



Fernández-Ramos, M.D., Moreno-Puche, F., Escobedo, P., García-López, P.A., Capitán-Vallvey, L.F. and Martínez-Olmos, A. (2020) Optical portable instrument for the determination of CO₂ in indoor environments. *Talanta*, 208, 120387. (doi:[10.1016/j.talanta.2019.120387](https://doi.org/10.1016/j.talanta.2019.120387))

There may be differences between this version and the published version. You are advised to consult the publisher's version if you wish to cite from it.

<http://eprints.gla.ac.uk/197775/>

Deposited on: 04 October 2019

Enlighten – Research publications by members of the University of Glasgow
<http://eprints.gla.ac.uk>

Optical portable instrument for the determination of CO₂ in indoor environments

M.D. Fernández-Ramos^{*a,e}, F. Moreno-Puche^a, P. Escobedo^b, P.A. García-López^c, L.F. Capitán-Vallvey^{a,e}, A. Martínez-Olmos^{d,e}

^a *Department of Analytical Chemistry, University of Granada, Spain.*

^b *BEST Group, Department of Electronics and Nanoscale Engineering, University of Glasgow, United Kingdom.*

^c *Department of Statistics and Operations Research, University of Granada, Spain.*

^d *Department of Electronics and Computer Technology, University of Granada, Spain.*

^e *Unit of Excellence in Chemistry applied to Biomedicine and the Environment of the University of Granada, Spain.*

**e-mail: mdframos@ugr.es*

Abstract

A portable device based on a colorimetric sensor to determine the atmospheric level of CO₂ gas is presented in this work. The system is based on a low-cost, low-power System on a Chip (SoC) microcontroller with integrated Wi-Fi. A user-friendly application was developed to monitor and log the CO₂ measurements when the system is connected to a Wi-Fi network. The sensing membrane is directly deposited on the surface of the colour detector, thus reducing the complexity of the system. This sensing membrane is formed by a pH indicator α -naphtholphthalein, tetramethylammonium hydroxide pentahydrate, 1-ethyl-3-methylimidazolium tetrafluoroborate, Tween 20 and hydroxypropyl methylcellulose as the hydrophilic polymer. The system has been fully characterized, obtaining response and recovery times of 1.3 and 2.5 s, respectively, a limit of detection of 51 ppm, and an average resolution of 6.3 ppm. This portable device was applied for the in-situ determination of CO₂ gas in the atmosphere inside classrooms in several secondary schools. The measurements were taken during complete workdays and the results were statistically compared with the same measurements taken using a commercially available non-dispersive infra-red (NDIR) device. No significant statistical differences were found between the results obtained using both devices. A complete statistical treatment of the measurements made with the proposed portable device was carried out. The obtained results show that the

1 concentration of CO₂ gas in some schools was higher than the desired concentration,
2 with regard to influencing the student's health, safety, productivity and comfort. This
3 demonstrates the need to control this parameter to ensure appropriate indoor
4 environmental quality (IEQ).
5
6

7
8 **Keywords:** Portable device; colorimetric CO₂ gas sensor; indoor environmental
9 quality; autonomous monitoring.
10

