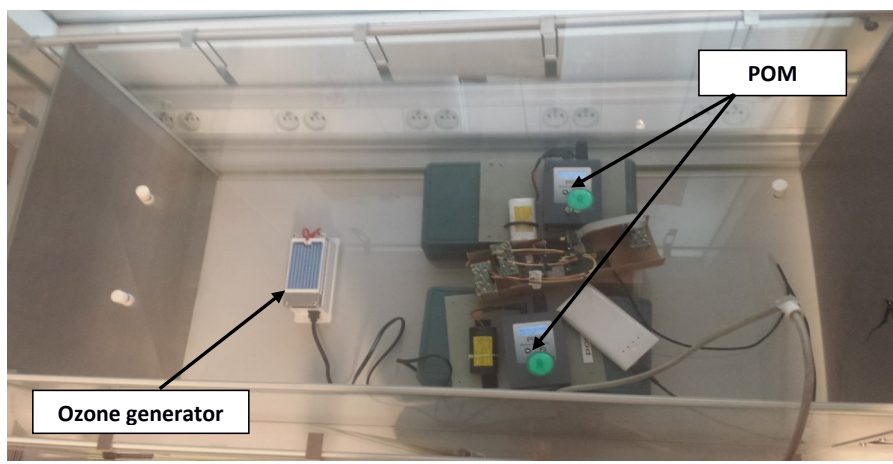



Figure 1: Exposure chamber

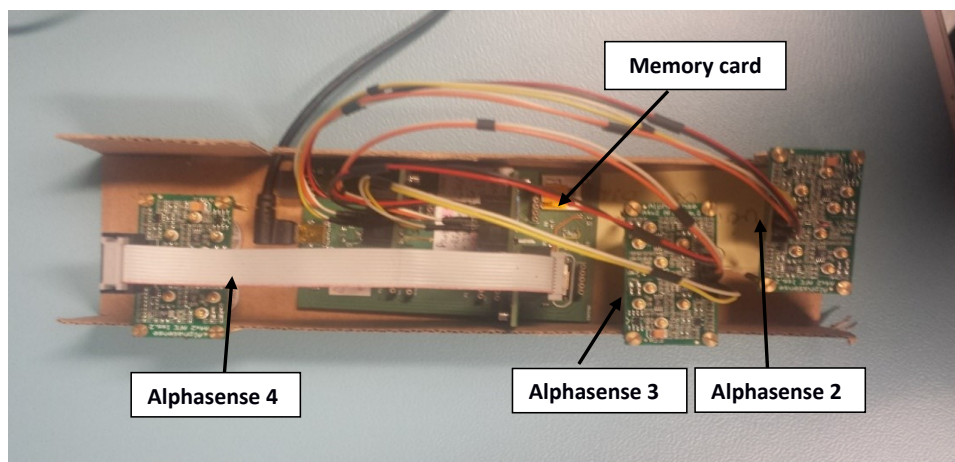



Figure 2: Cluster of sensors ozone prototype

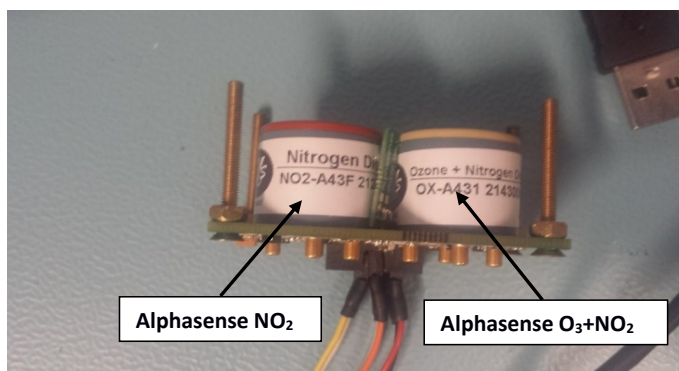



Figure 3: OX-A431 Alphasense

Figure 4: Metal oxide semiconductors sensor MICS-2614

