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Water based-ionic liquid carbon dioxide sensor for applications in the food industry

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ABSTRACT

A new water-based sensor for carbon dioxide containing an ionic liquid is presented. The sensor is based on the acidity of the CO_2 molecule. The sensor incorporates an ionic liquid in the matrix, which enhances CO_2 solubility, and minimising the response and recovery times of the sensor. The entire concentration range (0–100%) of CO_2 in water has been studied. The sensor is more sensitive at low CO_2 concentrations as is usual in this kind of optical sensor. As the sensor is intended for smart food packaging, one of the most important characteristics is stability, and this has been studied under different conditions of light, temperature and relative humidity. The sensor was found to be stablef or more than 14 days, which is the period of use for the intended application.

Pork chops were packed at 4 °C and the production of CO_2 studied in conjunction with total bacterial counts over a period of 14 days. The results show that the concentration of CO_2 dioxide increases in time, in correlation with bacterial counts. As the threshold of CO_2 content for human consumption of this meat is 20%, the sensor has been optimised for detection around this concentration.

1. Introduction

The importance of CO_2 is evident in different fields such as environmental [1], clinical [2], biological [3] and industrial [4,5]. In recent years, the determination of CO_2 has attracted great interest, along with other gases such as oxygen and nitrogen in confined spaces [6]. This is especially interesting for the control of insect pests in art and archaeological items in museums, through controlled atmosphere treatment (CAT), in which CO_2 gas is used to displace oxygen within a sealed enclosure to a percentage low enough to kill all stages of the insect life-cycle [7]. The treatment time is typically four-weeks, over which it is imperative that the CO_2 does not fall below 60%, and therefore the strict control of CO_2 level is essential during that period of time. The use of climate chambers with modified atmospheres is becoming popular among art museums and collections to avoid the deterioration of items [8]. Controlled Atmosphere Storage is also used in food industry, for example for fruits and vegetables and has great importance in extending their postharvest life [9].

Another example of the importance of CO_2 in confined environments is tracking of CO_2 in modified atmospheres of packaged food and particularly meat products. In a normal environment, meat products are packed in a modified atmosphere, which typically consists of a mixture of nitrogen, oxygen and CO_2 which has been optimised [10] to expend the lifetime of the food. This modified atmosphere inhibits the early deterioration of meat products, allowing for longer shelf life, maintaining freshness, colour stability and the inhibition of microbial spoilage [11,12].

The CO_2 levels inside meat packages can be used as indicator of freshness. A change in CO_2 concentration during storage is a clear indication that bacteria are growing inside the container and/or the package is not properly sealed and the modified atmosphere has been compromised. However, a non-destructive method for determining the CO_2 concentration within such packages has not, as yet, been reported.

In order to integrate smart materials as sensor systems in packaging, they need to be compatible with printing technology for mass production used in the industry, as this is required to maintain low unit-cost relative to the value of the food product. In addition, printing is an attractive option for sensor fabrication due to ease to use, accuracy and precision, reliability, and alignment with food safety requirements. The major restrictions that impede the use of current sensors in food are: instability of chemistry used, toxicity of sensor materials, difficulty of integration into food packages at an acceptable cost, and difficulty of detection [13]. Recently it has been reported by Puligunda et al. that "the development of efficient CO_2 sensors that can intelligently monitor the gas concentration changes inside a food package and specific to food packaging applications is essential" [14].

Most existing CO_2 optical sensors are based on absorption by the gas at the 4.26 μm IR absorption band [15]. However, there are two

