SAW-based differential sensor exploiting metallocorroles properties for the selective measurement of carbon monoxide.

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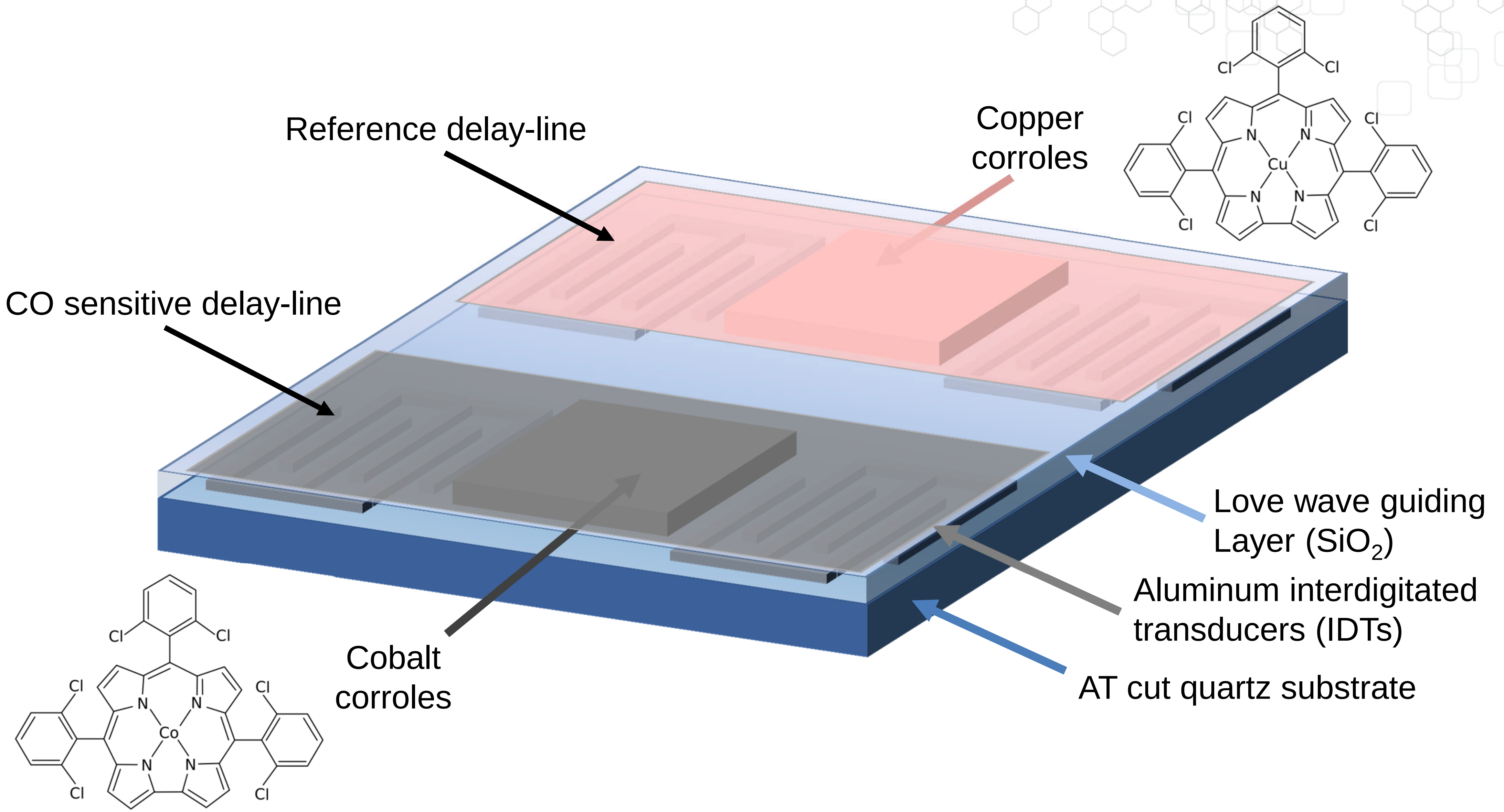
SENSORDEVICES 2020

Presenter resume

Meddy VANOTTI (M) was born on 23-11-1985 in Le Chenit (Switzerland). He obtained the master's degree of physics in 2010 at the University of Franche-Comté (UFR-ST) in France. Meddy obtained his PhD degree in Engineering Sciences at the University of Franche-Comté in 2015 under the supervision of Sylvain Ballandras during which he studied the development of SAW devices for the detection of toxic gases in the air. After a post-doctoral position at the UCL (Belgium), working on the design of surface acoustic wave resonators for the detection of bacteria in liquid phase, Meddy joined back the FEMTO-ST institute to work as a research engineer on SAW based gas sensors.

