CALIBRATION OF SMALL RESISTIVE COMMERCIAL SENSORS TO MEASURE OZONE WITH THE INTERFERENCE OF TEMPERATURE AND HUMIDITY

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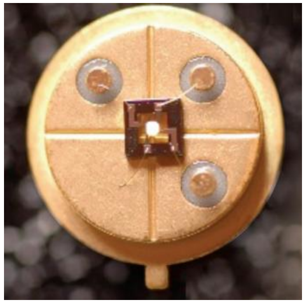
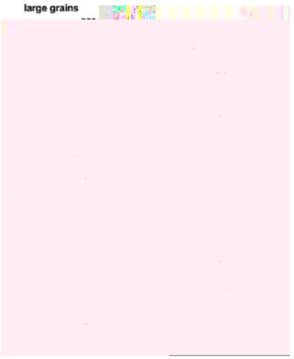
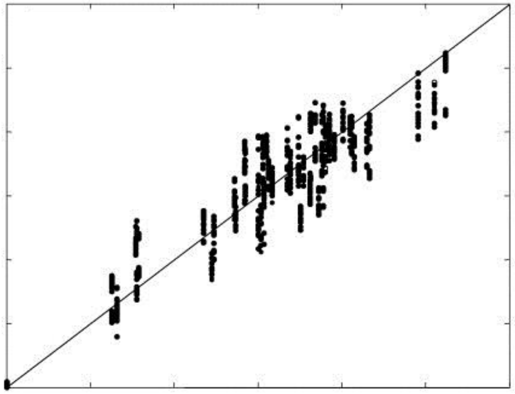
INTRODUCTION

There are a great number of small resistive commercial sensors to measure ozone in the market but most of the manufacturers do not specify calibration procedures or calibration curves.

This work presents a combination of a resistive sensors model of humidity and temperature influence and a PLS regression.



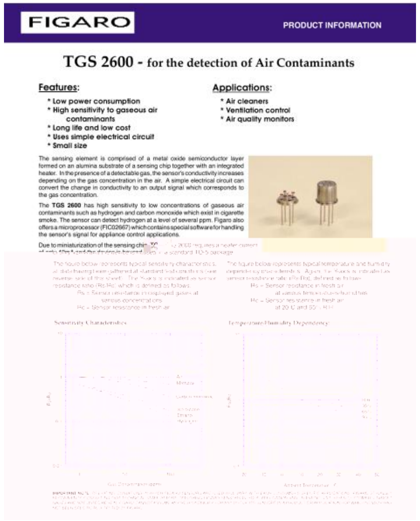




INTRODUCTION

Moreover the ambient humidity and temperature are important interferences that usually are not taken into account in manufacturer specifications or research articles.

Also the comparison between sensors is difficult since the calibration methods can add or subtract a great amount of uncertainty to the measurements.



FIGARO PRODUCT INFORMATION

TGS 2600 - for the detection of Air Contaminants

Features:

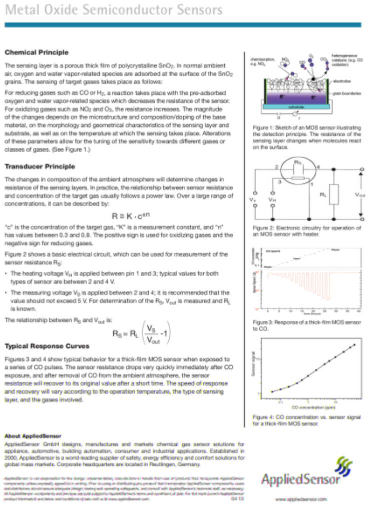
- Low power consumption
- High sensitivity to gaseous air contaminants
- Long life and low cost
- Uses simple electrical circuit
- Small size

Applications:

- Air cleaners
- Ventilation control
- Air quality monitors

The sensing element is comprised of a metal oxide semiconductor layer formed on an alumina substrate of a sensing chip together with an integrated heater. In the presence of a detectable gas, the sensor's conductivity increases depending on the gas concentration in the air. A simple electrical circuit can convert the change in conductivity to an output signal which corresponds to the gas concentration.

The **TGS 2600** has high sensitivity to low concentrations of gaseous air contaminants such as hydrogen and carbon monoxide which exist in cigarette smoke. The sensor can detect hydrogen at a level of several ppm. Figaro also offers a microprocessor (FIC02667) which contains special software for handling the sensor's signal for appliance control applications.