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important drawbacks to this approach: (i) the strong interference by water vapour and (ii) the cost of the sensors. In recent years, there have been many publications on CO_2 sensor development based on absorbance [16–18] or luminescence [19,20] in combination with acid-based indicators, but none of these sensors have been investigated for application in smart packaging technologies. Optical CO_2 sensors based on the acidity of this molecule are normally solvent-based sensors, but in the food packaging industry these suffer from the drawback of long-term instability, arising from decomposition of the commonly used quaternary ammonium hydroxide derivatives [18,21]. In this work, we have avoided using these compounds. Instead, water based sensors have been prepared using meta cresol purple sodium salt as the indicator, glycerol as plasticizer and sodium hydrogencarbonate as buffer in a matrix of hydroxyethyl cellulose. In this way, the lifetime is increased and also this composition creates an easily printable ink. To our knowledge, this type of water based sensor for CO_2 has been reported only once previously, by Mills et al. [16]. However, in an additional development, we have included ionic liquids (IL) in the matrix, making the sensor more selective to CO_2 than other gases due to its higher solubility. Ionic liquids have been used previously in solvent based CO_2 sensors [22,23]. In the first case, the sensors prepared were liquid sensors[22], and could not be used as a smart material for the food industry. In the second case [23], the IL was used together with 1-hydroxy-3,6,8-pyrenetrisulfonate (HPTS) and tetraoctylammonium hydroxide (TOAOH) in a matrix of ethyl cellulose to generate a fluorescence-based analytical signal. However, these sensors are highly difficult to implement in the food industry because (i) they need be spread over the substrate in the basic form and (ii) the system of detection is not a simple device, making it difficult to implement as a food freshness indicator. In contrast, the sensing chemistry for CO_2 studied in this paper is based on plastic solid-state sensor membranes that respond to the acidity of the CO_2 molecule. In this system, an acid–base indicator (MCP) is included in a CO_2 permeable membrane containing hydrogen carbonate as an internal buffering system to (i) ensure the indicator is predominantly initially the deprotonated form and the basic form is stabilised as a hydrated ionic pair and (ii) to enable the uptake of CO_2 from the atmosphere by forming a hydrogencarbonate buffer. The change in the position of the acid–base equilibrium by CO_2 in the membrane is transduced into a change in colour/absorbance of the indicator immobilised in the membrane.

The gaseous CO_2 dissolves in water according to the following equations:

$$CO_2\,(g) \leftrightarrows CO_2\,(l) \quad K_D = 3.3\cdot 10^{-2} \quad (1)$$

$$CO_2\,(l) + H_2O \leftrightarrows H_2CO_3 \quad K_h = 2.6\cdot 10^{3} \quad (2)$$

$$H_2CO_3 + H_2O \leftrightarrows HCO_3^- + H_3O^+ \quad K_1 = 1.72\cdot 10^{-4} \quad (3)$$

$$HCO_3^- + H_2O \leftrightarrows CO_3^{2-} + H_3O^+ \quad K_2 = 5.59\cdot 10^{-11} \quad (4)$$

A change in the pH of the medium is detected by a pH indicator HIn present in the same medium that changes colour:

$$\underset{colour\ 1}{HIn} + H_2O \leftrightarrows \quad \underset{colour\ 2}{H_3O^+ + In^-} \quad (5)$$

The pKa of the indicator selected should be adequate to change the position of the equilibrium in the presence of protons generated by the dissociation of carbonic acid originating from the CO_2 (Eq. (3) above). It has been reported that the preferred pK_a should be around 7.0–8.3 and for this reason, the appropriate pH indicators used to sense CO_2 include α-naphtholphthalein [29], thymol blue, and bromo thymol blue [30].

To the best of our knowledge, this is the first report of a water based colorimetric CO_2 sensor for use in smart food packaging that has unique advantages arising from an ionic liquid in the matrix.

2. Experimental

2.1. Reagents and materials

2-Hydroxyethyl cellulose (HEC, average Mv ~90,000), meta-cresol purple sodium salt (MCP), glycerin, sodium hydrogencarbonate and the ionic liquid 1-ethyl-3-methyl-imidazolium chloride were all sourced from Sigma–Aldrich Química S.A. (Spain). For microbiology buffered peptone water (LAB046), maximum recovery diluent (LAB103), Plate Count Agar (PCA) LAB149, pseudomonas agar base (LAB108), violet red bile agar (VRBA) (LAB031) all from LAB M Heywood (Lancashire, UK) were used. All aqueous solutions were made using reverse-osmosis quality water (Mili-RO 12 plus Milli-Q station from Millipore, conductivity 18.2 MΩ cm).

Pork boneless chops were bought from the Butchers Shop (Omni shopping centre, Santry, D9, Ireland) and high barrier bag material BB3055 specific for meat products were obtained from Sealed Air (Seville, Spain).

Additionally an homogeniser Stomacher AGB Scientific Ltd, (Dublin Ind Est Dublin 11 Co. Dublin, Ireland), a heat sealer PFS-300MM Electric Impulse Sealing Machine C. (Media w.s. trade sl Barcelona, Spain) and a CheckPoint – Handheld Gas Analyzer (O_2/CO_2) Dansensor A/S (Rønnedevej 18, DK-4100 Ringsted, Denmark) to O_2 and CO_2 measurements inside meat packages, were used.

