A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

DCU

I.M. Pérez de Vargas-Sansalvador[a], C. Fay[b], T. Phelan[b], M.D. Fernández-Ramos[a], L.F. Capitán-Vallvey[a], D. Diamond[b], F. Benito-Lopez[b,]

A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

- Fast analysis
- Portable instrumentation
- Low cost
- Real-time analysis

A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Environmental Monitoring

Active packaging and Modified-atmosphere technologies

CO_2

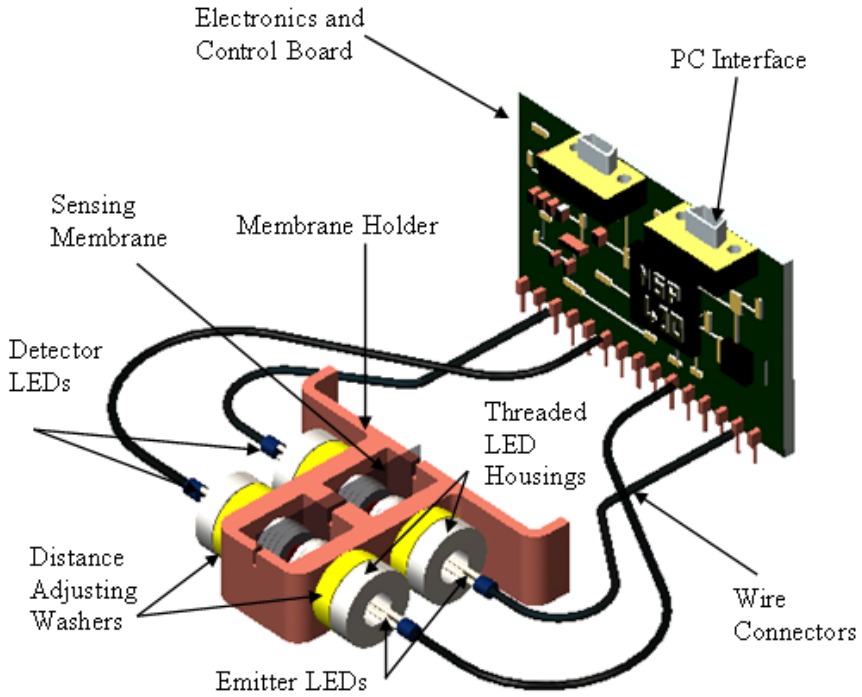
Pollution Control

Agro-food industry

A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Portable electronic system

- Paired emitter-detector diode (PEDD) arrangement as a colorimetric chemical detection system.



Analytical signal

Discharge time (μs)

A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Mechanism

- CO_2 Acidic properties

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightleftharpoons HCO_3^- + H_3O^+$$

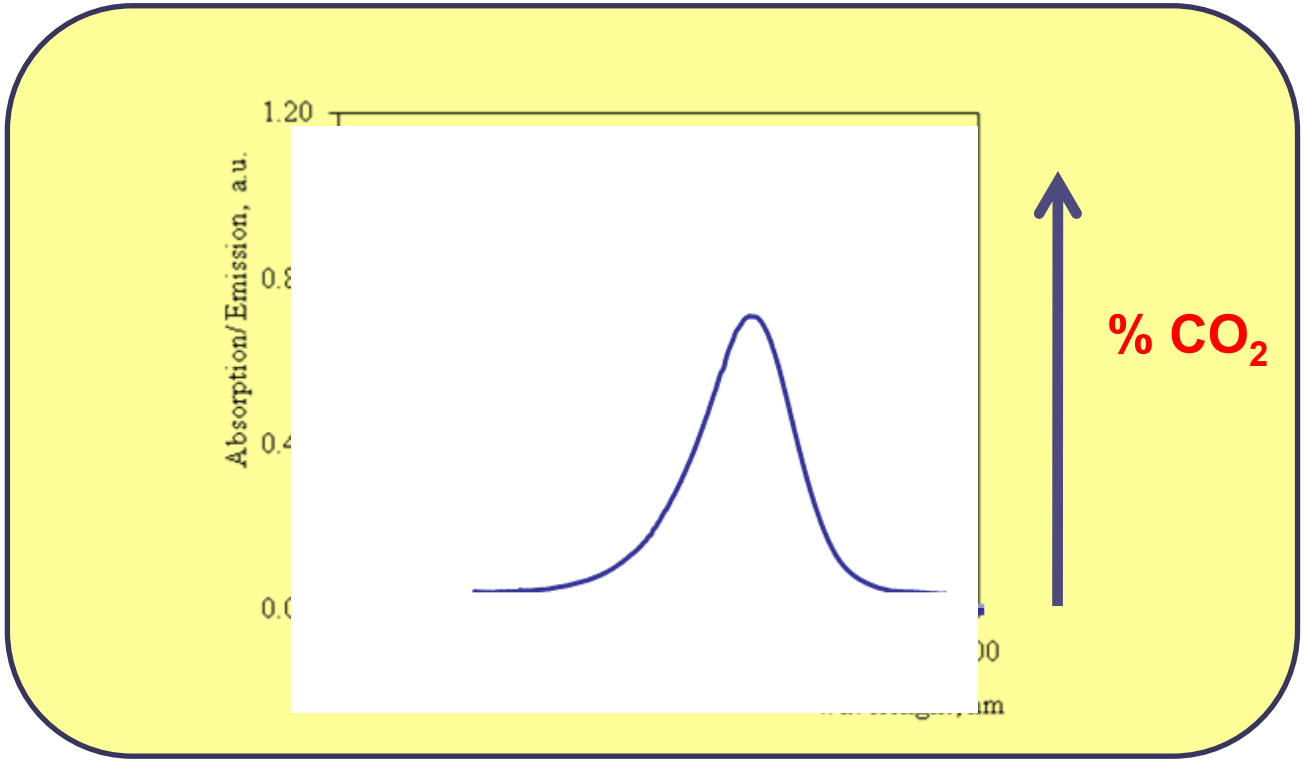
- ion-pair α-naphtholphthalein - tetraoctylammonium