11 12 13 14 15 **1. Introduction**

16
17 Air quality monitoring is essential to ensure a good quality of life. Not only is outdoor
18 air quality important, but also indoor air quality, since nearly everybody spends a lot of
19 time indoors. Poor indoor air quality is mainly caused by inadequate ventilation, as a
20 consequence of not bringing enough outdoor air inside to dilute emissions from indoor
21 sources, as well as not carrying indoor air pollutants outside. High values of temperature
22 and humidity can also increase some pollutant concentrations. Children and young
23 adults are especially vulnerable, because they spend a lot of time in classrooms, usually
24 with a high occupancy. Some research has found negative health effects from prolonged
25 exposure to various gases and particles in schools, which makes it necessary to control
26 and monitor them [1]. Stationary analytical devices used in the routine quality analysis
27 of atmospheric air are expensive and complex to transport and install on site [2]. As an
28 alternative, portable analysers exist to detect and identify specific compounds or groups
29 of compounds present in the air, both indoors and outdoors [3-6]. They are normally
30 equipped with a USB or COM interface for quick and easy communication and data
31 transfer to a desktop computer or laptop, their own rechargeable or replaceable power
32 supply, a built-in cache for storing measurement data and LCD displays [7]. Low-cost
33 devices for data collection and analysis are a very interesting option that can make
34 indoor environmental quality (IEQ) assessment affordable. In this respect, some sensing
35 systems for IEQ control based on an Arduino platform have been developed, basically
36 consisting of an Arduino Uno board, an SD memory card for data storage, and a number
37 of low-cost sensors for temperature, relative humidity, occupancy, lighting, and CO₂
38 concentration [8]. The integration of wireless communication into these systems reduces
39 the setup time by avoiding the need for additional wires between the sensors and the
40 central data acquisition system, also offering the possibility to collect all the data in one
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 node for storage in a central computer [9, 10]. In addition to these advantages in
2 portable indoor air quality measurement systems, other platforms use the cloud-based
3 VOLTRON software, which can be included in open-source designs. This platform has
4 been used to develop an Xbee agent for the VOLTRON software that enables robust
5 wireless data collection, demonstrating its application in IEQ evaluation in real
6 buildings [11].
7
8
9

10
11 The popularity of this kind of portable instrumentation is increasing due to its good
12 performance in terms of short response times, automatic operation for long periods of
13 time, high resolution, low cost and easy operation. In some cases, the instruments are
14 even supplied with self-calibration devices, filling-up systems, auto-regeneration of
15 reagents and independent power supply systems. Moreover, thanks to the on-site use of
16 field portable instruments, errors resulting from sample transport and storage can be
17 eliminated [12]. They are also very useful in process monitoring applications and
18 scenarios that require an emergency response. Ideally, these systems should be noiseless
19 so that they do not bother the building occupants, and can, thus, obtain spatially and
20 temporally representative air pollution data. However, they also have some
21 disadvantages, such as higher detection limits and lower sensitivity than the data
22 obtained in laboratory conditions, a strong influence of environmental factors on the
23 instrument performance and a high possibility of sample contamination in the field.
24
25
26
27
28
29
30
31
32
33
34
35

36 Among the main gases and pollutants usually monitored for air quality evaluation, CO₂
37 is undoubtedly one of the most important. In normal conditions, the CO₂ present in the
38 atmosphere is around 300 ppm, which does not pose a threat to human health. Levels up
39 to 1000 ppm are considered permissible in closed spaces [13], and this the typical level
40 found in occupied spaces with good air exchange. However, levels of CO₂ between
41 2000 and 5000 ppm can cause of headaches, sleepiness, bad concentration, an increased
42 heart rate and slight nausea. Finally, CO₂ levels above 5000 ppm can lead to loss of
43 oxygen, which can cause permanent brain damage [14].
44
45
46
47
48
49
50

51 In closed spaces holding many people, CO₂ levels can exceed those recommended for
52 health reasons, due to the increase of CO₂ from exhaled air. Therefore, it is highly
53 advisable to have a quick way to determine the CO₂ level in closed crowded places [15,
54 16]. There have been some studies to monitor the levels of CO₂ inside classrooms to
55
56
57
58
59
60
61
62
63
64
65

1 determine whether air quality regulations are being complied with, using continuous
2 commercially available CO₂ sensors [17, 18].
3

4 This study verifies the feasibility of a portable instrument based on an optical membrane
5 previously developed by us [19] to determine the evolution of CO₂ during activities in
6 secondary school classrooms. The results obtained by our platform are compared with a
7 commercially available device that is used as the gold standard to measure CO₂
8 concentration.
9
10
11
12

13 **2. Materials and methods**

14 *2.1. Reagents and Materials*

15
16
17 Hydroxypropyl methylcellulose (HPMC, Methocel E-5, LV USP/EP premium grade)
18 from Dow Chemical Iberia S.L. (Tarragona, Spain) was used as hydrophilic polymer. 1-
19 ethyl-3-methylimidazolium tetrafluoroborate, α -naphtholphthalein,
20 tetramethylammonium hydroxide pentahydrate (TMAOH), and Tween 20, from Sigma-
21 Aldrich Química S.A. (Madrid, Spain). Sheets of Mylar-type polyester from
22 Goodfellow (Cambridge, UK) were used as support for the membranes.
23
24
25
26
27
28
29
30
31
32