The standard mixtures for instrument calibration and characterization were prepared using N_2 as the inert gas by controlling the flow rates of the different high purity gases CO_2 and N_2, entering a mixing chamber using a computer-controlled mass flow controller (Air Liquid España S.A., Spain) operating at a total pressure of 760 Torr and a flow rate of 500 $cm^3\ min^{-1}$.

To produce different humidity conditions (from 14 to 100% RH), a CEM system was used. This system consists of a mass flow controller for measurement and control of the carrier gas flow (mixtures of N_2 and CO_2), a mass flow meter for liquids (MiniCoriflow) with a range of 0.4–20 g/h of liquid (water in this case), and a CEM 3-way mixing valve and evaporator for control of the liquid source flow and mixing the liquid with the carrier gas flow resulting in total evaporation. Moreover, it contains a temperature-controlled heat-exchanger to add heat to the mixture to produce complete evaporation of the liquid (100 °C was selected for water).

2.2. Preparation of CO_2 sensing membranes

Sensing membranes for CO_2 were prepared from a cocktail containing 12.5 mg of HEC, 1.4 mg MCP, 2.25 mg $NaHCO_3$ and 37.5 mg glycerin all dissolved in 1 mL of water, using an ultrasonic bath. Two versions were studied, with and without addition of ionic liquid (IL). In the case of IL addition, 80 μL was taken from the sensor cocktail and 2 μL of the IL added and homogenised. The sensor preparation consists of casting the membrane on one side of a Mylar support (Goodfellow, Manchester, UK) from 20 μL of the cocktail. After that, the support was left to dry in darkness in a box for 6 h at room temperature.

2.3. Spectrophotometric measurement

For the characterization of the sensing membranes, steady-state measurements were performed using a Hewlett Packard diode array

spectrophotometer (model 8453; Nortwalk, CT, US) for absorption measurements. The measurements of the sensing films were performed using a homemade cell holder, so that the gas flux was directed to the sensing membrane.

2.4. Colour measurement

The membranes were imaged using a Sony DSC-HX300 digital camera (Japan) placed inside of a homemade wooden enclosure (see Fig. 1) illuminated with two LED-lamps (6500 K, illumination inside of the box = 9680 Lx) placed at 90° with respect to the digital camera to minimise any interference from external light.

The optimised settings used to photograph the sensing membrane were ISO 80, shutter speed 1/320 s, aperture value f/4, focal distance 14 mm; white balance, automatic; resolution, 3648 × 2736; mode, macro.

The hue or H component of the hue, saturation, value (HSV) colour space of the region of interest (ROI) of the membranes were determined using Image J software (National Institutes of Health) along with the Color Space Converter plugin to generate the median values of the H parameter from the pixels (around 153000) that compose the ROI. ROI is defined as the area of the digitalised membrane selected to perform the colorimetric analysis in order to get analytical information.

2.5. Microbiology experiments

Raw pork was purchased fresh from a butcher, packaged in 500 g quantities inside CO_2/O_2 impermeable bags, and sealed using an impulse bag sealer. The samples were stored at 4 °C and analysed over time for the presence of total aerobic count and members of the families *Pseudomonadaceae* and *Enterobacteriaceae*.

For the bacteriological analysis of packaged raw pork, 27 g of sample was weighed into a sterile petri dish using an aseptic technique, transferred into 243 mL of Buffered Peptone Water and homogenised using a stomacher for 30 s. Serial dilutions of 9 mL aliquots of Maximum Recovery Diluent were prepared and suitable dilutions were plated in triplicate and poured with plate count agar (PCA-Total aerobic count), Pseudomonad agar (*Pseudomonads*) and VRBA (*Enterobacteriaceae*). Plates were incubated as follows: PCA 22 °C for 48 h and 37 °C for 24 h, pseudomonads 30 °C for 24 h and VRBA 37 °C for 24 h. Following incubation plates were counted and the result expressed as numbers of organisms/g. pork.

3. Results and discussion

3.1. Correlation bacteria count versus concentration of CO_2. bacteriological analysis of packaged raw pork

The intended use of this sensor is as a freshness indicator in pork meat, and therefore the first experiments carried out were performed in order to find out the concentrations of CO_2 that can be correlated with the state of the packaged meat. In order to know the state of the meat, the correlation of the gases inside the package with bacteria present must be studied. *Pseudomonas* spp., *Enterobacteriaceae* [24] and TVC [25] (Total Viable Count) are key parameters to evaluate this. It has been accepted that 10^7 cfu/g/mL or cm^2 is the threshold for indicating meat spoilage [26]. It has been previously demonstrated [14] that the increase in the percentage of CO_2 in packaged food can be correlated with the freshness state in kimchi [27], pea and tomato soup [28], salads [13] and meat. Rukchon et al. found an increase in CO_2 percentage in chicken breast during its spoilage [24], the experiments suggesting that chicken breasts stored at 4 °C remained stable for 6 days.