Differential SAW sensor structure



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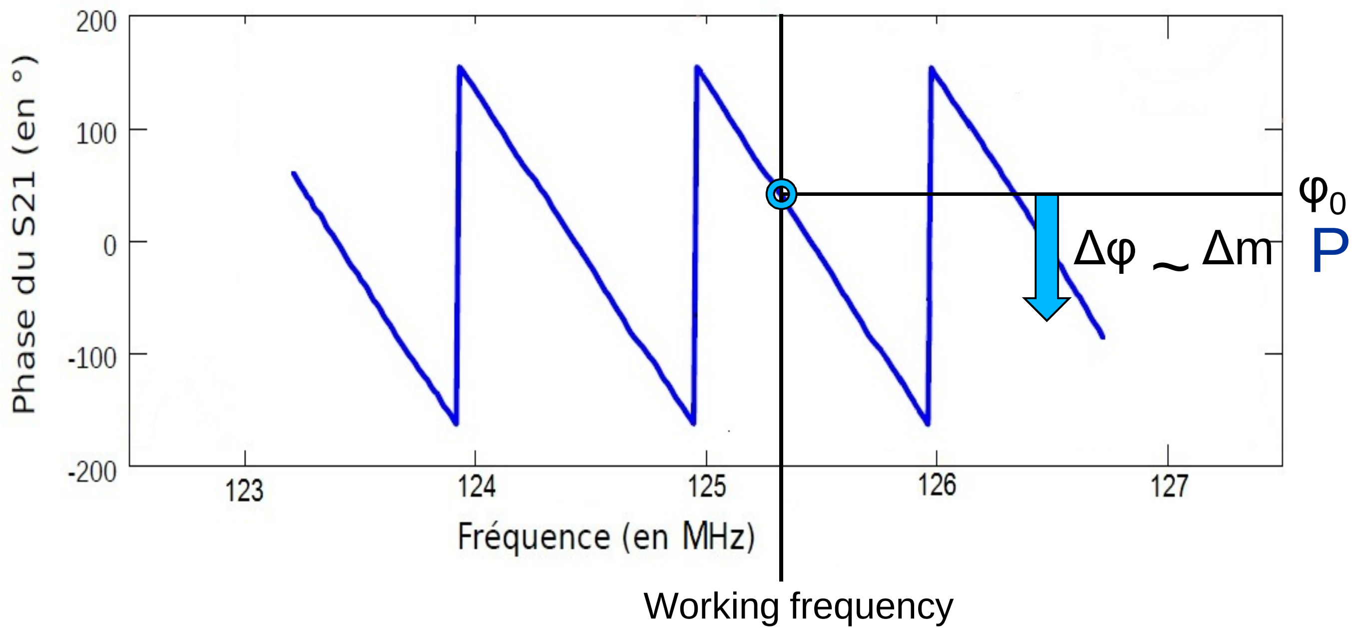
A double delay-line configuration allowing for differential measurements was selected.
The sensitive line and reference line are respectively cover by cobalt corroles and copper corroles.