$$TOA^+N^- \cdot xH_2O + CO_2 \overset{K}{\longleftrightarrow} TOA^+HCO_3^- \cdot (x-1)H_2O \cdot HN$$

Deprotonated form α-naphtholphthalein

Protonated form α-naphtholphthalein

A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS



% CO_2

A α-NP

Light LED

Discharge time

A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Cocktail 1

- PtOEP (luminophore)
- PVCD (O_2 impermeable)
- THF

Cocktail 2

- α-naphtholphthalein
- EC
- TBP
- TOAOH
- Tol:EtOH

A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

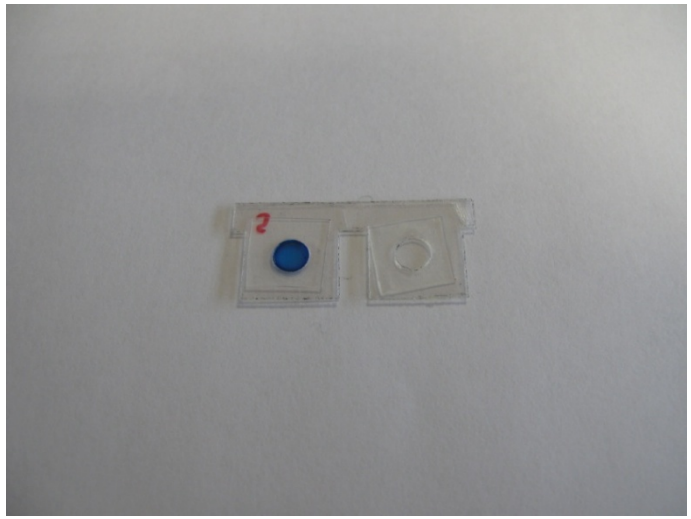
Configurations studied

Configuration 1

Opposite side configuration