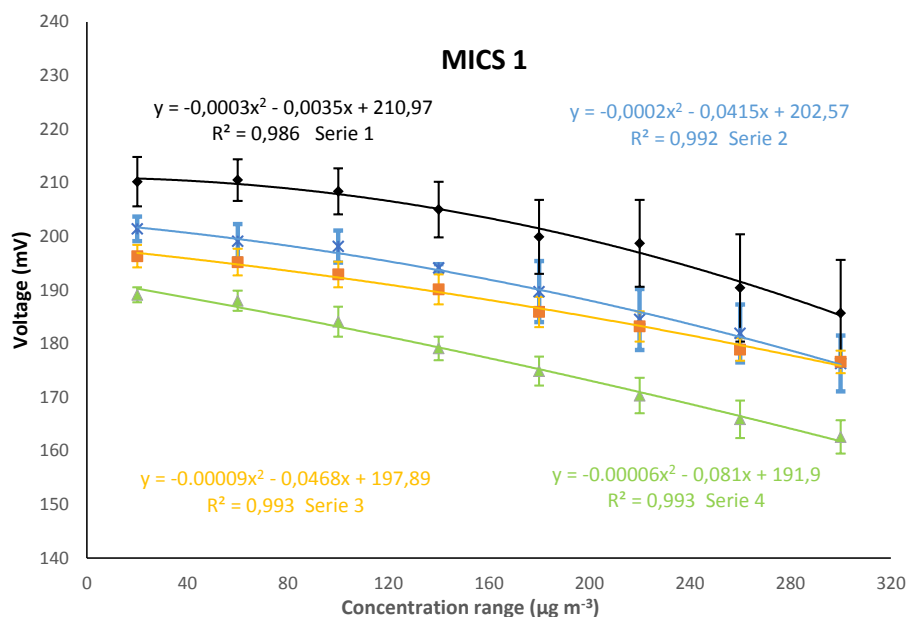



Figure 5: Short time drift and temperature effect of MICS 1 sensor

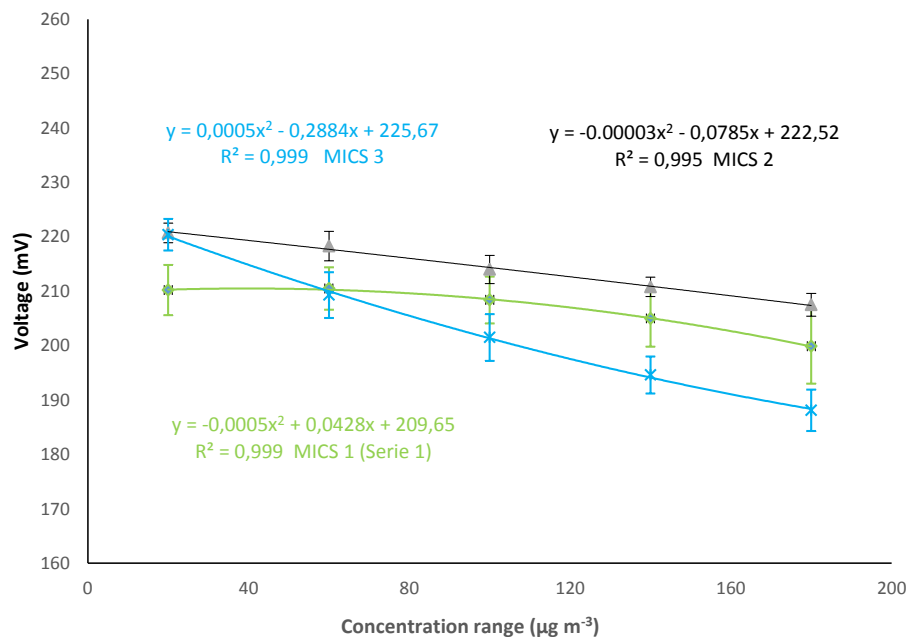



Figure 6: Voltage response with the concentration for 3 MICS sensors at room temperature
Note: For the MiCS 1 we represent the voltage response for the Serie 1.