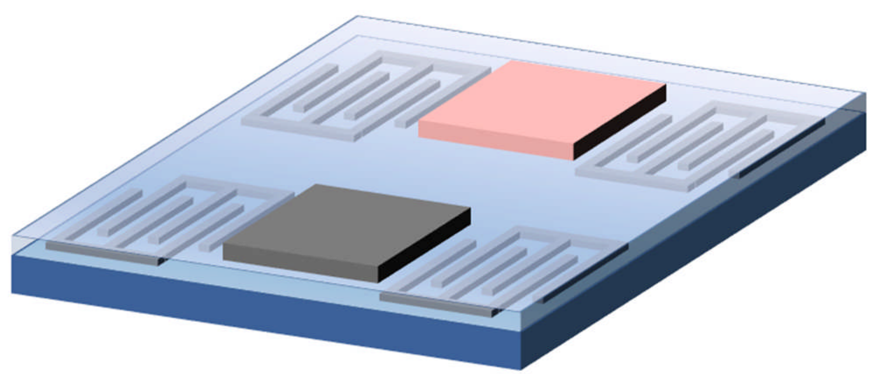
Interrogation strategy

Phase measurement



Phase shift Δφ induced by gravimetric effect

CO gas



CO adsorption (Δm) on cobalt corroles

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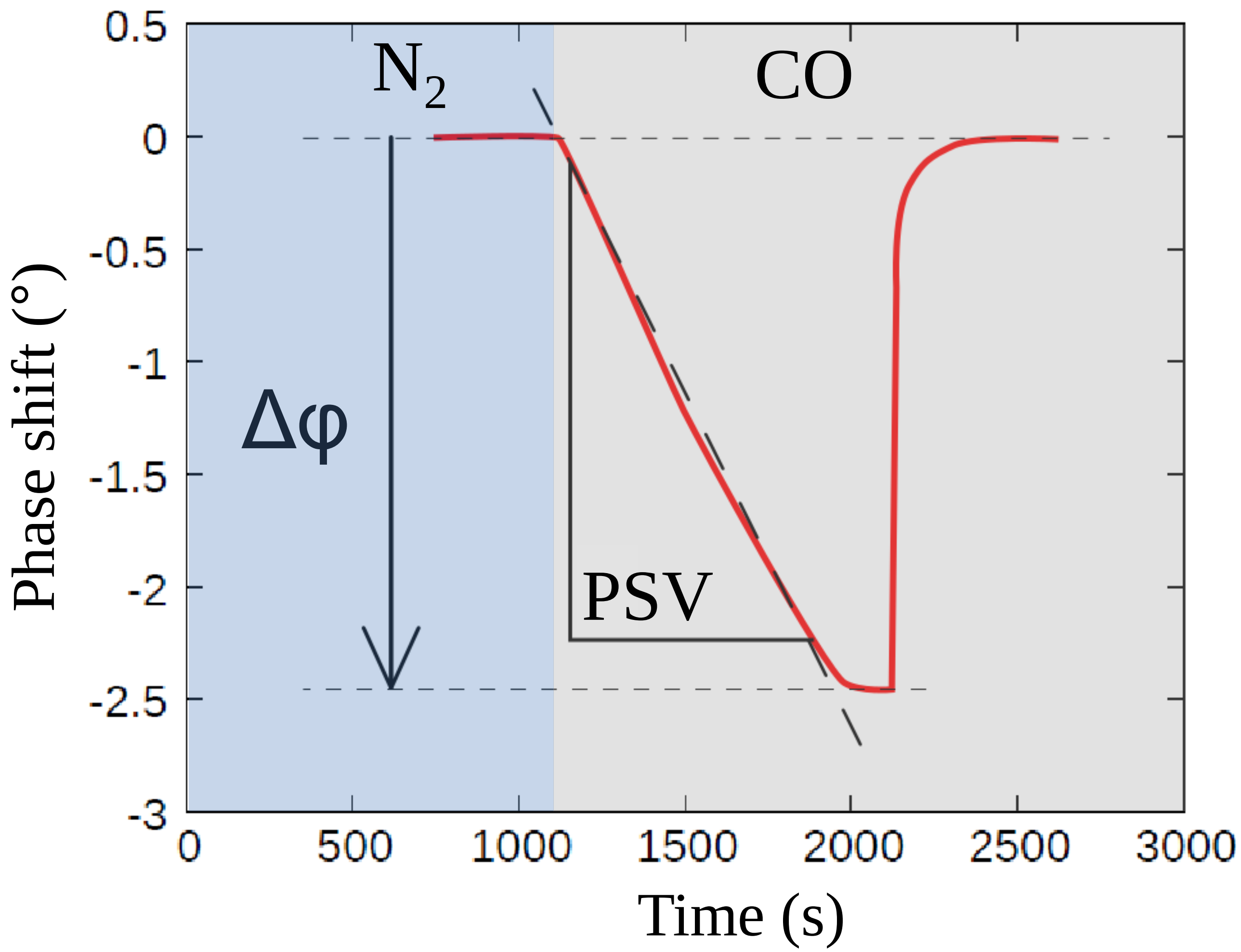
The sensor is based on Love wave gravimetric sensitivity. An open-loop interogation strategy consising in a phase shift measurement at constante frequency was chosen to monitor the frequency down shift of the delay line.

Signal characterization



Typical phase response of the sensor.

The gravimetric sensitivity of the sensor, deduced from the Sauerbrey formula [0], is given by following equation :