Prevention degradation of PtOEP in the presence of TOAOH

Inner filter effect



Configuration 2

Elimination of cocktail 1 membrane

Simplification of the system

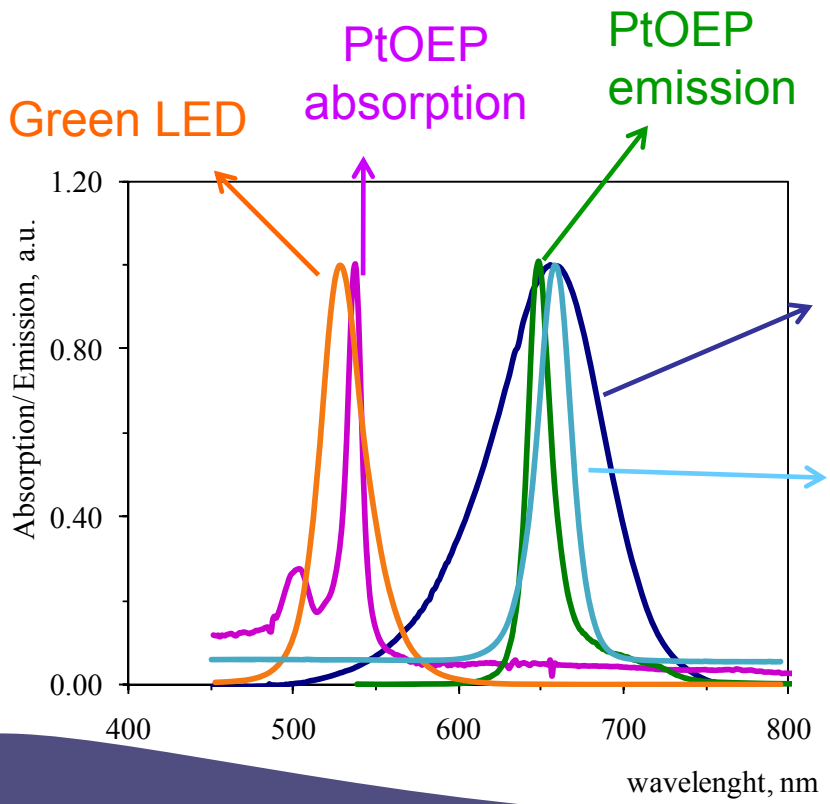
Membrane Cocktail 2

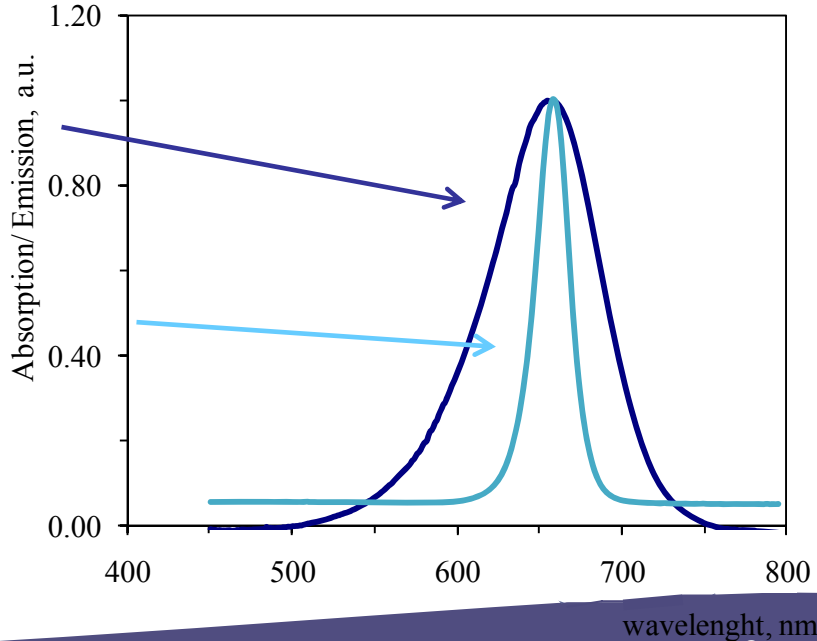
A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Configurations studied

Configuration 1

Configuration 2

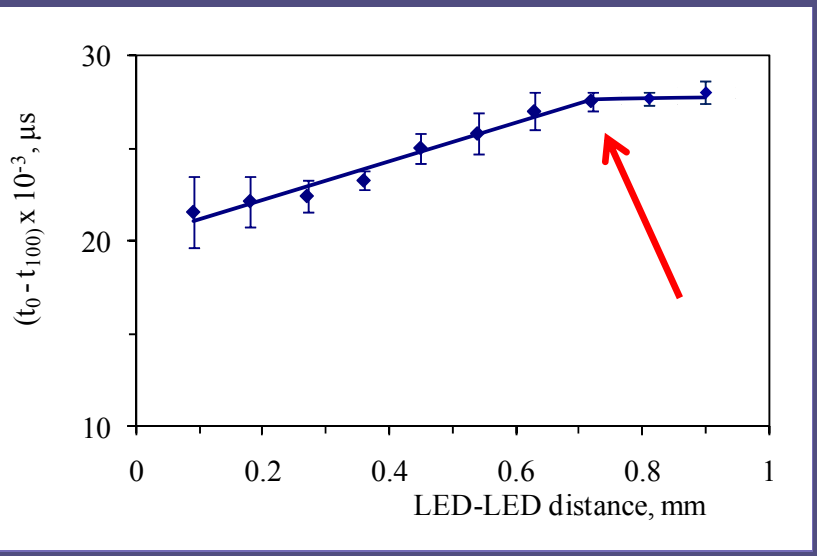




A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Distance LED-LED influence

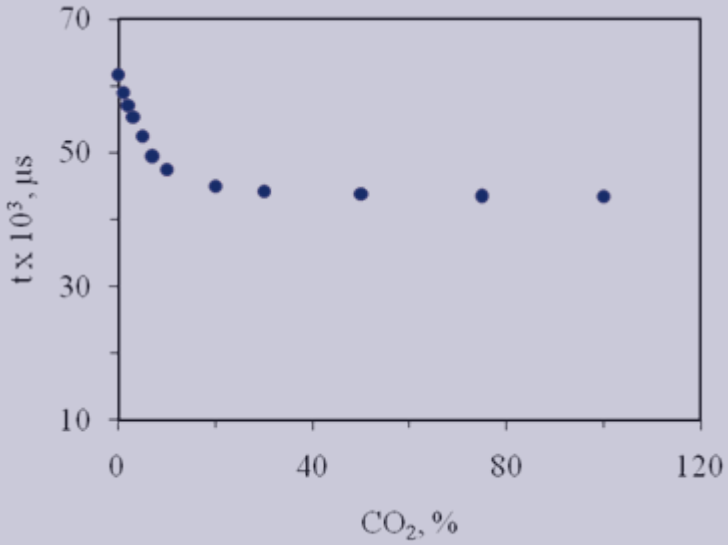
- To determine the optimum distance between LEDs tips
- Study of the response at different distances at pure N_2 and pure CO_2