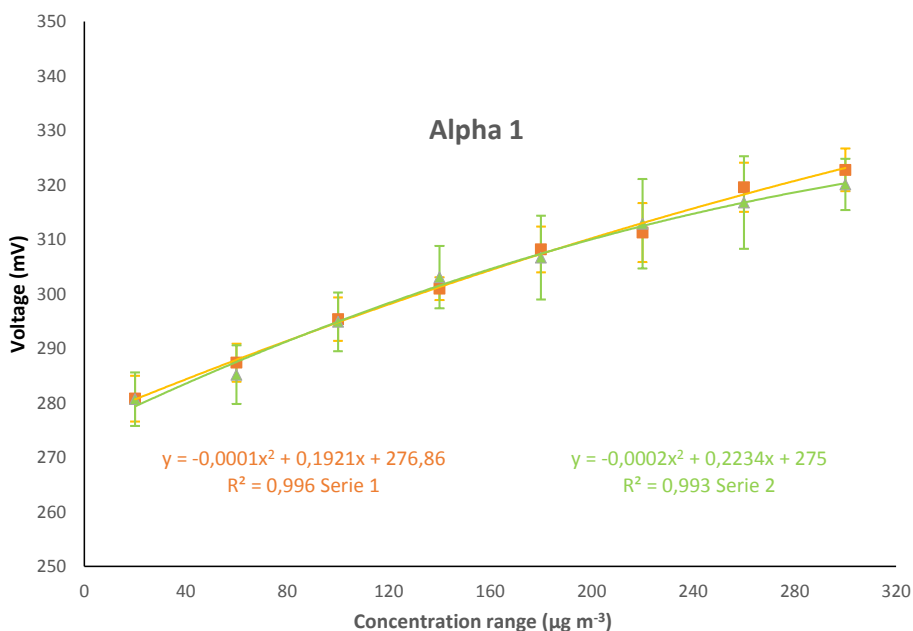



Figure 7: Short time drift of Alpha 1 sensor at room temperature

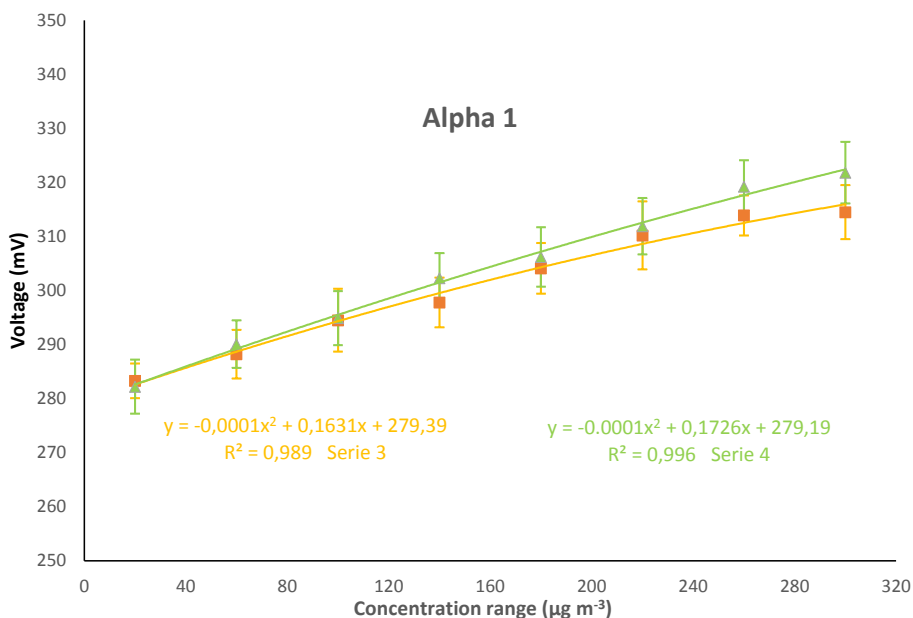



Figure 8: Short time drift of Alpha 1 sensor at T= 309K

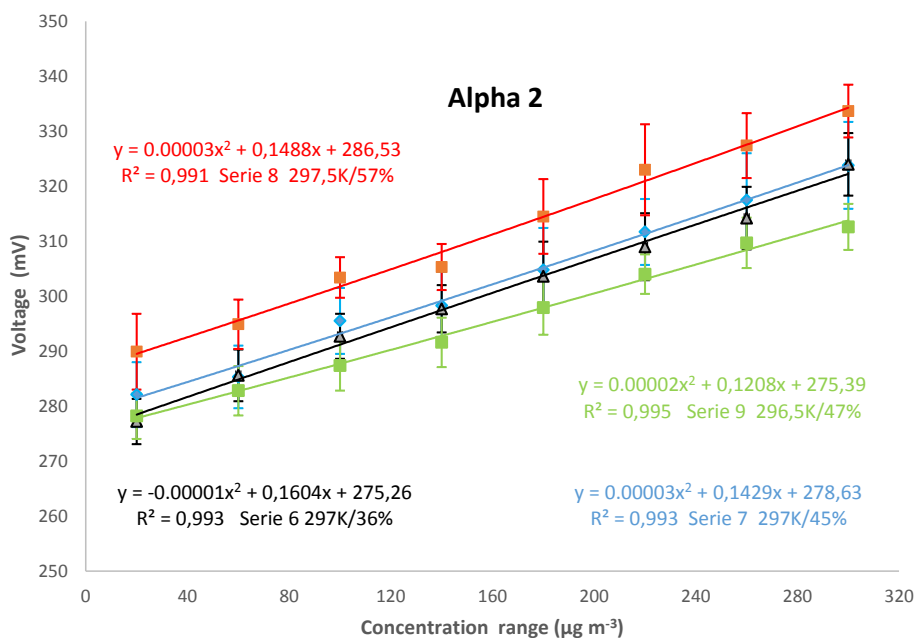