33
34 The standard mixtures to characterize the membranes were prepared using N₂ as the
35 diluting gas, controlling the flow rates of the high purity CO₂ and N₂ gases that enter the
36 mixing chamber with computer-controlled mass flow controllers (Air Liquide España
37 S.A.). The system works at a total pressure of 760 Torr and a flow rate of 500
38 cm³·min⁻¹.
39
40
41
42
43

44 *2.2. Instruments and software*

45
46 To compare the experimental results obtained with the portable device developed in this
47 study, the commercial NDIR carbon dioxide gas sensor data logger Perfect Prime
48 CO2000 (EU) (Solomon Smart Ltd, Hong Kong) was used.
49
50
51
52

53 To characterize the CO₂ sensing membranes, steady-state luminescence measurements
54 were performed using a Cary Eclipse Varian Inc. (Palo Alto, CA, USA) luminescence
55 spectrometer. The measurements were made using a homemade cell holder composed of
56 two metallic triangular prisms that support the membrane and lead the gas flow towards
57 it. The phosphorescence of the membranes was measured using a gate time (t_g) of 10 ms
58
59
60
61
62
63
64
65

1 and a delay time (t_d) of 0.15 ms, with excitation and emission slit widths of 2.5 and 5
2 nm, respectively, working at $\lambda_{ex} = 537$ nm and $\lambda_{em} = 650$ nm. All measurements were
3 made in triplicate to check for experimental errors.
4

5
6 Software Jasp v.0.8.4 was used in the statistical treatment of the measurements made
7 with the proposed device and with the commercial device.
8
9

10 *2.3. Sensing membrane preparation*

11
12 The sensing membranes for CO₂ were prepared using a cocktail containing 0.02 % of
13 the indicator α -naphtholphthalein, 0.7 % HPMC, 0.84 % TMAOH, 0.38% Tween 20 and,
14 0.069% 1-ethyl-3-methylimidazolium tetrafluoroborate [20]. The CO₂ sensor was
15 prepared by casting 10 μ l of this cocktail in two separate amounts of 5 μ L directly on
16 the colour detector sensing surface of the portable instrument. After that, the membrane
17 was left to dry for one day at room temperature.
18
19
20
21
22
23
24

25 *2.4. System description*

26
27 The block diagram of the instrument is shown in Figure 1. It consists of two
28 differentiated parts: the sensing module and the microcontroller unit (MCU).
29
30
31

32 **Figure 1**

33
34 In the sensing module, the CO₂ sensitive membrane is placed on the surface of a digital
35 colour detector model S11059-02DT (Hamamatsu Photonics, Japan), an I2C interface-
36 compatible colour detector sensitive to red ($\lambda_{peak}=615$ nm), green ($\lambda_{peak}=530$ nm), blue
37 ($\lambda_{peak}=460$ nm), and infrared ($\lambda_{peak}=855$ nm) radiation. This device codifies the
38 measured incident radiation in four digital words of 16 bits. An LED model SML-
39 010VTT86 (ROHM Semiconductors, Japan) with peak emission at 650 nm is used as
40 light source. This device is aligned with the sensitive membrane and the colour detector
41 at a fixed distance of 2 mm. In order to produce a stable emission, the LED is voltage-
42 biased using a regulator model NCP1117 (ON Semiconductor, USA), which provides a
43 stable voltage of 2 V. A temperature and humidity sensor model SHT15 (Sensirion AG,
44 Switzerland) is included for the compensation of the thermal and humidity dependence
45 of the sensing membrane.
46
47
48
49
50
51
52
53
54
55
56

57
58 The MCU is embedded in an ESP32 module (Espressif Systems, China). The ESP32 is
59 a low-cost, low-power, Dual-Core 2.4 GHz Wi-Fi Dual-Mode Bluetooth (BT) System-
60
61
62
63
64
65

1 on-Chip (SoC) combo MCU designed for mobile, wearable electronics and Internet of
2 Things (IoT) applications [21, 22]. It features an Xtensa Dual-Core 32-bit LX6 CPU
3 operating up to 240 MHz, 520 kB SRAM, 12-bit SAR ADC up to 18 channels, a built-
4 in Wi-Fi card that supports IEEE 802.11 b/g/n standards, Bluetooth v4.2 BR/EDR and
5 Bluetooth Low Energy (BLE). In addition, the ESP32 module has 40 general purpose
6 I/O pads that can be used to connect external components and sensors. It also includes
7 SPI and I2C interfaces.
8
9