Metal Oxide Semiconductor Sensors

Chemical Principle

The sensing layer is a porous thick film of polycrystalline SnO_2. In normal ambient air, oxygen and water vapor-related species are adsorbed at the surface of the SnO_2 grains. The sensing of target gases takes place as follows:

For reducing gases such as CO or H_2, a reaction takes place with the pre-adsorbed oxygen and water vapor-related species which decreases the resistance of the sensor. For oxidizing gases such as NO_2 and O_3, the resistance increases. The magnitude of the changes depends on the microstructure and composition/doping of the base material, on the morphology and geometrical characteristics of the sensing layer and substrate, as well as on the temperature at which the sensing takes place. Alterations of these parameters allow for the tuning of the sensitivity towards different gases or classes of gases. (See Figure 1.)

Transducer Principle

The changes in composition of the ambient atmosphere will determine changes in resistance of the sensing layers. In practice, the relationship between sensor resistance and concentration of the target gas usually follows a power law. Over a large range of concentrations, it can be described by:

$$R \cong K \cdot c^{\pm n}$$

"c" is the concentration of the target gas, "K" is a measurement constant, and "n" has values between 0.3 and 0.8. The positive sign is used for oxidizing gases and the negative sign for reducing gases.

Figure 2 shows a basic electrical circuit, which can be used for measurement of the sensor resistance R_S:

- The heating voltage V_H is applied between pin 1 and 3; typical values for both types of sensor are between 2 and 4 V.
- The measuring voltage V_S is applied between 2 and 4; it is recommended that the value should not exceed 5 V. For determination of the R_S, V_{out} is measured and R_L is known.

The relationship between R_S and V_{out} is:

$$R_S = R_L \left(\frac{V_S}{V_{out}} - 1 \right)$$

Typical Response Curves

Figures 3 and 4 show typical behavior for a thick-film MOS sensor when exposed to a series of CO pulses. The sensor resistance drops very quickly immediately after CO exposure, and after removal of CO from the ambient atmosphere, the sensor resistance will recover to its original value after a short time. The speed of response and recovery will vary according to the operation temperature, the type of sensing layer, and the gases involved.

Figure 1: Sketch of an MOS sensor illustrating the detection principle. The resistance of the sensing layer changes when molecules react on the surface.

Figure 2: Electronic circuitry for operation of an MOS sensor with heater.

Figure 3: Response of a thick-film MOS sensor to CO.

Figure 4: CO concentration vs. sensor signal for a thick-film MOS sensor.

About AppliedSensor

AppliedSensor GmbH designs, manufactures and markets chemical gas sensor solutions for appliance, automotive, building automation, consumer and industrial applications. Established in 2000, AppliedSensor is a world-leading supplier of safety, energy efficiency and comfort solutions for global mass markets. Corporate headquarters are located in Reutlingen, Germany.

AppliedSensor

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MEASUREMENTS

MEASUREMENTS

1-110 ppb of O_3 (stability of 3 ppb)

40-80 % Humidity (stability of 2 %)

12-32 ºC Temperature (stability of 1 ºC)

The measurements consisted on:

- Several scales of ozone.
- Scales of humidity.
- Scales of temperature.

To avoid hysteresis we presented the gas mixture concentrations in mixed order.