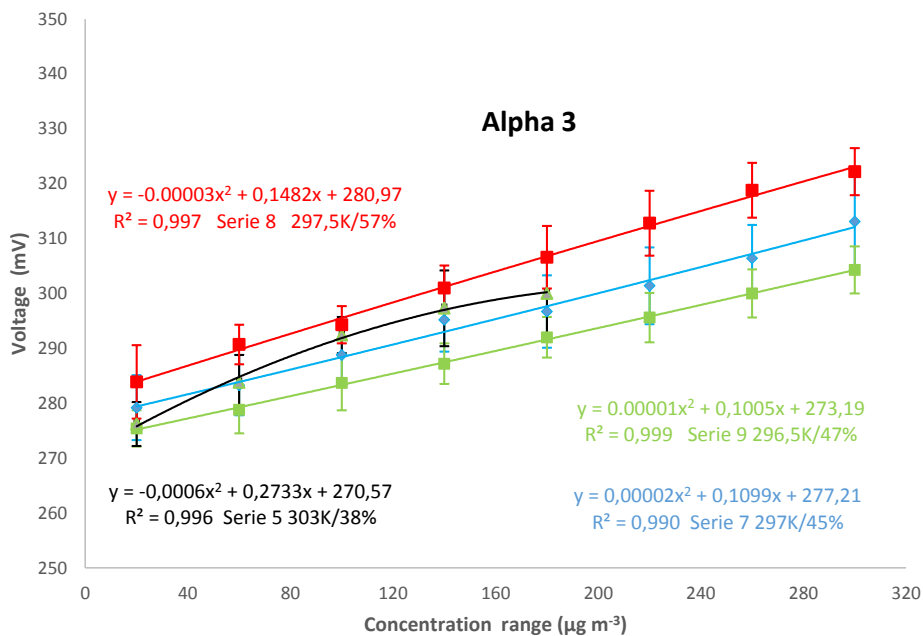



Figure 9: Humidity effect on Alpha 2 sensor at room temperature (Second Period of tests)

5   **Figure 10: Humidity effect on Alpha 3 sensor at room temperature (First and Second Period of tests)**