Therefore, the following experiments were carried out to correlate bacteria count versus concentration of CO_2 for the new sensor. Each day of analysis, one of the stored meat packages was selected and before opening to perform the bacteriological analysis, the concentration of CO_2 was measured by the Checkpoint analyser. Experiments were performed at days 0, 2, 5, 7, 9, and 12. Fig. 2 shows the increase in CO_2 and bacteria count over time.

The correlation between bacterial counts and gas release is clearly shows that from day 5 and the CO_2 concentration rises above ca. 20% and simultaneously the bacterial count crosses the threshold of 10^7 cfu/g/mL or cm^2. It can be observed from Fig. 2 that the concentration of oxygen decreases until day 7, at which point all oxygen has been used for bacterial growth, and from that day on the bacterial count and concentration of CO_2 remain practically constant.

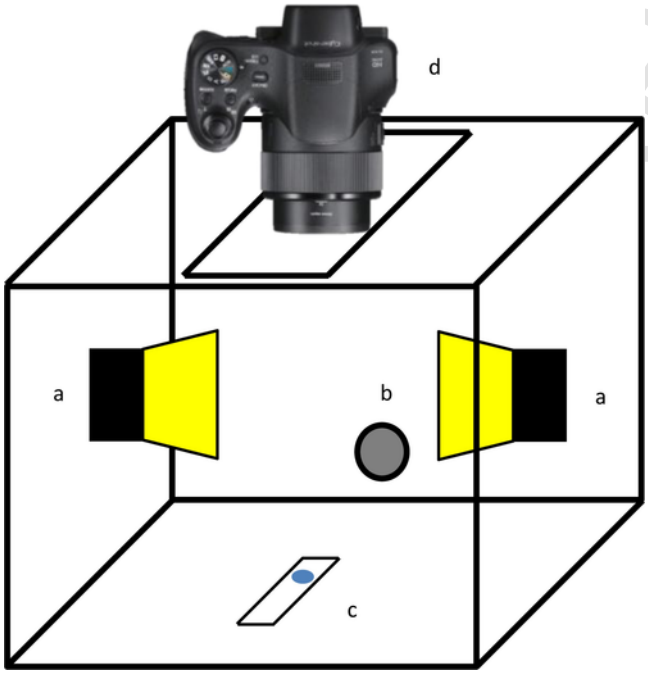

Fig. 1. Homemade light box used to digitalize the membranes. a) LED-lamps; b) gas inlet; c) membrane and d) digital camera.

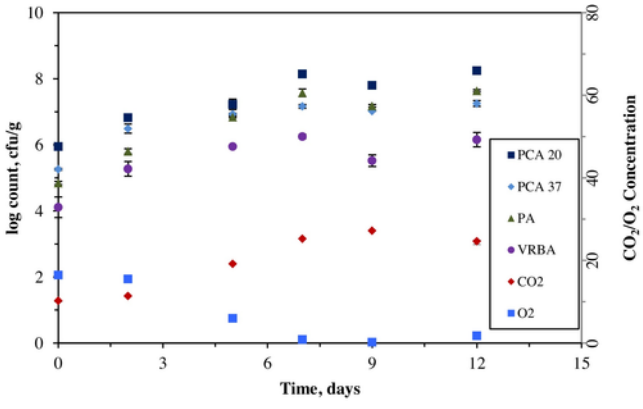

Fig. 2. Bacterial growth versus time (x axis) and O_2/CO_2 concentration (y_2 axis) inside packages. PCA 20 (Total aerobic count at 20 °C), PCA 37 (Total aerobic count at 37 °C), PA (Pseudomonads), VRBA (Enterobacteriaceae).

It can be concluded from this experiment that the CO_2 sensor should be highly sensitive for concentrations up to 20% CO_2 and the stability should be greater than 10 days (2 weeks). In this study, meat spoilage occurred after 5 days, but twice this period was selected for the sensor lifetime to cover extended meat lifetimes due to modified atmosphere packaging.