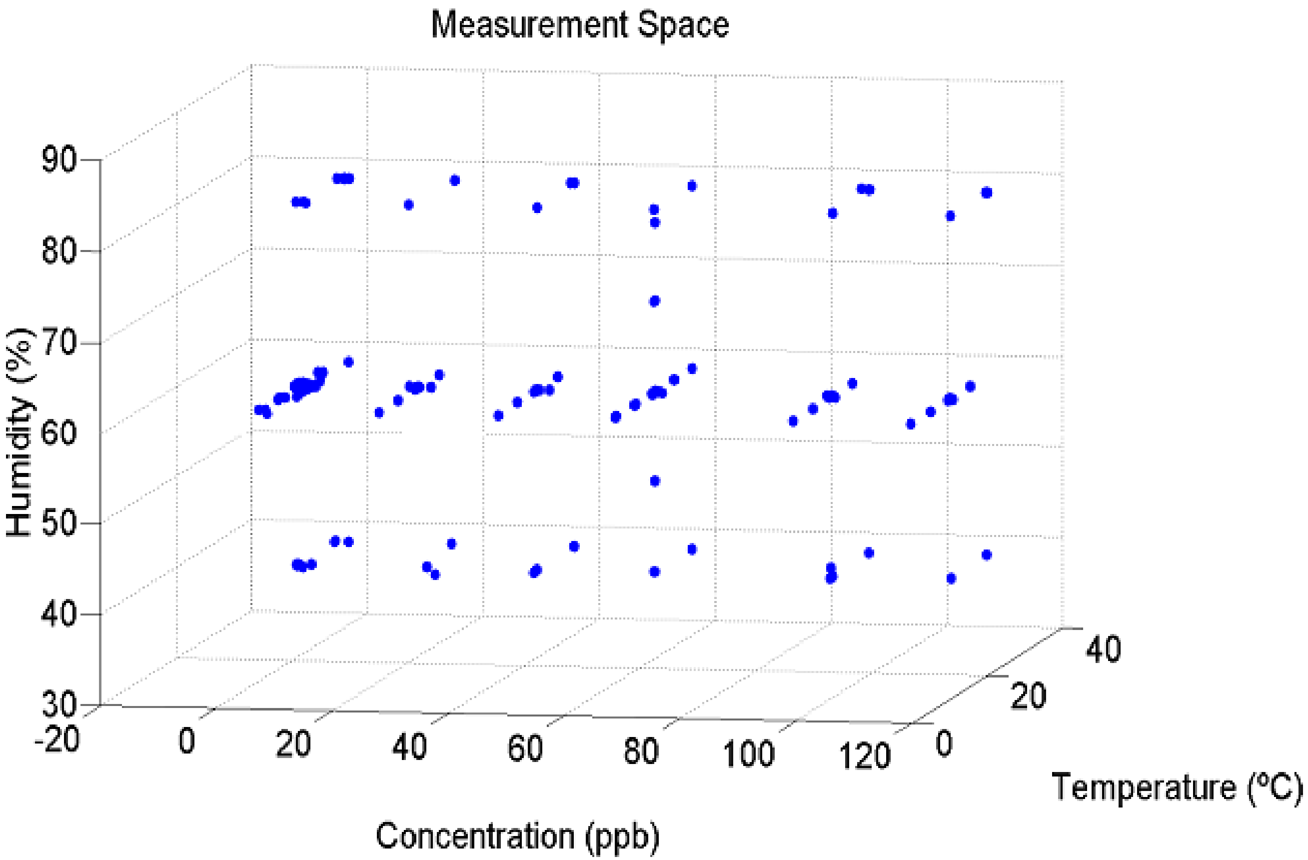
MEASUREMENTS

This testing chamber generated the mixtures by pre mixing dynamically the ozone and synthetic air and delivering them at a known concentration to the sensors.

These measurements did follow the procedures specified on the ISO-6145.

The concentration of the target gas was not just calculated from the mixture but actually measured by a reference analyzer in order to low the uncertainty of the calibrations.

MEASUREMENTS



MEASUREMENTS

Sensor Model	Enterprise
Unitec Sens 3000 1	Unitec s.r.l
Unitec Sens 3000 2	Unitec s.r.l
IMN2P 1	IMN2P
IMN2P 2	IMN2P
SP61 1	FIS
SP61 2	FIS
MICS 2610 1	e2V
MICS 2610 2	e2V
NanoEnvi 1	Ingenieros Asociados
NanoEnvi 2	Ingenieros Asociados
MICS OZ47 1	e2V
MICS OZ47 x	e2V
MICS OZ47 9	e2V

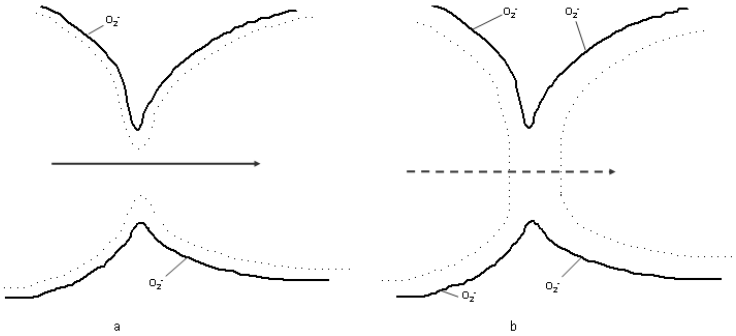
MODELIZATION

MODELIZATION

The resistive gas sensor consists on layers of metal oxide, usually tin oxide, that change their electrical properties when exposed to different gases.

The parameter more widely measured to detect these changes is the resistance.

This change of resistance or conductance is usually modeled by the metal oxide grain to grain conductivity.