$$S = \frac{df}{f_0} . \frac{A}{dm}$$

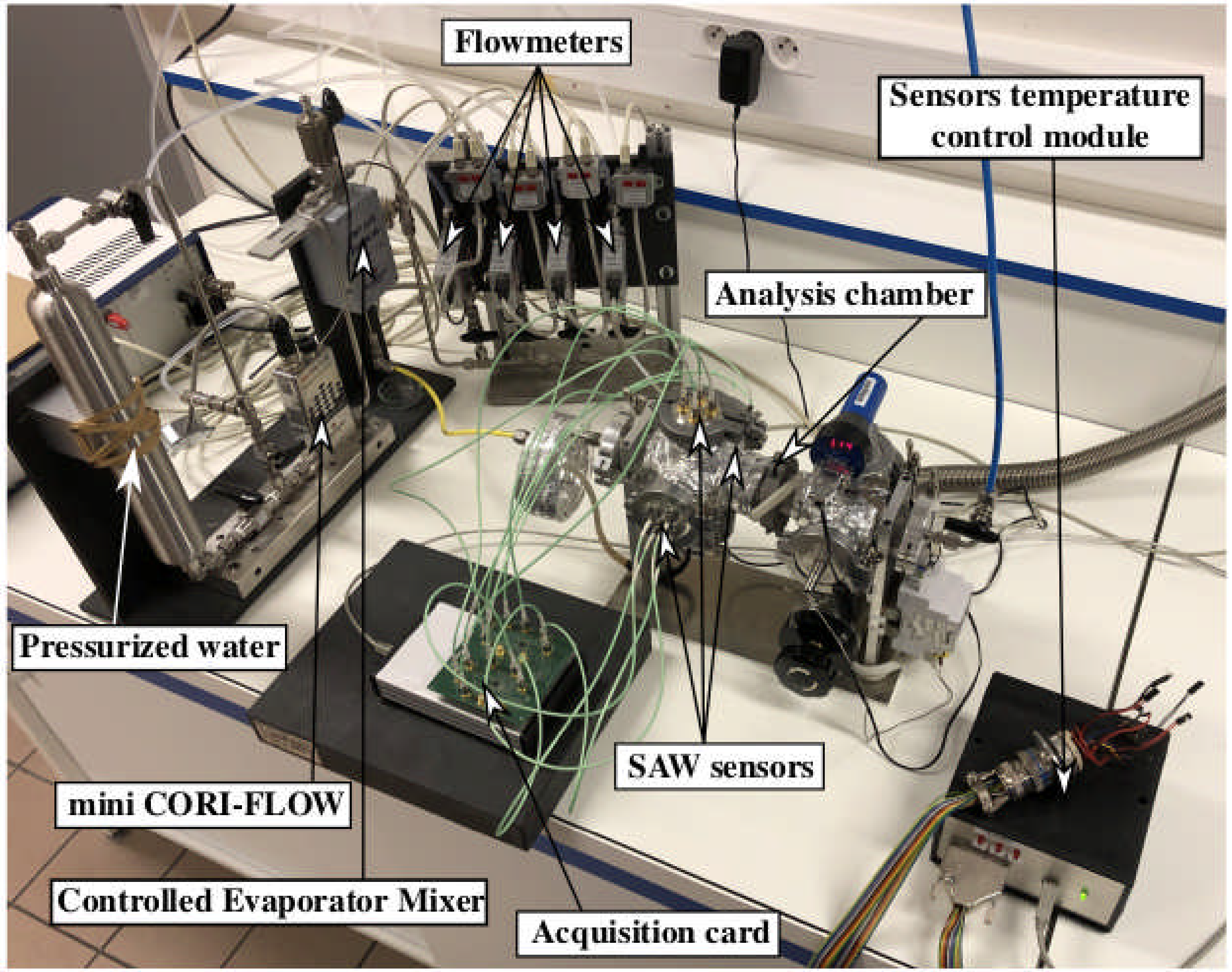
The CO concentration and flow rate being kept constant during the exposure, the gas concentration is proportional to the phase variation in respect of time:

$$C \sim \frac{d\varphi}{dt} .$$

CO concentrations can consequently be determined by means of the derived phase at the beginning of its decrease. This derived phase is referred to as 'Phase Shift Velocity' (PSV). This approach allows to measure gas concentrations within a few tens of seconds.

[0] G. Sauerbrey, Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung, Z. Physik. 155 (1959) 206–222. https://doi.org/10.1007/BF01337937.

Experimental bench



Four mass-flow meters operating in the range 2-500 $mL.min^{-1}$ were used to generate the mixture from gas cylinders with calibrated concentration of target molecules. A Controlled Evaporation Mixing module (CEM) was used to generate a controlled relative humidity in the gas flow. The latter then flowed through a dedicated test chamber, which volume is approximately one liter, with a constant flow rate equal to 500 $mL.min^{-1}$.

A dedicated electronic [1] that delivers similar information to that from a network analyzer was implemented to monitor the phase signals.