3.2. CO_2 sensing membrane characterisation

The ideal sensor characteristics for this application encompass the following easily printable ink compatible with the food packaging process, sufficient sensitivity over the relevant CO_2 concentration range (20% target concentration) and high stability, especially in ambient light.

The absorption spectrum of the CO_2 sensor membranes was monitored by UV–vis absorption spectroscopy as a function of CO_2 concentration, and exhibited two peak maxima; one at 420 nm that increases with CO_2 concentration, and another at 595 nm, that decreases with CO_2 concentration, and together with an isosbestic point at 495 nm, indicating the existence of an equilibrium between both dye forms (blue/yellow) with equal molar absorptivity at this wavelength.

Fig. 3 shows the response of the sensing membranes at different concentrations of CO_2 ranging from 0 to 100% at 595 nm. From this, the typical decay function of absorbance versus CO_2 concentration can be obtained [31,32]. Fig. 3 shows the sensor sensitivity is higher at low concentrations of CO_2, and as the threshold established by bacteriological analysis was around 20% the composition of the cocktail has been optimised to maintain a high sensitivity at low concentrations of CO_2. This depends on the kind of modified atmosphere used for the packaged food as, if high concentrations of CO_2 are used, the sensitivity of the CO_2 sensor should be moved towards higher concentrations. In this example, no modified atmosphere has been used and 20% is the preferred threshold for detection.

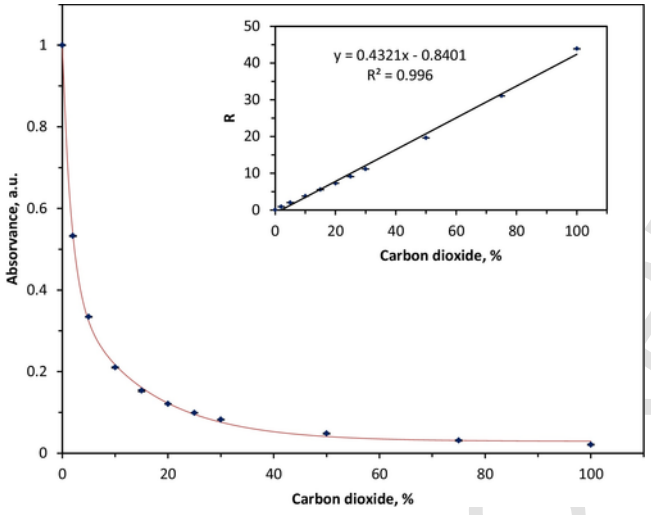

Fig. 3. Absorbance at 595 nm versus CO_2 concentration from 0 to 100%. Inset. R versus the concentration of CO_2.

In order to obtain a linear function, the parameter R can be described as the ratio of the concentrations of the protonated to deprotonated forms of the indicator [32] and calculated using the absorbance at 0% of CO_2 (A_o), at 100% of CO_2 (A_∞) and at any intermediate value measured at the wavelength of the maximum for deprotonated indicator (Eq. (6)).

$$R = \frac{A_o - A}{A - A_\infty} = \frac{[HIn]}{[In^-]} \quad (6)$$

If R is plotted versus the concentration of CO_2, a straight line is obtained that confirms the reaction ratio 1:1 between CO_2 and MCP.

The inclusion of the IL 1-ethyl-3-methyl-imidazolium chloride is key in making the sensor more selective to CO_2 than other gases due higher CO_2 solubility [33] which reduces the response and recovery times of the sensor. A study of the dynamic response of the sensing membranes when exposed to alternating atmospheres of pure CO_2 and pure N_2 was carried out. The response time was calculated from between 10% and 90% of the maximum signal. Table 1 shows the differences between the dynamic behaviour of sensing membranes having IL or not in their matrix.

As can be observed in Fig. 4. A and B, the response and recovery times are much quicker in the case A than B, where a membrane containing IL has been used.

The limit of detection (LOD) was calculated from the calibration function (inset Fig. 3), by using the conventional approach defined by $LOD = R_0+3s0$, where R_0 is the blank or average value in the absence of CO_2 and s_0 is the critical level or standard deviation of the blank, which was determined from six replicate measurements. The limit of quantification (LOQ) of the instrumental procedure was obtained by using $LOQ = R_0 + 10s_0$. The LOD found by using this approach was 0.36% CO_2 and the LOQ was 0.37% CO_2.

Table 1
Response and recovery times of sensing membranes containing (A) and not containing IL (B). n = 3.