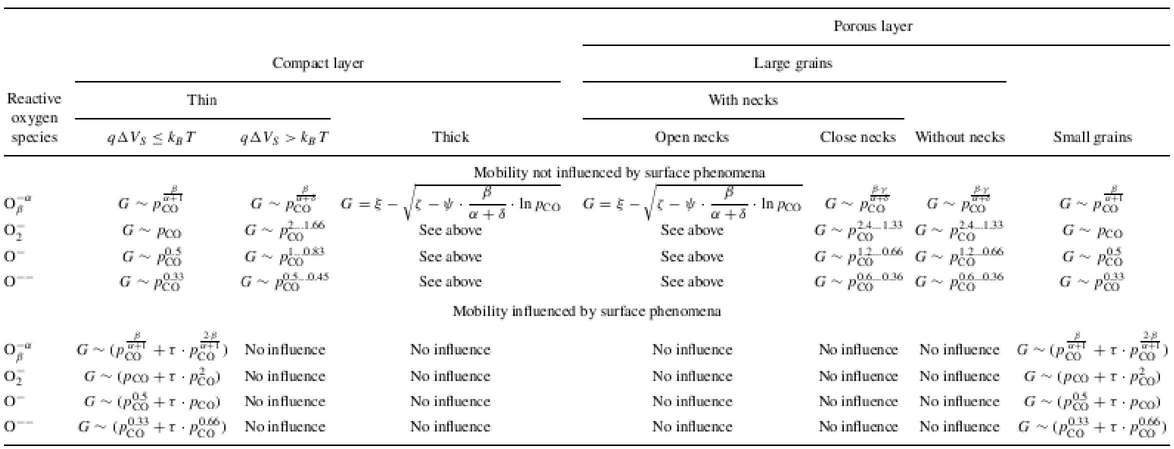


MODELIZATION

In presence of an oxidizing gas, normally oxygen in ambient air, the molecules of the gas react with the oxide trapping electrons of the surface creating a charged space that act as a barrier for the conductivity

There are different morfologies that affect to the conductivity:

- Layer thickness.
- Size grain.
- Compactness.
- Porosity.
- Form factor.



				Porous layer			
	Compact layer			Large grains			
Reactive oxygen species	Thin			With necks			
	$q\Delta V_S \leq k_B T$	$q\Delta V_S > k_B T$	Thick	Open necks	Close necks	Without necks	Small grains
			Mobility not influenced by surface phenomena				
$O_\beta^{-\alpha}$	$G \sim p_{CO}^{\frac{\beta}{\alpha+1}}$	$G \sim p_{CO}^{\frac{\beta}{\alpha+\delta}}$	$G = \xi - \sqrt{\zeta - \psi \cdot \frac{\beta}{\alpha+\delta} \cdot \ln p_{CO}}$	$G = \xi - \sqrt{\zeta - \psi \cdot \frac{\beta}{\alpha+\delta} \cdot \ln p_{CO}}$	$G \sim p_{CO}^{\frac{\beta \cdot \gamma}{\alpha+\delta}}$	$G \sim p_{CO}^{\frac{\beta \cdot \gamma}{\alpha+\delta}}$	$G \sim p_{CO}^{\frac{\beta}{\alpha+1}}$
O_2^-	$G \sim p_{CO}$	$G \sim p_{CO}^{2...1.66}$	See above	See above	$G \sim p_{CO}^{2.4...1.33}$	$G \sim p_{CO}^{2.4...1.33}$	$G \sim p_{CO}$
O^-	$G \sim p_{CO}^{0.5}$	$G \sim p_{CO}^{1...0.83}$	See above	See above	$G \sim p_{CO}^{1.2...0.66}$	$G \sim p_{CO}^{1.2...0.66}$	$G \sim p_{CO}^{0.5}$
O^{--}	$G \sim p_{CO}^{0.33}$	$G \sim p_{CO}^{0.5...0.45}$	See above	See above	$G \sim p_{CO}^{0.6...0.36}$	$G \sim p_{CO}^{0.6...0.36}$	$G \sim p_{CO}^{0.33}$
			Mobility influenced by surface phenomena				
$O_\beta^{-\alpha}$	$G \sim (p_{CO}^{\frac{\beta}{\alpha+1}} + \tau \cdot p_{CO}^{\frac{2 \cdot \beta}{\alpha+1}})$	No influence	No influence	No influence	No influence	No influence	$G \sim (p_{CO}^{\frac{\beta}{\alpha+1}} + \tau \cdot p_{CO}^{\frac{2 \cdot \beta}{\alpha+1}})$
O_2^-	$G \sim (p_{CO} + \tau \cdot p_{CO}^2)$	No influence	No influence	No influence	No influence	No influence	$G \sim (p_{CO} + \tau \cdot p_{CO}^2)$
O^-	$G \sim (p_{CO}^{0.5} + \tau \cdot p_{CO})$	No influence	No influence	No influence	No influence	No influence	$G \sim (p_{CO}^{0.5} + \tau \cdot p_{CO})$
O^{--}	$G \sim (p_{CO}^{0.33} + \tau \cdot p_{CO}^{0.66})$	No influence	No influence	No influence	No influence	No influence	$G \sim (p_{CO}^{0.33} + \tau \cdot p_{CO}^{0.66})$

MODELIZATION

The potential barrier has an effect on the conductivity that can be expressed as:

$$G=G_o \cdot \exp(-q \cdot V_s/k \cdot T)$$

Where q is the electronic charge, k the Boltzmann constant, T is the absolute temperature, G_0 a constant term that depends on the geometry and material and V_s is the potential barrier between the grains.