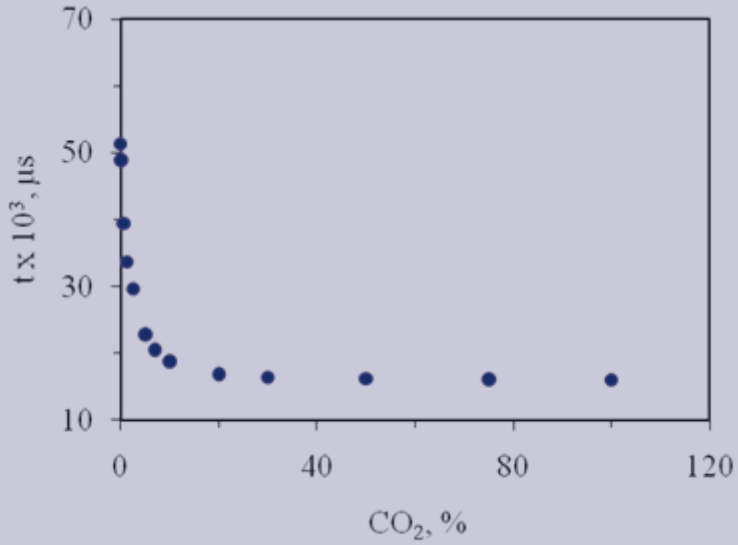
A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Instrument response to carbon dioxide

Configuration 1



Configuration 2



A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Instrument response to carbon dioxide

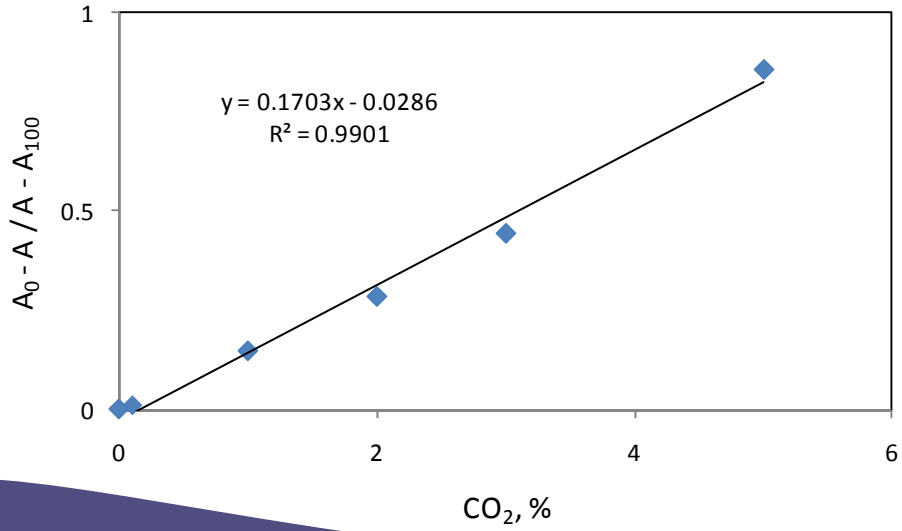
$$\frac{\left[TOA^+HCO_3^- \cdot (x-1)H_2O \cdot HN\right]}{\left[TOA^+N^- \cdot xH_2O\right]} = K\left[CO_2\right] = \frac{A_0 - A}{A - A_{100}}$$

$$A = \log\frac{I^0}{I} = -\log\frac{t^0}{t}$$

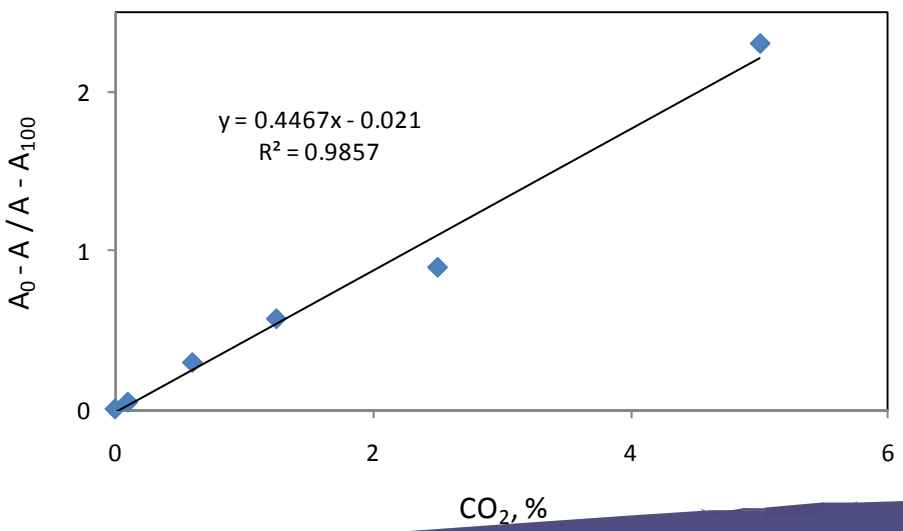
A_0 : A at 0 (deprotonated form)
A_{100} : A at 100 % CO_2 (protonated form)
A: A at any concentration.

t^0: t in the absence of the indicator membrane
t: membrane included at any CO_2 %