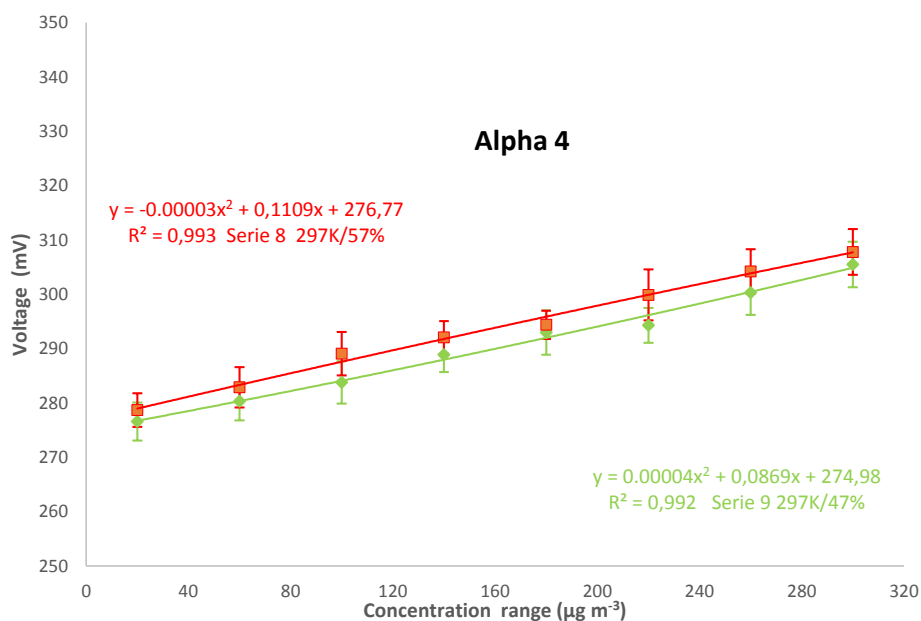
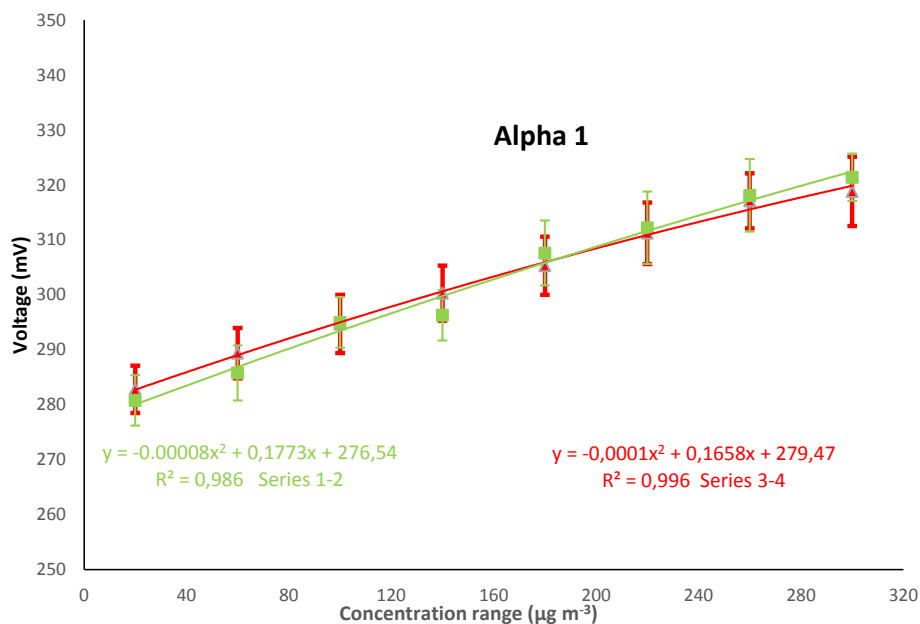



Figure 11: Humidity effect on Alpha 4 sensor at room temperature (Second Period of tests)

5   **Figure 12: Variation of the voltage of the Alpha 1 sensor according concentration for room temperature and T = 309 K.**