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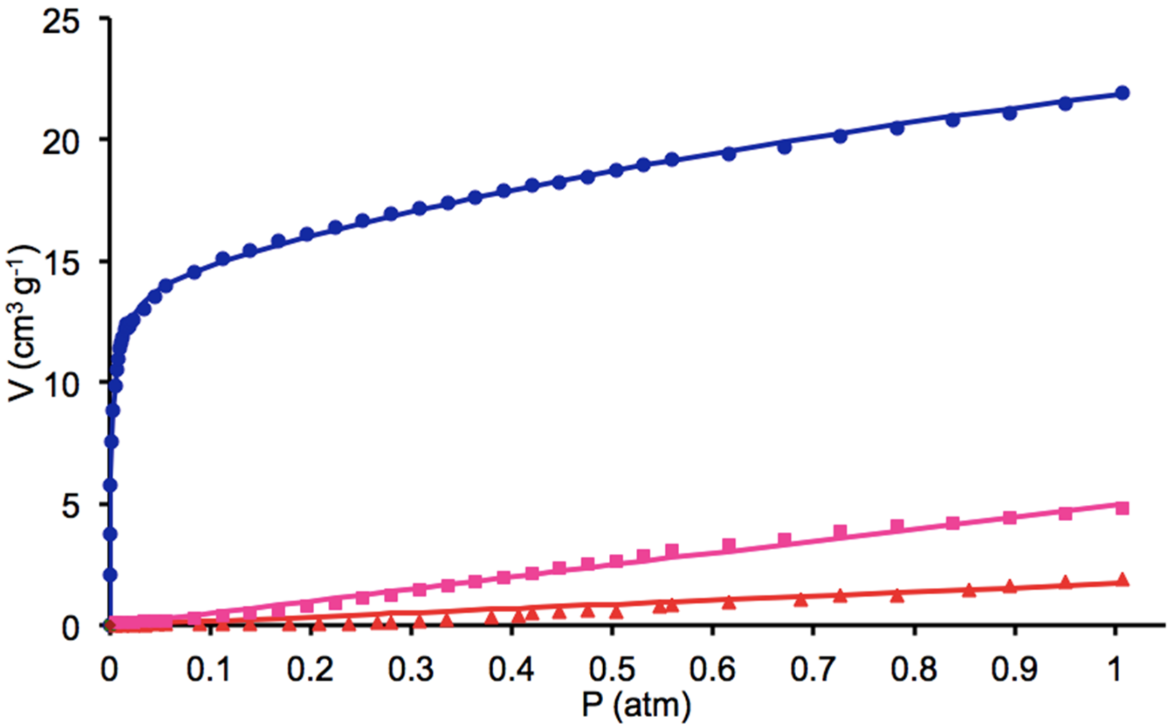
[1] D. Rabus, G. Martin, E. Carry, S. Ballandras, Eight channel embedded electronic open loop interrogation for multi sensor measurement, 2012 European Frequency and Time Forum. (2012). https://doi.org/10.1109/EFTF.2012.6502420.

Metallocorroles as functionalizing layers

Cobalt corrole as sensitive layer:



Adsorption isotherms of CO (blue), O_2 (pink) and N_2 (red) for cobalt corrole recorded at 298 K.

Cobalt corrole presents a high CO uptake and low adsorption capacities for N_2 and O_2. For these two last gases, the uptake values are equal to 1.9 $cm^3.g^{-1}$ and 4.8 $cm^3.g^{-1}$, respectively, and the sorption is best described by a Henry-type behavior with an overall low affinity. Conversely, the cobalt corrole shows a CO sorption volume equal to 21.9 $cm^3.g^{-1}$ (2.7% (w/w)) at 1 atm and the isotherm can be described by a combination of two different processes. The first one is assigned to an adsorption phenomenon with a high affinity in the low-pressure range (0-0.05 atm) thanks to the coordination of one carbon monoxide molecule on the cobalt center.