Configuration 1



Configuration 2



A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Calibration function

In order to linearise the response

Relative signal

t_{100}: t at 100 % CO_2

t_0: t at 100% N_2

t: t at any % CO_2

$(t_{100} - t_0) / (t - t_0)$ → R

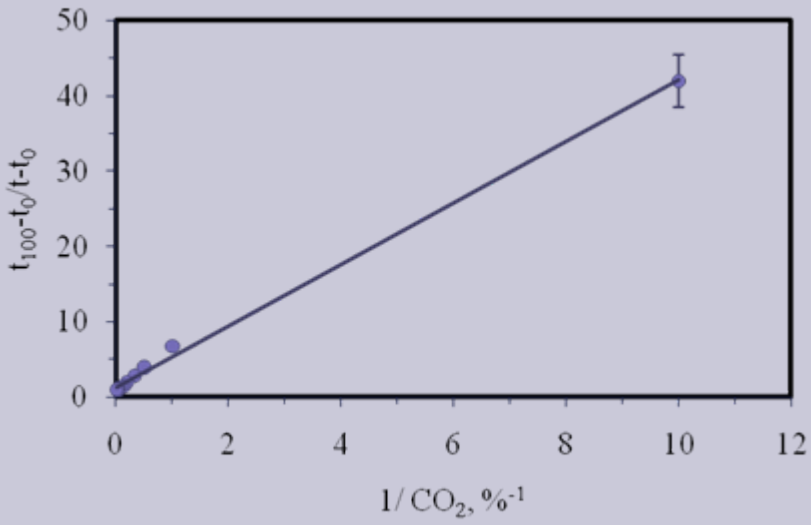
VS

$1/[CO_2]$

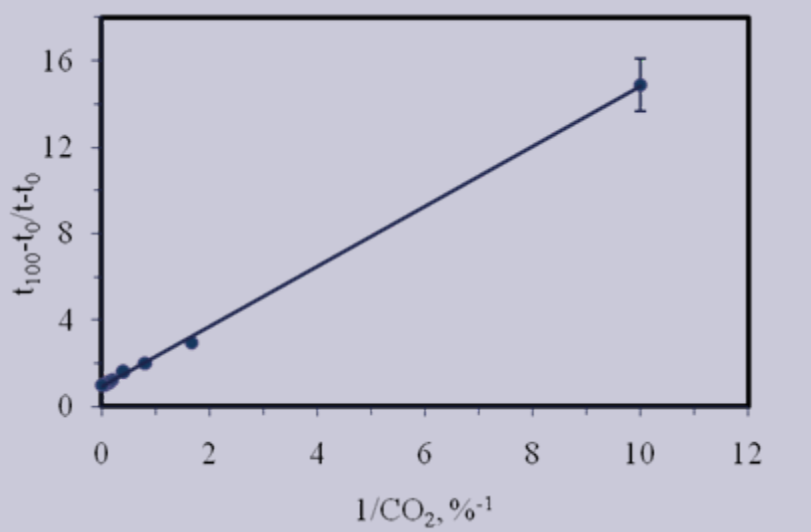
A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Calibration function

Configuration 1



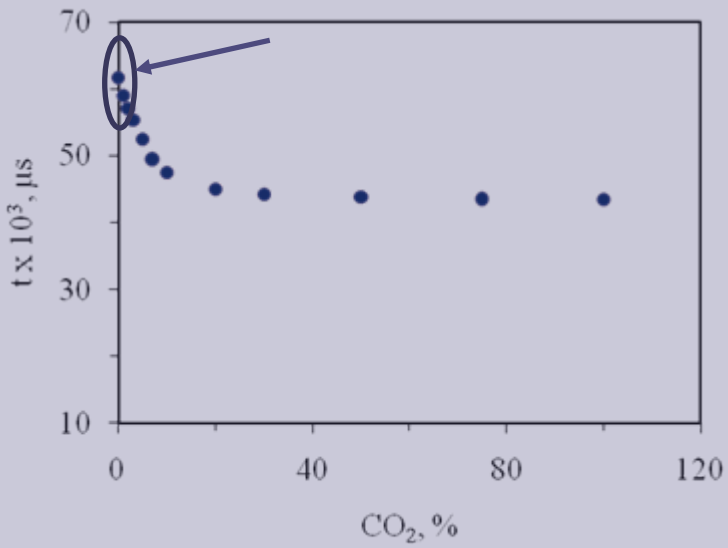
Configuration 2



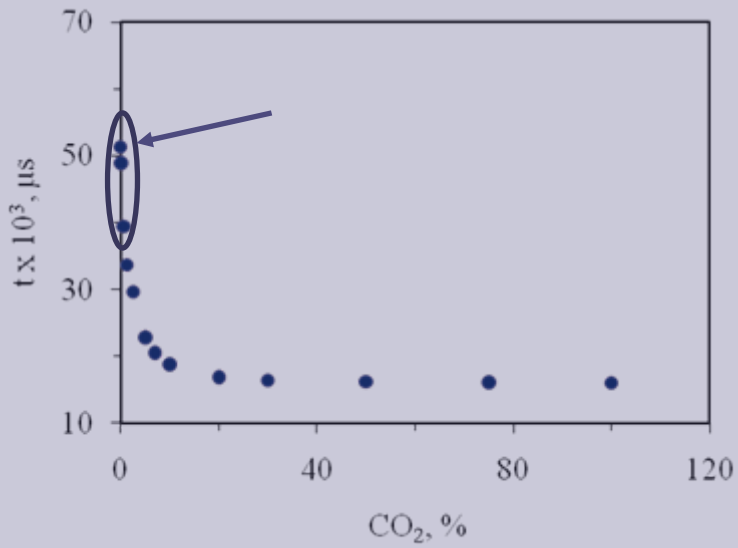
A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