MODELIZATION

The conductivity dependence on the temperature is sometimes modeled by:

$$R=R_0\cdot \exp(-T\cdot \chi)$$

In witch R is the resistance of the sensor, R_0 is the resistance of the sensor without the temperature influence, T is the temperature and χ is the constant of the model that needs to be fitted.

The ambient temperature will modify the sensor temperature:

$$R=R_0\cdot \exp(T\cdot \beta+\delta)$$

MODELIZATION

The humidity is more complex as it dissociates on protons and OH^- groups and can form other species as H_2CO in the surface.

A general approach is to consider the water vapor as another species that has an influence on the response of the sensor.

This behavior is described by the equation

$$R=R_0\cdot Hd^{\alpha}$$

In witch Hd is the humidity of the ambient, R_0 the resistance of the sensor without the humidity influence and α is the parameter that needs to be fitted.

MODELIZATION

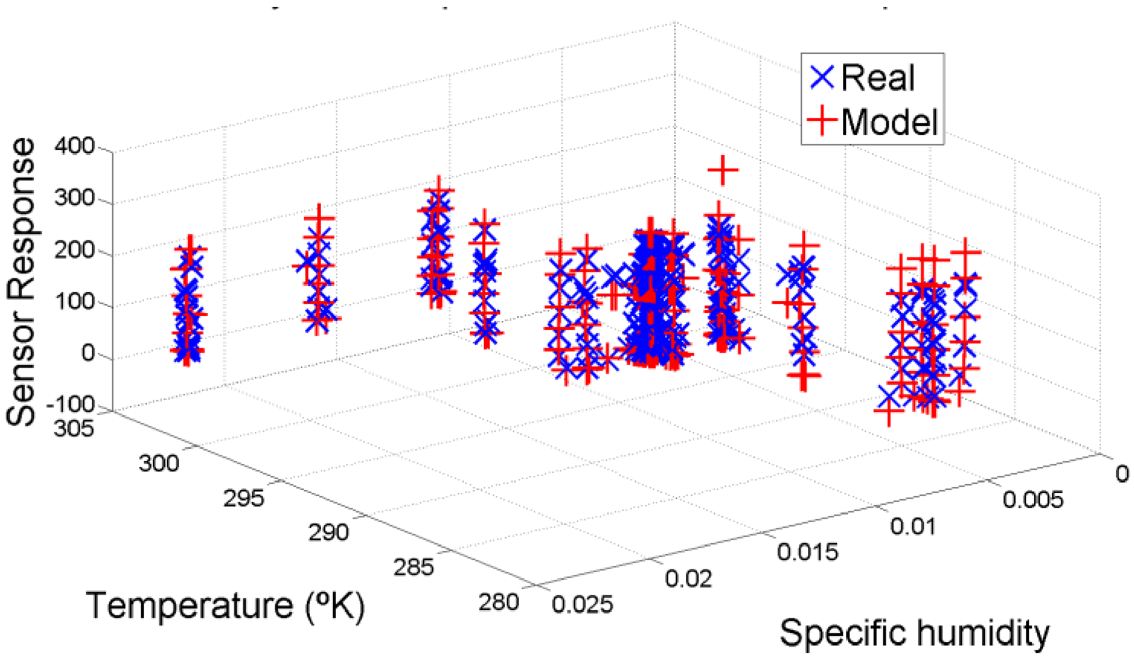
Combining both equations we obtain:

$$R=R_0 \cdot Hd^{\alpha} \cdot \exp(T \cdot \beta+\delta)$$

To fit our model we search the parameters α and β by a Nelder-Mead unconstrained nonlinear optimization programmed in Matlab.