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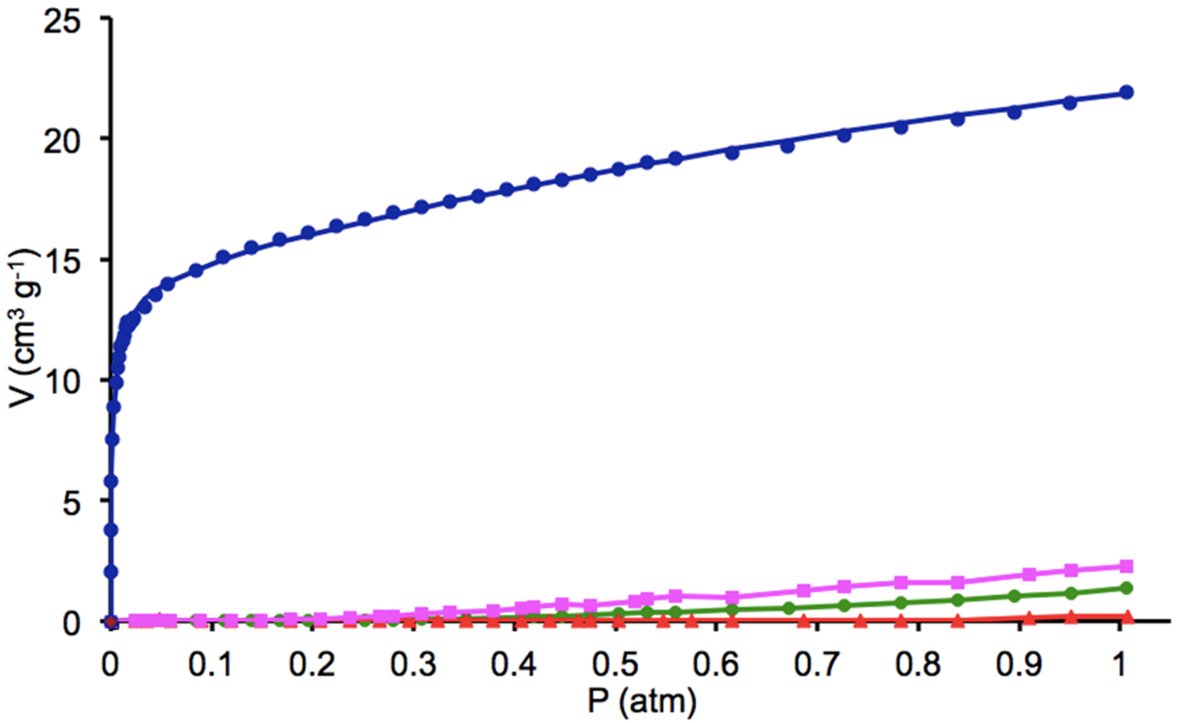
[2] A. Ghosh, Electronic Structure of Corrole Derivatives: Insights from Molecular Structures, Spectroscopy, Electrochemistry, and Quantum Chemical Calculations, Chem. Rev. 117 (2017) 3798–3881. https://doi.org/10.1021/acs.chemrev.6b00590.
[3] G. Herzberg, Molecular spectra and molecular structure. Vol.1: Spectra of diatomic molecules, New York: Van Nostrand Reinhold, 1950, 2nd Ed. (1950). http://adsabs.harvard.edu/abs/1950msms.book.....H (accessed August 25, 2020).

Metallocorroles as functionalizing layers

Copper corrole as reference:



Adsorption isotherms of CO (blue) for cobalt corrole compared to CO (green), O_2 (pink) and N_2 (red) for copper corrole recorded at 298 K

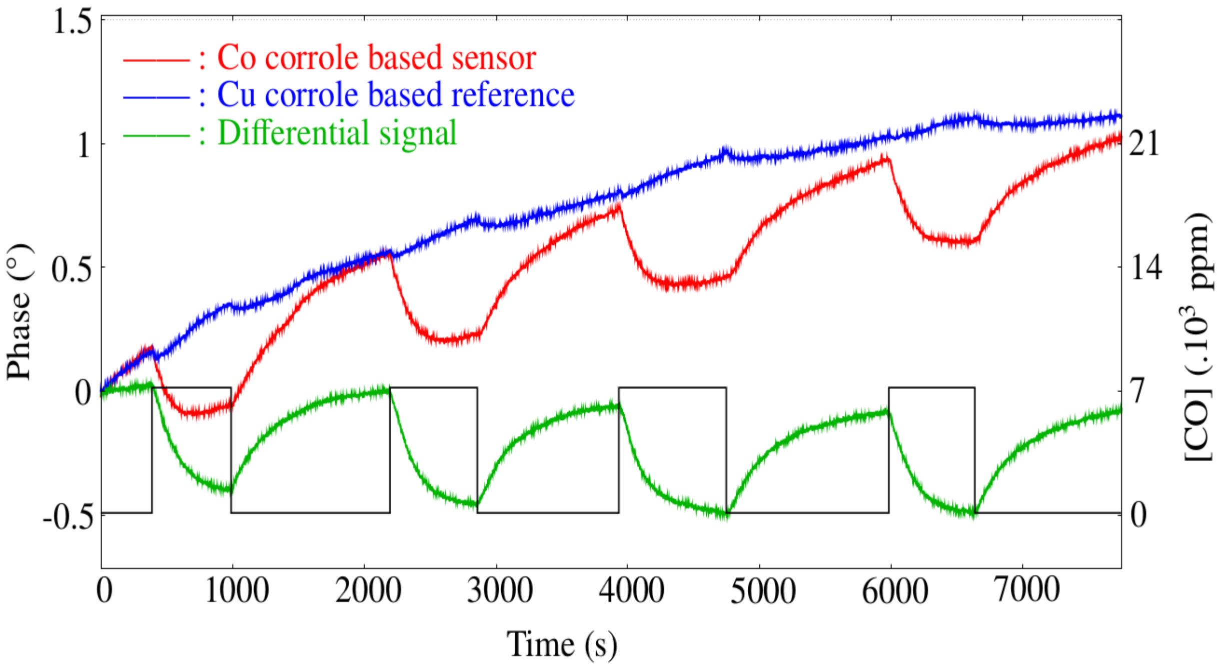
In view to design our double delay-line differential sensor, the use of an accurate organic layer with no affinity for CO is required for the functionalization of the reference.