LOD

Configuration 1



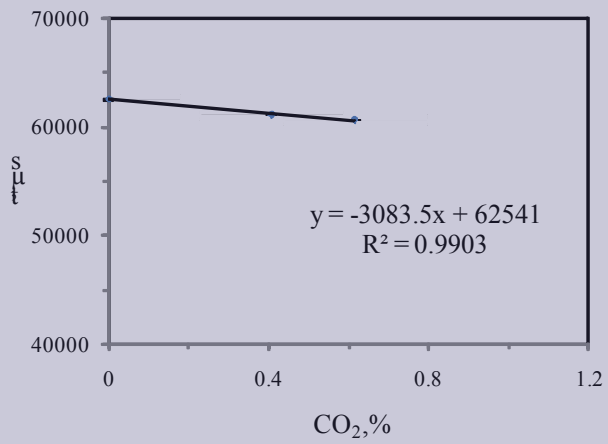
Configuration 2



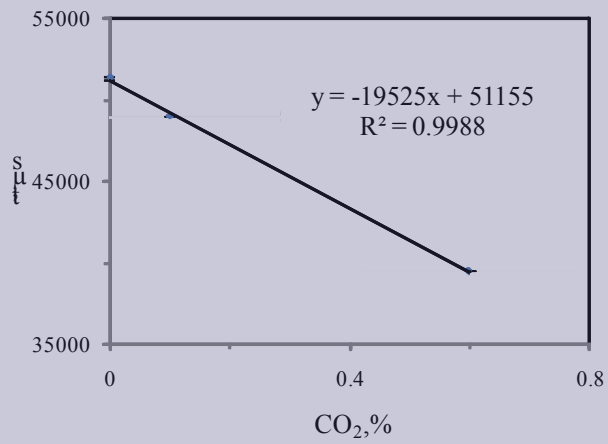
A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Limit of Detection

Configuration 1



Configuration 2



A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Limit of Quantification

LOQ ⇒ Calibration function

s_0: critical level

$$t_{LOQ} = t_0 - 10s_0$$

$$R_{LOQ} = \frac{t_{100} - t_0}{10s_0}$$

A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

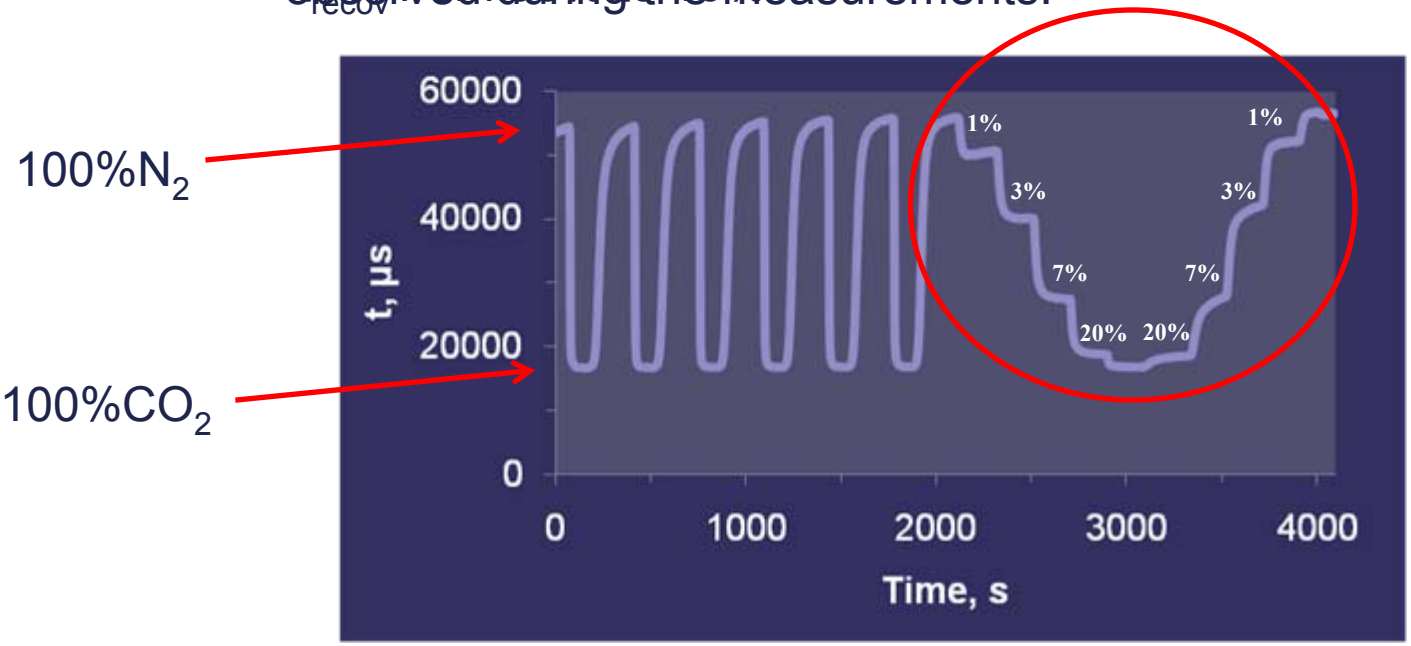
Comparison between both configurations

	t_0-t_{100} (µs)	Slope	LOD (%)	LOQ (%)
Configuration 1	18,175	5.962	0.0082	5.86
Configuration 2	35,358	1.379	0.0066	2.67

A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Dynamic response

- Alternating atmospheres of pure CO_2 and pure nitrogen
- The signal changes were fully reversible and hysteresis was not observed during the measurements.