Membrane containing IL (A)		Membrane no containing IL (B)	
Response Time	Recovery Time	Response Time	Recovery Time
17 ± 1 s	105 ± 4 s	530 s ± 20 s	540 s± 32

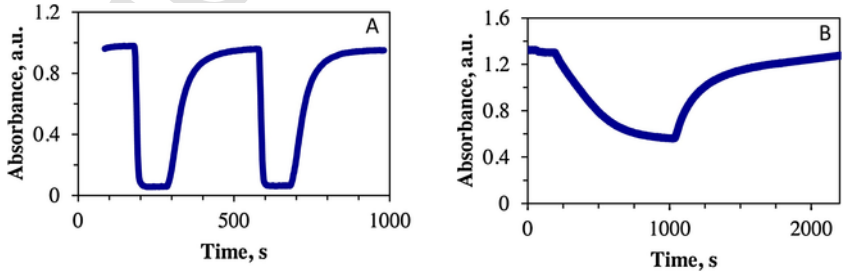

Fig. 4. Dynamic behaviour of sensing membranes. (A) containing IL (B) without IL.

3.3. Humidity dependence

Given the intended application of the sensor, high relative humidity is expected in the packaged meat so dependence to humidity must be studied. A serial of calibrations were carried out in triplicate from 0 to 100% of RH (Fig. 5). As can be observed from Fig. 5 the dependence is not very high compared to other CO_2 sensors [16]. In fact, the response is only slightly unaffected (the slope of the calibration function varies between 0.1864 and 0.235), and this can be explained by the use of the ionic liquid in the sensor matrix. If the sensitivity (as slope of calibration function) is plotted versus the concentration of CO_2 (Fig. 6) a slight decrease is observed when the relative humidity increases, but it is a really small change (slope = −0.0005/%RH). However, it does affect the sensor stability (see following section).

3.4. Stability of sensing membrane

The stability of the sensor is a crucial variable for maximizing the duration of service and is a key factor in its future application. The application in meat packages for the food industry requires at least 2 weeks lifetime to be implemented in real situations. Different environments were studied using a set of three sensors for each experiment: a) conventional light conditions, RT (room temperature), b) darkness, RT and high humidity, c) darkness and RT d) darkness high humidity and 4 °C. The results are summarised in Table 2. It can be concluded from this set of experiments that light does not significantly affect the performance of the sensor, and is much less compared to solvent based sensors for CO_2 [16,20,34]. Actually, there is no observable difference for sensors kept under ambient light conditions and those kept in darkness. However, relative humidity has a high effect on the stability of the sensor, but high relative humidity together with low temperature does not appreciably affect the stability of the sensor, and under these conditions it can perform satisfactorily for more than 2 weeks (i.e. the stability required for the intended application can be met under the storage conditions typically used).

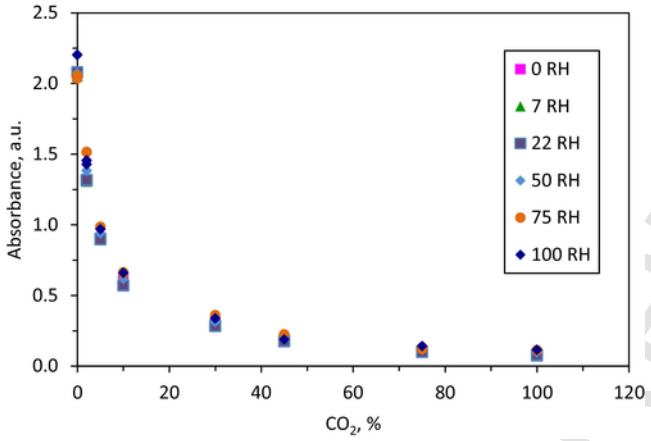

Fig. 5. Absorbance versus CO_2 concentration at different values of RH.

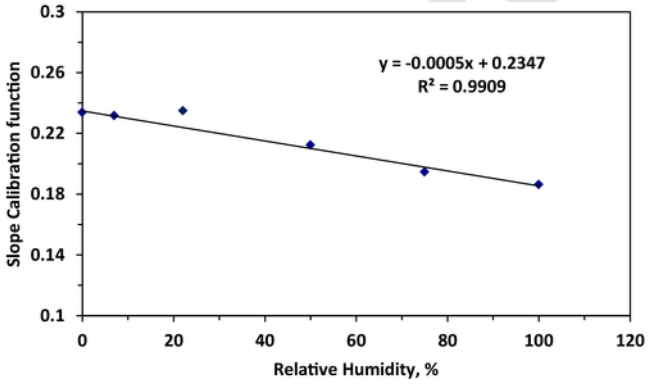

Fig. 6. Sensitivity of calibration functions obtained at different percentages of RH.