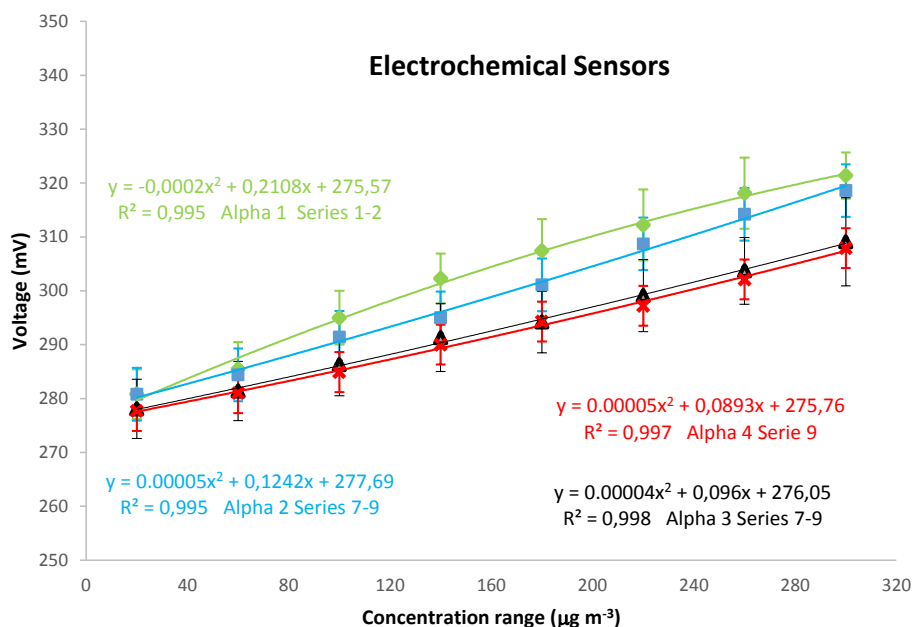



Figure 13: Voltage response with the concentration for 4 Electrochemical sensors of Alphasense at room temperature

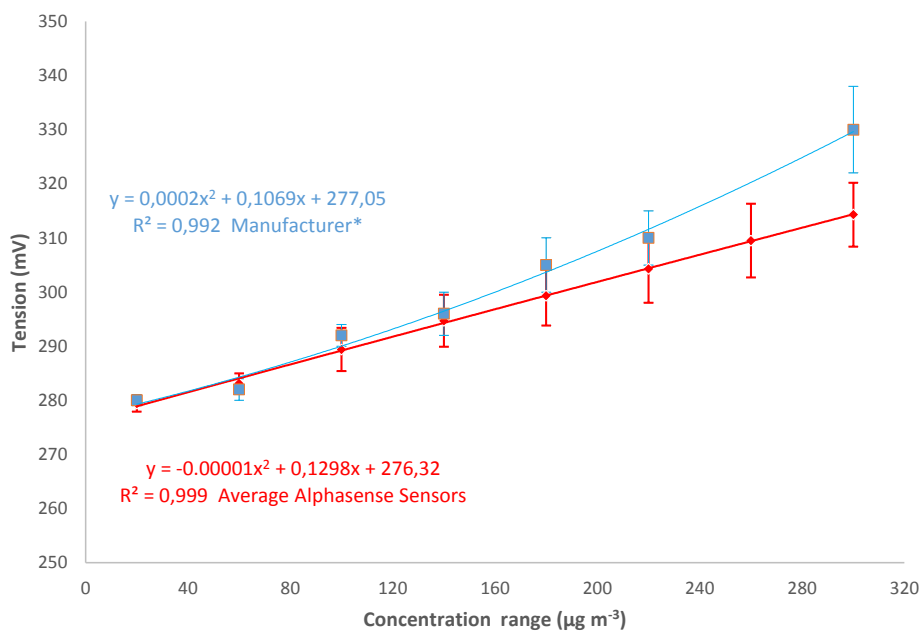



Figure 14: Comparison between average sensitivity of Electrochemical sensors and the manufacturer values
*curve obtained with technical specification OX-A431