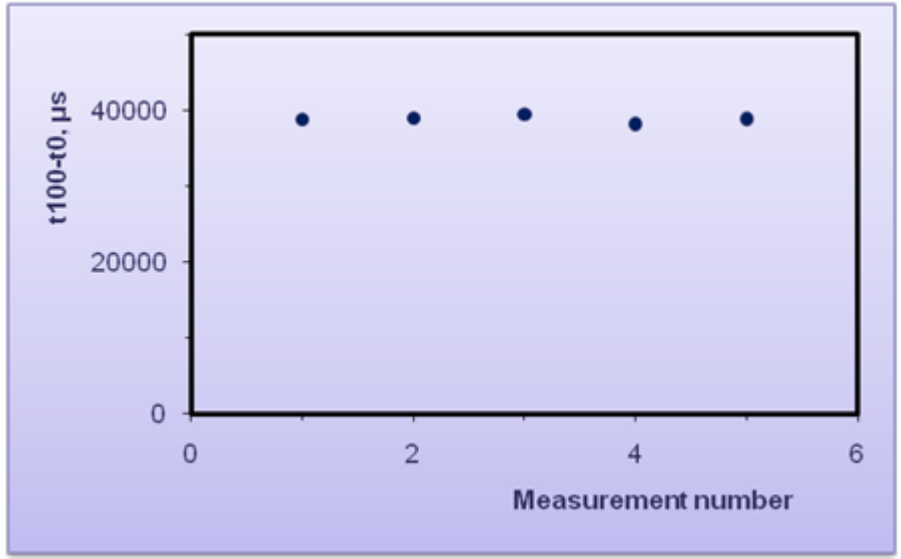
t_{resp} 11.0 ± 0.9 s
t_{recov} 55.3 ± 4.8 s

A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Precision of the system

Intra-day | Intra-day | Inter-day

- 5 measurements at 100% N_2 and 100% CO_2 using the same membrane
- 45 minute intervals with 8 replicates each.
- RSD 1.15%