Table 2
Summary of lifetime of the CO_2 sensor under different conditions.

Conditions	Stability
Conventional light conditions,RT	1 month
Darkness, RT	1 month
High relative humidity, darkness and RT	1 week
High relative humidity, darkness and 4 °C	2 months

The stability durations shown in Table 2 have been calculated for the sensors stored under the same conditions through the entire study. After the stability duration is exceeded, the sensor calibration function starts to change (becomes curved), so the sensors still respond to CO_2 over the whole range, but with different sensitivity. The criterion for stability is that the slope of the calibration function changes by more than 10% from the original calibration on day 1. is a variability of the slope of the calibration function less than 10%.

Calibrations were carried out twice a week during the whole period studied for each set of membranes kept under the different conditions studied. Fig. 7 shows the calibration function for each set of experiments. Each calibration function shown is representative of the entire stable lifetime.

The stability of sensor is a key parameter as this will define its applicability. Often in the literature, such sensors are kept under special storage conditions such as in desiccators and under specially controlled humidity or light conditions. But if the sensor is intended for real applications, more realistic storage conditions should be studied. Table 3 shows the stability shown for different CO_2 sensors found in literature.

3.5. Applicability

The intended application of this sensor is as freshness indicator that could be monitored using a simple digital camerawith the ultimate aim to create an Android application that could be implemented in a mobile phone.

The hue or H component of the hue, saturation, value (HSV) colour space is calculated here instead the well-known and often used RGB coordinates, due to. The reason why the H is selected is because the robust nature and superior precision when tracking colour changes in digital images. This parameter has been demonstrated to be 2–3 times superior than RGB, due to small variations in signal with indicator concentration, membrane thickness, detector spectral responsivity, and illumination [36,37].

Calibration functions were carried out at different concentrations of CO_2 and pictures were taken at each concentration. Images were analysed using the program ImageJ and the hue (H) coordinate calculated. Fig. 8. shows the colours obtained at different concentration of CO_2 and Fig. 9 the H coordinate versus the percentage of CO_2.

Data can be fitted to an exponential growth function (red line), which returns the following equation $y = -0.49705^{\frac{x}{-7.76348}} + 1.16483, r^2 = 0.99015$. Results obtained are in concordance agreement with the those obtained using the Spectrophotometer, with higher changes at low CO_2 concentrations and

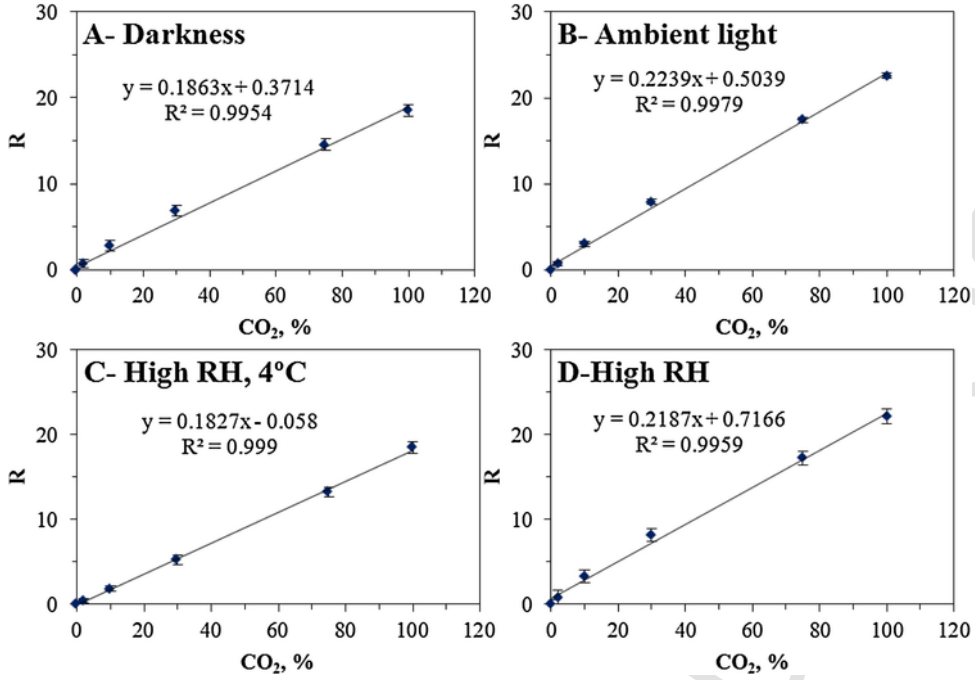

Fig. 7. R versus CO_2 concentration. Calibrations obtained at different conditions A) Darkness B)Ambient light C) High RH and 4 °C and D) High RH. The points represent the average of all measurements across respective CO_2 concentrations, error bars are the standard deviation, and a linear fit is given as the black lines.