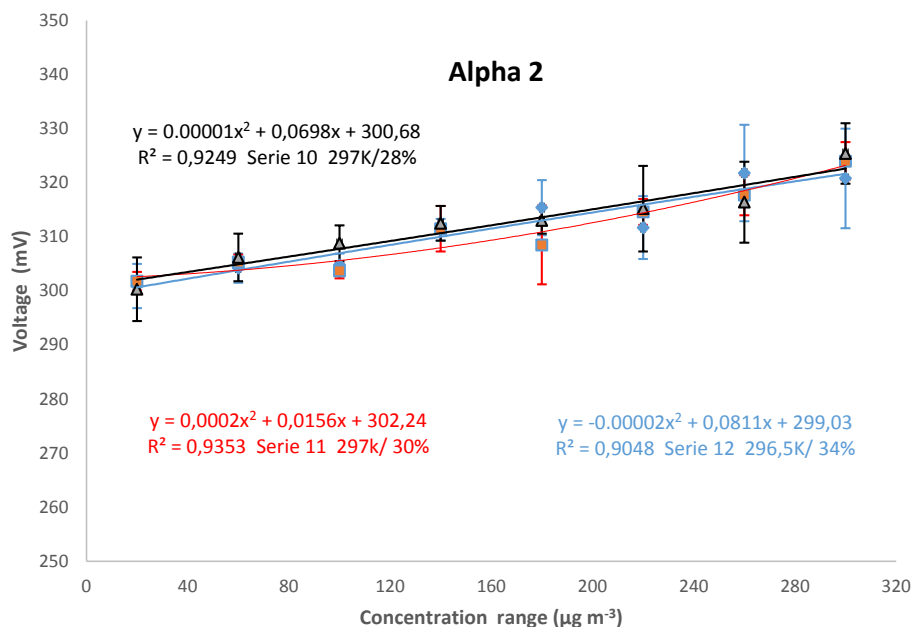
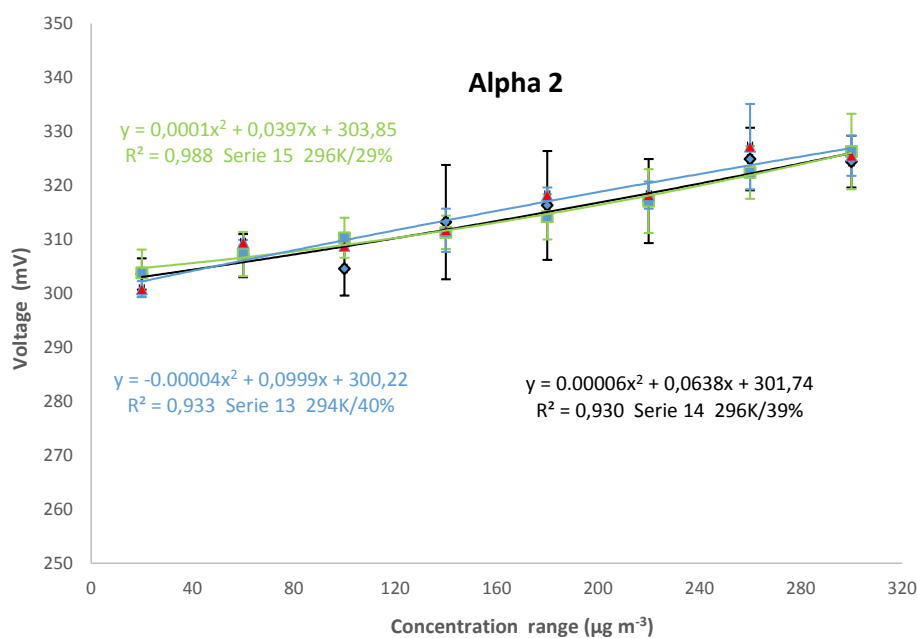



Figure 15: Alpha 2 sensor (third Period of tests)