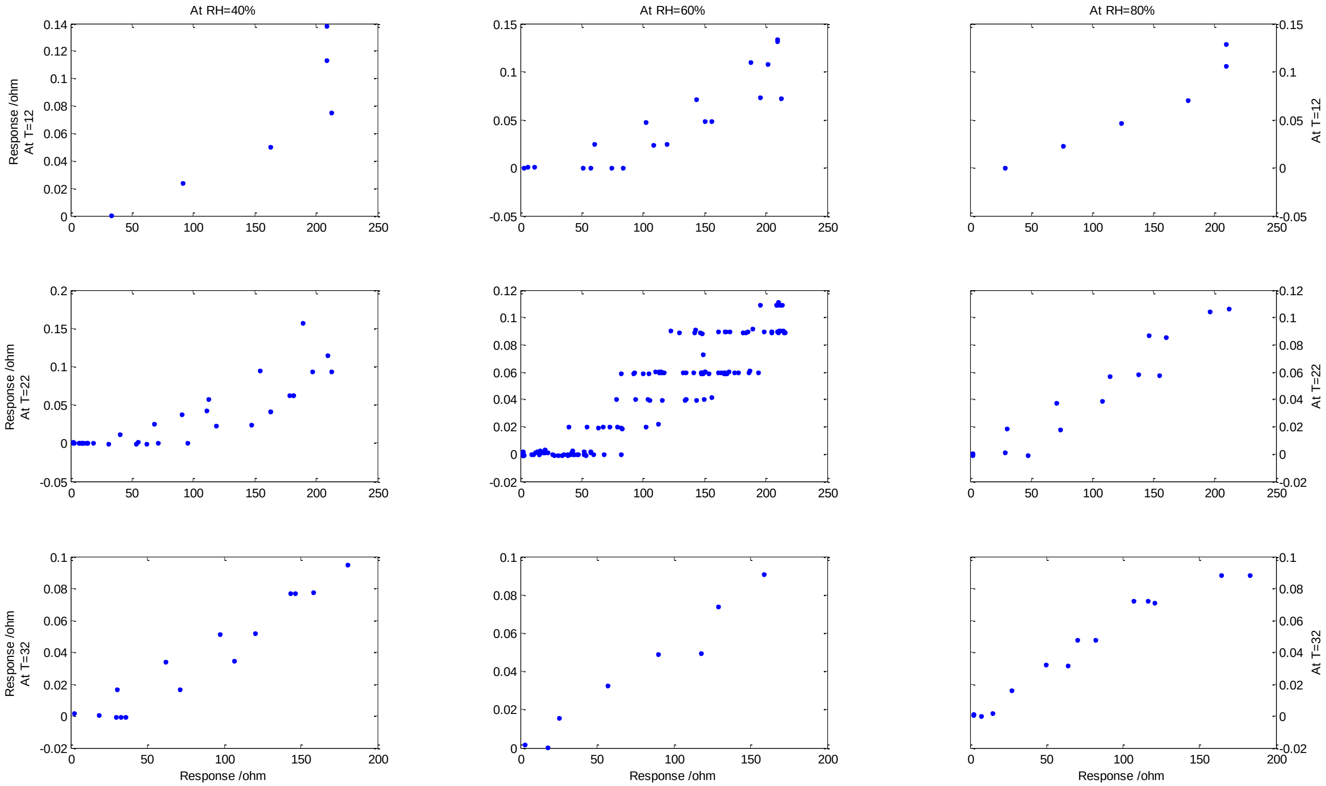
Inspecting the obtained values for α and β we can conclude that even for sensor of the same model the values have a high variability indicating that for every different sensor a new calibration must be done.

MODELIZATION



MODELIZATION

FIS 2



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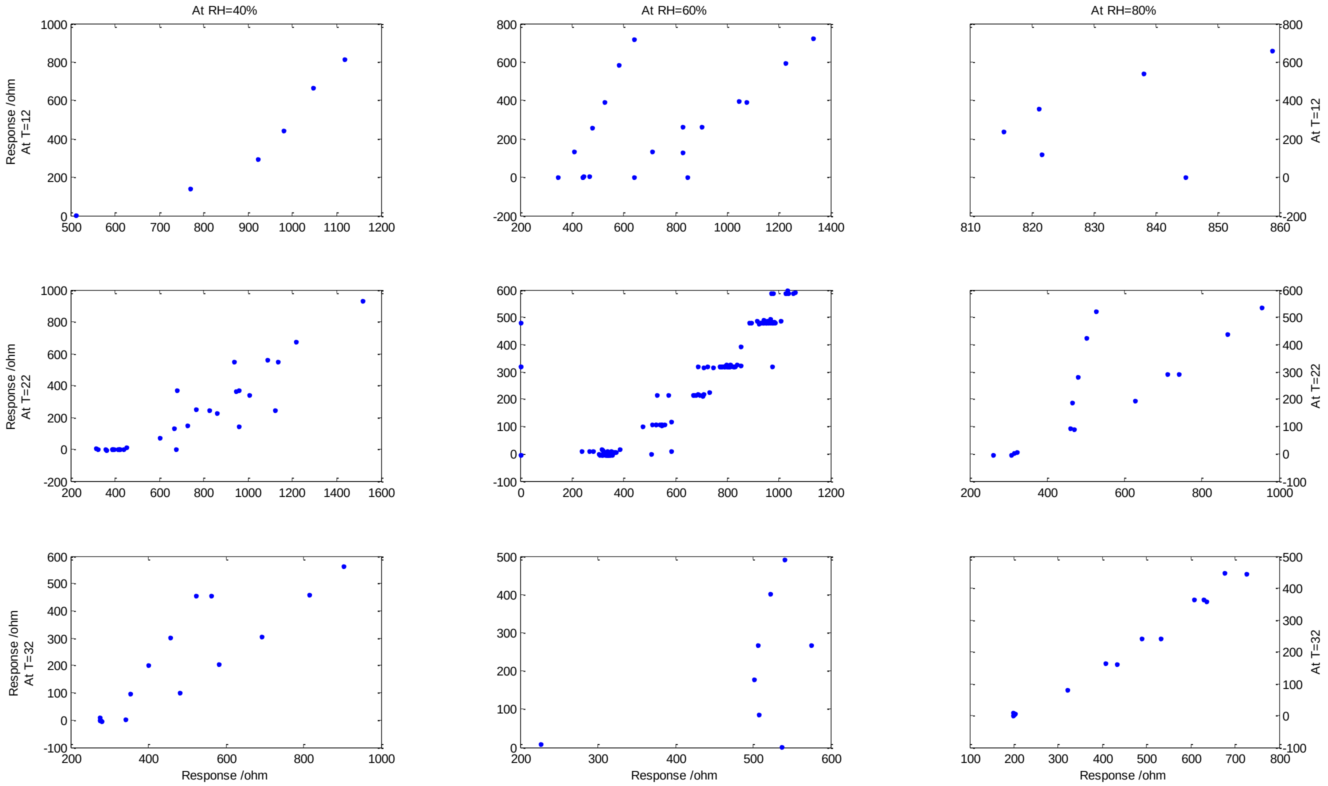
MODELIZATION