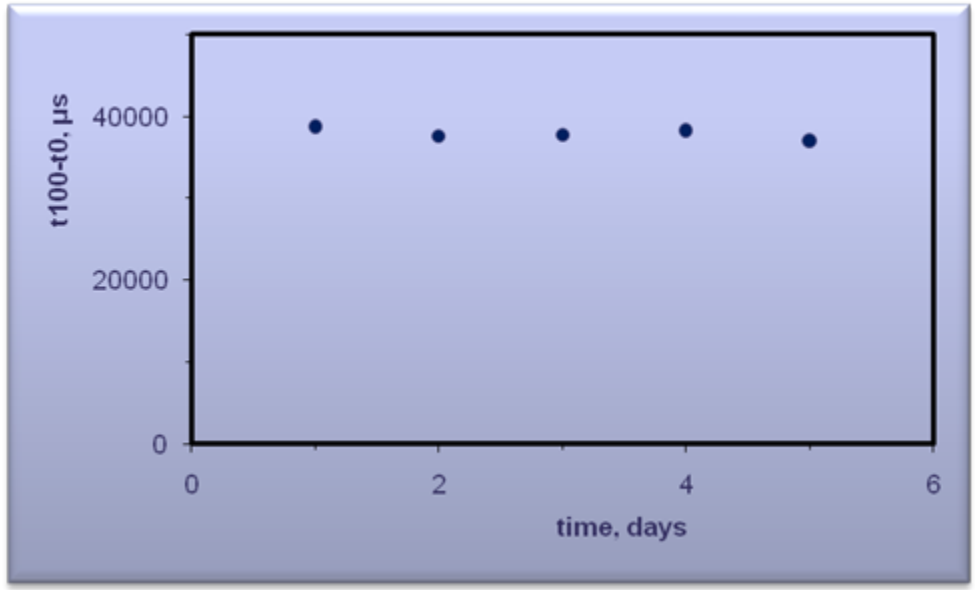


A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Precision of the system

Inter-day

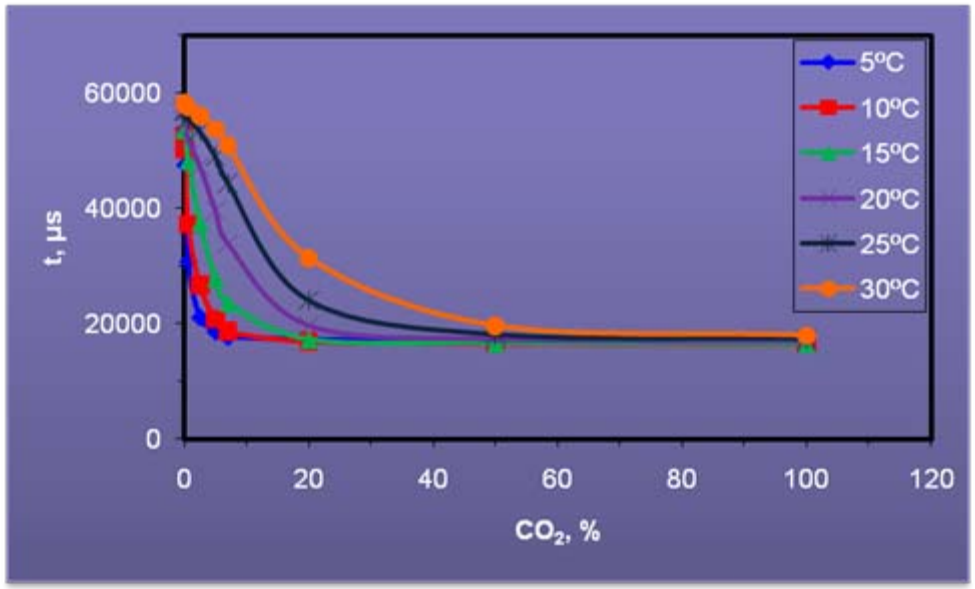
- 5 measurements at 100% N_2 and 100% CO_2 using the same membrane
- 5 days in a row
- RSD 1.77%



A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Temperature influence 5-30ºC

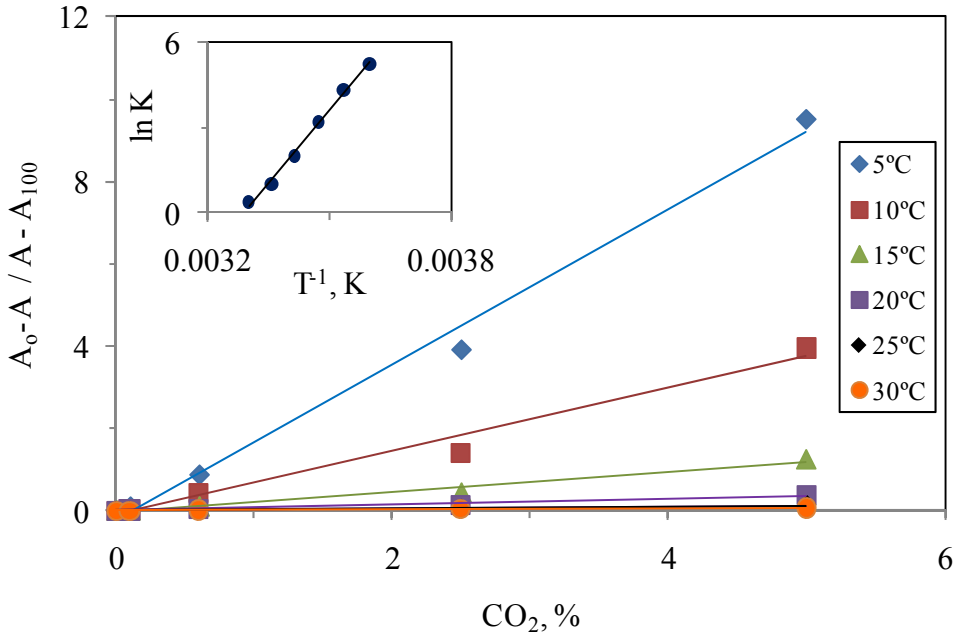
- Considerable influence on the sensitivity of CO_2 sensors
- The slope decreases with increasing T



A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Temperature influence 5-30ºC

- Model of T
- ΔG<0, that means that the reactions are spontaneous

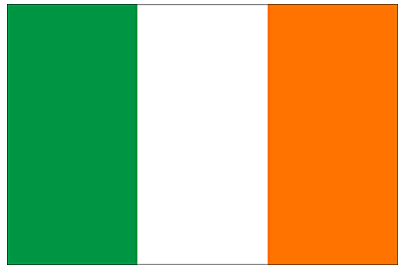


ΔH = -142 KJ/mol
ΔS = -208 J/mol·K

A NEW LED-LED PORTABLE CO_2 GAS SENSOR BASED ON AN INTERCHANGEABLE MEMBRANE SYSTEM FOR INDUSTRIAL APPLICATIONS

Conclusions

- This system could form the basis of versatile handheld instrument for industrial applications
- Two configurations studied, the most sensitive was selected
- The sensing membranes were prepared on interchangeable supports to give an extra degree of freedom
- Complete analytical characterization with good results



ECsens Group

Adaptive Sensors Group

ACKNOWLEDGEMENTS

- Prof. Dermot Diamond
- Dr. Fernando Benito-López
- People of the Adaptive Sensors Group

Financial support

- Ministerio de Ciencia e Innovación, Dirección General de Investigación y Gestión del Plan Nacional de I+D+i (Spain) (Projects CTQ2009-14428-C02-01 and CTQ2009-14428-C02-02)
- Junta de Andalucía (Proyecto de Excelencia P08-FQM-3535)
- European Regional Development Funds (ERDF)
- Science Foundation Ireland under grant 07/CE/I1147
- I.M. Pérez de Vargas-Sansalvador wants to thank Junta de Andalucía for incentivo estancias breves 3/2009

Thanks for your attention

¡Gracias!