smaller changes at high CO_2 concentrations. At 20% of CO_2 the signal is ca. 90% of the total response of the H value.

4. Conclusions

The work documented in this paper has detailed the development of a CO_2 sensor based on a colorimetric membrane incorporating an IL and targeting applications in the food industry (pork meat). The inclusion of an ionic liquid in the matrix improves the dynamic response. This sensor was studied using a spectrophotometer and a digital camera, with the latter showing a strong correlation between gas concentration and hue coordinate. This represents the basis of a smartphone based detection system that could be used by consumers and food industry workers. A study related to the correlation between the gas generated by pork meat over time versus the total bacteria count identified 20% of CO_2 as the threshold for indicating pork meat spoilage in unmodified atmosphere packaged samples. The feasibility of this new sensor was studied under different conditions showing that at high humidity and 4 °C (conditions of commercialised packed meat) a stability of more than two weeks was obtained, which meets the requirements for the intended application.

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Table 3
Examples of CO_2 sensor found in literature.

Type of measurement	Components of the membrane	Storage conditions	Lifetime	Reference
Absorbance	MCP, $NaHCO_3$, HEC, Gly, IL	Ambient light	30 days	Current study
		Darkness	30 days	
		High RH	7 days	
		High RH, 4 °C	60 days	
Phosphorescence	TBP, α-NP, TMAOH, EC	Darkness	515 days	[35]
	TBP, α-NP, TMAOH, DBU		20 days	
	TBP, α-NP, TMAOH, HPMC		390 days	
	α-NP, TMAOH, HPMC, TWEEN 20		300 days	
Phosphorescence	PtTFPP, α-NP, CTAOH, EC	4 °C	14 days	[13]
		RT	7 days	
		4 °C and MA	21 days	
Absorbance	MCP, HEC, Gly, NaHCO3	Laboratory conditions	After 21 days starts to fade	[16]
Phosphorescence	PtOEP, α-NP, TOAOH, EC	33% RH	Half-signal 4–7 days	[20]
		95% RH + light	Half-signal 4–7 days	
		95% RH + darkness	Half-signal 11 months	
Fluorescence	HTPS, EC, EMIMBF4	Laboratory conditions	Lost in signal by 10–24% after 95 days	[23]
Fluorescence	HTPS, EC, TOAOH	Desiccator + Sodium carbonate	16,2% signal drift after 5 days	[31]

TBP: Tributhylphosphate, α-NP: α-naphtholphthalein, TMAOH: tetramethylammonium, EC: Ethylcellulose, DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene, HPMC: MethocelE-5 Premium, PtTFPP: Pt-porphyrin, CTAOH: cetyltrimethylammonium hydroxide, PtOEP: Pt- Octaethyl porphyrin, HPTS, EMIMBF4: 1-ethyl-3-methylimidazolium tetrafluoroborate.

Fig. 8. Photographs of sensing membranes from 100 N_2 to 100 CO_2.

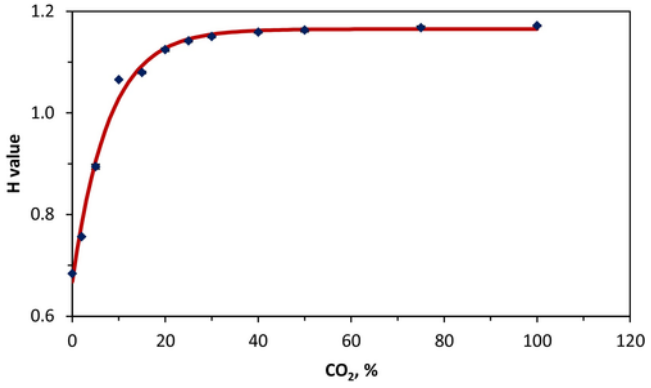

Fig. 9. H value versus CO_2 concentration, n = 3.

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