As the copper corrole shows no sorption properties of CO, this complex was chosen for the functionalization of the reference line.

[2] A. Ghosh, Electronic Structure of Corrole Derivatives: Insights from Molecular Structures, Spectroscopy, Electrochemistry, and Quantum Chemical Calculations, Chem. Rev. 117 (2017) 3798–3881. https://doi.org/10.1021/acs.chemrev.6b00590.
[3] G. Herzberg, Molecular spectra and molecular structure. Vol.1: Spectra of diatomic molecules, New York: Van Nostrand Reinhold, 1950, 2nd Ed. (1950). http://adsabs.harvard.edu/abs/1950msms.book.....H (accessed August 25, 2020).

Advantage of the differential configuration

Phase signal stability:



Comparison between phase signals from the sensitive line (in red), the reference line (in blue) and the differential signal (in green). The black curve represents the CO concentration in the test chamber.

The response profile of the CO sensitive line coated with cobalt corroles, shown by the red curve, shows clear responses to the target gas exposures but also a significant drift of the signal toward the high frequencies.

The signal from the reference line coated with copper corroles (blue curve) exhibits a similar drift of the phase signal and almost no response to the CO injections.

The differential signal, represented by the green curve, obtained by subtracting the signal from the reference line from that of the sensitive line.

The differential signal exhibits a remarkable compensation of the phase drift that results in a stable basic level.

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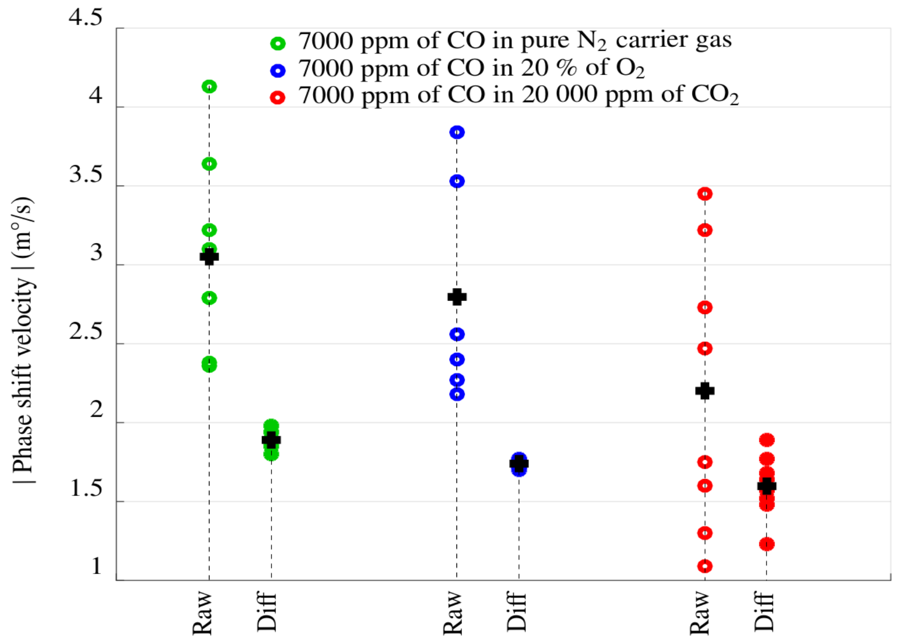
Advantage of the differential configuration

Improved repeatability



Measurements of 7000 ppm of CO in various carrier gases. Raw data are from the measurement line and Diff data from the differential signal. The mean values are represented by the crosses.

		PSV ($.10^{-3}$ °/s) [σ ($.10^{-6}$ °/s)] Raw data		Differential data	
Interferent	none (pure N_2)	-3.05	[610]	-1.89	[54.8]
	O_2 (20%)	-2.79	[704]	-1.74	[24.5]
	CO_2 (2%)	-2.20	[890]	-1.60	[199]

Statistical characterization of CO measurements in various conditions with (Differential data) and without (Raw data) the use of the differential system.

Here we observe a dramatic reduction of the measurements dispersion when using the differential system even in the presence of interferents is shown. The statistical characterization of these data, presented in the table, reveals that the deviation, σ, induced by CO_2 at 20 000 ppm is reduced by a factor 4.5. In the case of oxygen at 20%, which is one of the main interferents, the deviation is greatly reduced by a factor 30.