MICS 2610 1



CALIBRATION

CALIBRATION

PLS

Is a multiple regression approach that creates a linear combination of the inputs that best correlates with the output.

The goal of PLS regression is to predict Y from X and to describe their common structure.

It searches for a set of components that performs a simultaneous decomposition of X and Y with the constraint that these components explain as much as possible of the covariance between them.

Advantages

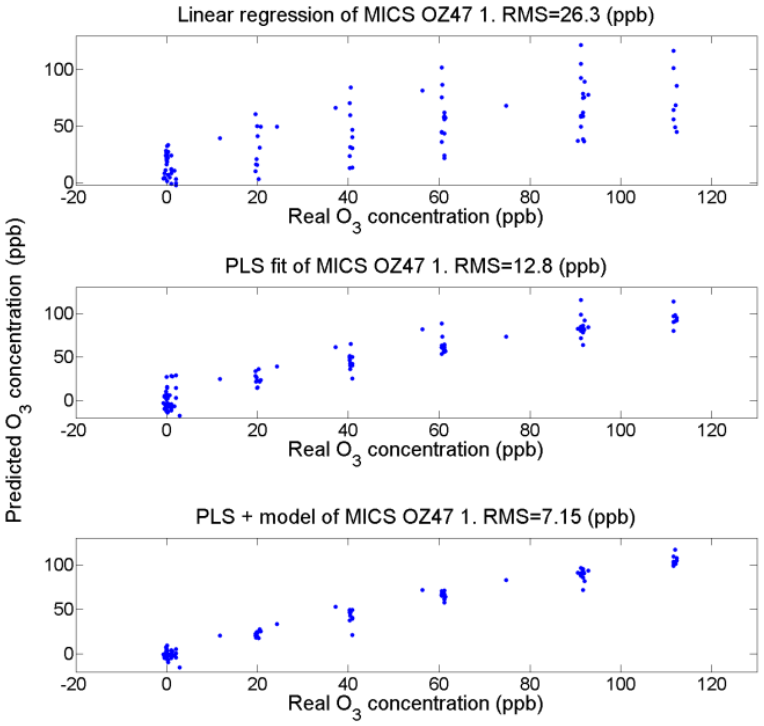
Dimension reduction
Less restrictive in terms of assumptions than other methods
    Distribution free
    No collinearity
    Independence of observations not required
Unlike PCR and Canonical Correlation PLS focus on the prediction

CALIBRATION

With the model fitted we make several calibrations to compare them.

- First we make a simple linear regression based on least squares.
  - In this regression we include only the resistance of the sensor as an independent variable.
- Then we make a multilinear PLS regression
  - Includes as independent parameters the resistances, absolute temperatures and specific humidities.
- Finally a multinear PLS that includes the model
  - Includes the resistances and the modeled influence of the temperature and the humidity.