5   **Figure 16: Alpha 2 sensor (Fourth Period of tests).**

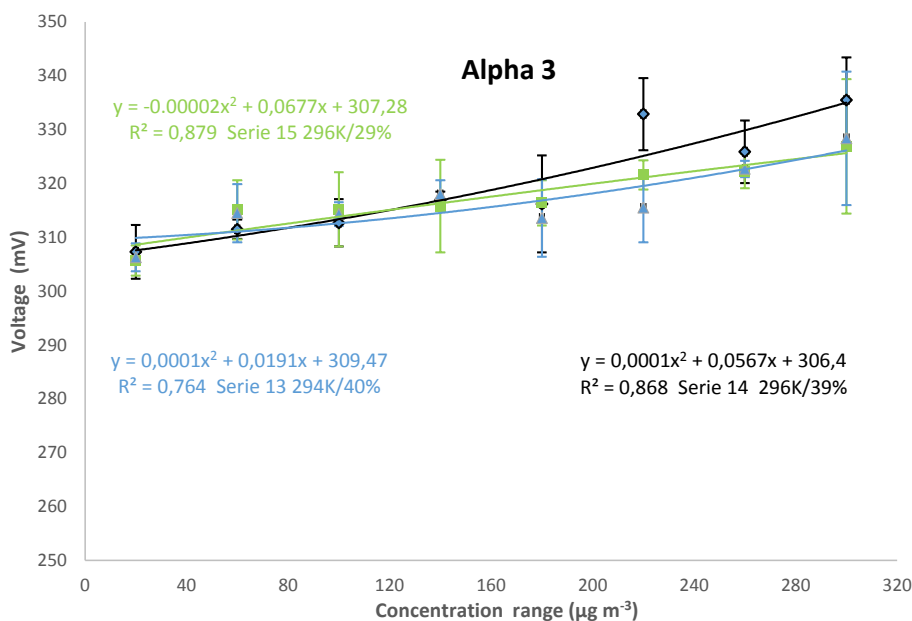



Figure 17: Alpha 3 sensor (Fourth Period of tests).

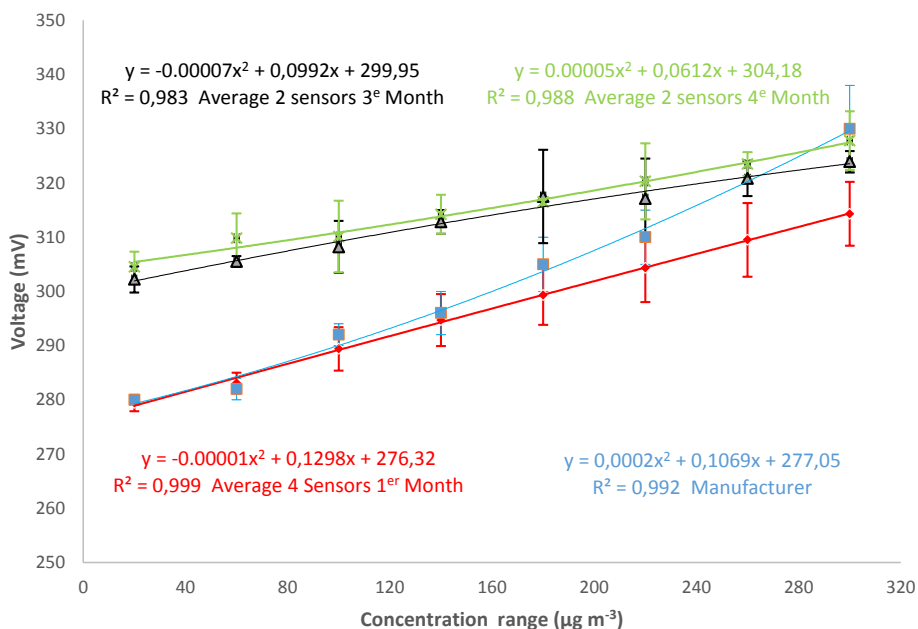



Figure 18: Long time drift of the sensors response with time for Electrochemical sensors