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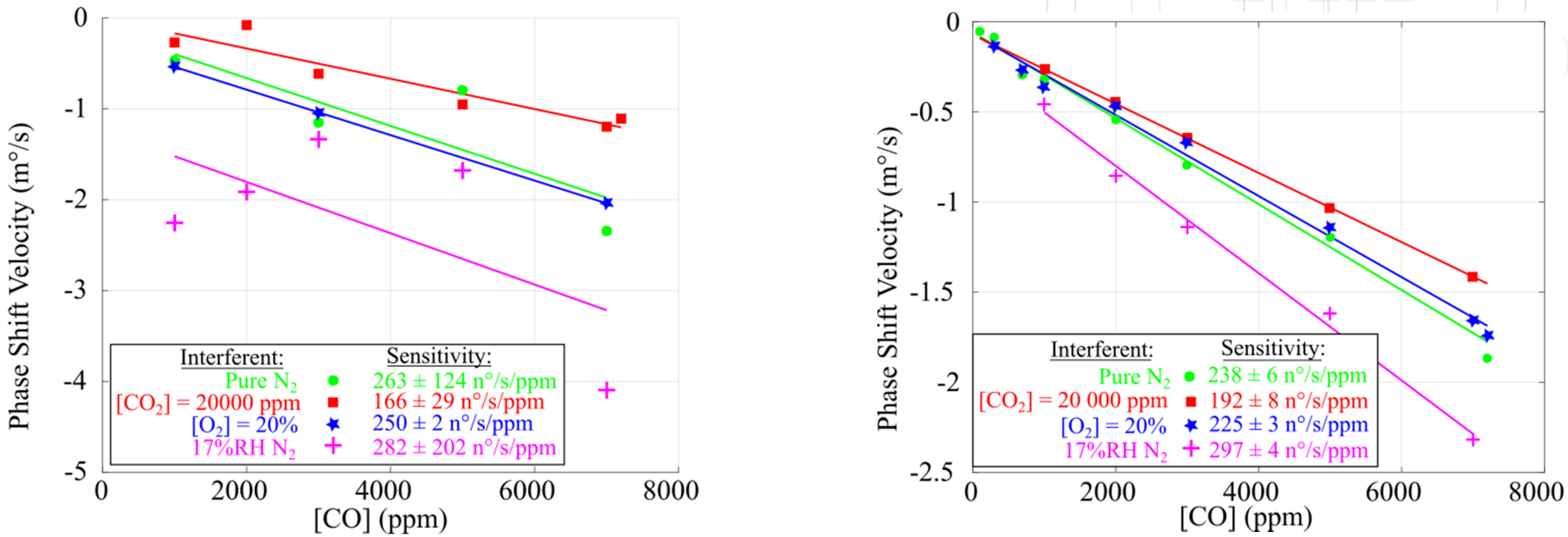
Advantage of the differential configuration

Improved stability:



Measurements of [CO] over a 100-7000 ppm range. (Left) Sensitivity characterization of the measurement line in presence of oxygen (blue), carbon dioxide (red) and humidity (pink) on the carrier gas. (Right) Sensitivity of the differential sensor in the presence of the same interferent.

As expected from previous works [4], a linear correlation between CO concentration and the phase shift velocity is observed. The uncertainty on the sensitivity drops dramatically in the case of the differential sensor. For example in the case of water interferent, the uncertainty on the sensitivity is divided by 50 when using the differential sensor.

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[4] M. Vanotti, C. Theron, S. Poisson, V. Quesneau, M. Naitana, V. Soumann, S. Brandès, N. Desbois, C. Gros, T.-H. Tran-Thi, V. Blondeau-Patissier, Surface Acoustic Wave Sensors for the Detection of Hazardous Compounds in Indoor Air, Proceedings. 1 (2017) 444. https://doi.org/10.3390/proceedings1040444

Conclusions

In this research, we developed an original sensor for carbon monoxide monitoring based on a differential configuration.

This approach takes advantage of the intrinsic high sensitivity to gravimetric phenomena of Love wave based SAW sensors, combined with CO selective sorption capabilities of the cobalt corroles.

Copper corroles have been successfully exploited for the development of a dedicated reference line.

We have shown that the use of a proper reference line as part of a differential sensor provides;

- **The stability of the sensor phase signal.**
- **Improvement in the repeatability of the measurements.**
- **A significant reduction of the uncertainty in the sensor sensitivity.**

These results pave the way for the detection of other gases with acoustic waves devices associated with dedicated functionalization compounds for the development of a multi-gas monitoring system.