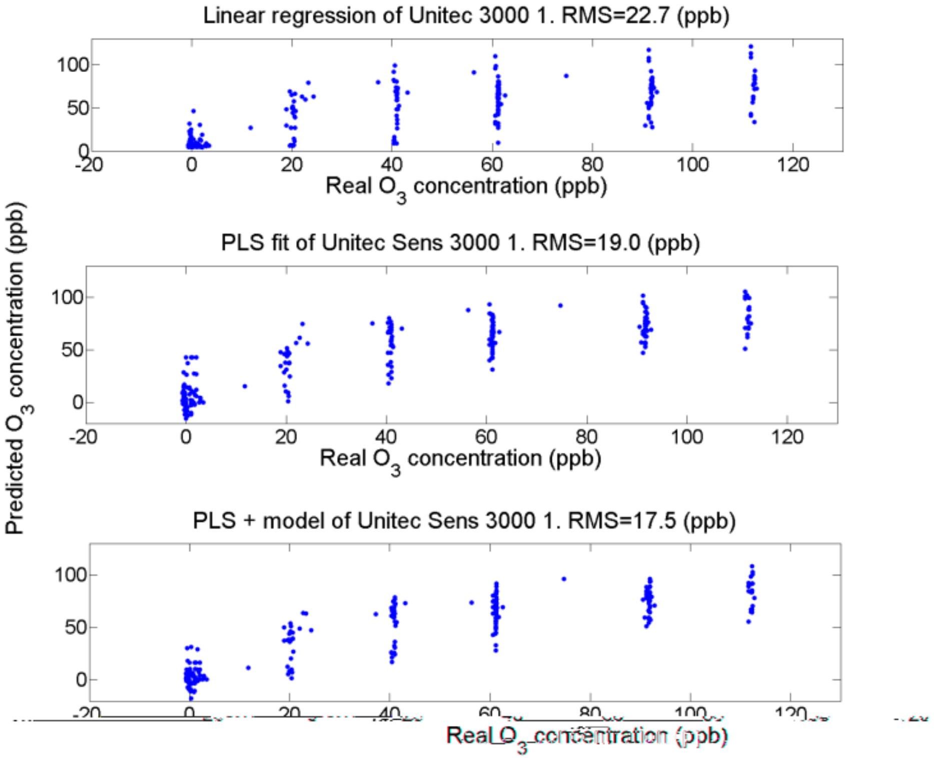
CALIBRATION



Linear regression of MICS OZ47 1. RMS=26.3 (ppb)

PLS fit of MICS OZ47 1. RMS=12.8 (ppb)

PLS + model of MICS OZ47 1. RMS=7.15 (ppb)



Linear regression of Unitec 3000 1. RMS=22.7 (ppb)

PLS fit of Unitec Sens 3000 1. RMS=19.0 (ppb)

PLS + model of Unitec Sens 3000 1. RMS=17.5 (ppb)

CALIBRATION

Sensor	RMS Regresion (ppb)	RMS PLS (ppb)	RMS Model+PLS (ppb)	PLS Improv. (%)	Model+PLS Improv. (%)
Uni. 3000 1	22.7	19.0	17.5	16.0%	22.6%
Uni. 3000 2	16.6	16.0	15.6	3.9%	6.1%
IMN2P 1	34.7	31.3	29.8	9.8%	14.1%
IMN2P 2	33.7	29.9	28.3	11.3%	16.0%
FIS SP61 1	16.3	15.1	14.6	7.3%	10.2%
FIS SP61 2	22.1	22.1	21.8	0.4%	1.4%
MICS 2610 1	23.9	18.6	16.1	22.1%	32.4%
MICS 2610 2	22.3	17.8	15.8	20.2%	29.2%
NanoEnvi 1	32.3	32.8	32.0	-1.5%	1.0%
NanoEnvi 2	38.2	37.7	31.8	1.2%	16.7%
MICS OZ471	26.3	12.8	7.2	51.5%	72.8%
MICS OZ472	28.2	22.8	21.7	19.2%	22.9%
MICS OZ473	25.5	20.8	19.9	18.4%	22.1%
MICS OZ474	24.0	20.0	19.2	16.4%	19.9%
MICS OZ475	25.0	20.6	19.7	17.8%	21.2%
MICS OZ476	38.9	38.2	37.3	1.8%	4.2%
MICS OZ477	30.9	25.1	22.8	18.8%	26.3%
MICS OZ478	28.7	25.0	23.6	12.9%	17.6%
MICS OZ479	23.4	20.1	18.9	14.4%	19.5%
Mean	**27.0**	**23.5**	**21.8**	**13.8%**	**19.8%**

CONCLUSION

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Just by taking into account the factors of temperature and humidity the linear calibration the improvement is clear, lowering the RMS a 13.8%.

When we add the model to the PLS regression the overall improvement on the RMS error is further increased by a 19.8%.

Some sensors present a higher improvement pointing at the fact that all the sensors present a high variability on its characteristics and this variability is significative even on sensors of the same model ad manufacturer.

THANK YOU

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