10
11
12
13 A very user-friendly application has been created using the myDevices Cayenne IoT
14 cloud platform to monitor and log the temperature and CO₂ measurements when the
15 ESP32 module is connected to a Wi-Fi network. MyDevices Cayenne (myDevices, CA,
16 USA) is a solution for building IoT applications based on well-known platforms such as
17 Arduino or Raspberry Pi. Very recently, this platform also added support for ESP32
18 based development boards, making it possible to programme the ESP32 chip in the
19 Arduino IDE in order to monitor and control this module from anywhere in the world
20 through a very intuitive dashboard. The communication between ESP32 and Cayenne is
21 done by means of a lightweight protocol called Message-Queue Telemetry Transport
22 (MQTT). The Cayenne Cloud acts as the MQTT ‘broker’, which is the mediator
23 between ESP32 and any other devices connected on the network (see Figure 1). The
24 Cayenne platform manages every sensor and actuator client device that wishes to send
25 and receive data using the Cayenne Cloud, so that users are able to monitor and control
26 the ESP32 and their connected devices from anywhere, simply by accessing the
27 Cayenne platform. The dashboard created for our application can be accessed anytime
28 from anywhere via a webpage using any Internet web browser (Figure 2a) or by means
29 of the Cayenne smartphone app (Figure 2b), which is available for both Android and
30 iOS devices. It consists of several custom widgets showing the desired information in
31 real time, that is, the current temperature and humidity and the current CO₂
32 concentration computed from the colour sensor measurements. The application also
33 saves a history log of every magnitude with timestamps, which can be exported to a file
34 and saved.
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52

53
54
55 **Figure 2**
56

57 **3. Results and Discussion**

58 59 *3.1. System characterization* 60 61

1 The Perfect-Prime CO2000 commercial sensor data logger was used as the gold
2 standard to measure the CO₂ concentration. Its response was checked when exposed to
3 different known concentrations of this gas. The instrument was proved to be suitable for
4 the study since the measurement range covers the atmospheric levels required for this
5 application.
6
7

8
9 The sensing membrane for CO₂ used in this study was previously developed on a plastic
10 solid-state sensor membrane containing a luminophore (PtOEP) that presents
11 phosphorescence quenching by the deprotonation form of a non-luminescent pH
12 indicator (α -naphtholphthalein) [23]. The sensing chemistry was placed on the
13 optoelectronic components: LED with the dye and photodetector with the pH indicator.
14 In this study, the design of the portable device is simplified by substituting the
15 membrane containing PtOEP placed on top of the 525 nm LED with an LED that emits
16 that PtOEP at the same wavelength (650 nm). This increases the stability of the sensing
17 area while eliminating a potential source of error. The instrument was calibrated in the
18 range of interest from 100 to 4500 ppm of CO₂ at room temperature by measuring six
19 replicas per point, resulting in a linear response, $y = 0.6216x + 14404.9906$, with good
20 fit ($R^2 = 0.9985$).
21
22
23
24
25
26
27
28
29
30
31

32
33 The limit of detection (LOD) was calculated as usual by using $LOD = t_0 + 3s_0$, where t_0 is
34 the average blank signal and s_0 is the critical level or standard deviation of the blank,
35 which is determined from eight replicas. The LOD found using this approach was
36 0.005% CO₂ (51.3 ppm). The limit of quantification (LOQ) was obtained assuming that
37 $LOQ = t_0 + 10s_0$, resulting 0.015% CO₂ (153.4 ppm). The resolution of the system was
38 obtained from the fitting function of calibration by taking derivatives in both terms and
39 approximating these derivatives to increments:
40
41
42
43
44
45

$$\boxed{\Delta CO_2 = \frac{\delta f}{\delta I} \Delta I} \quad (\text{eq. 1})$$

46
47 where f is the fitting function and ΔI is the error or uncertainty in the determination of
48 the intensity I . In this case, this error is taken as the standard deviation of the replicas in
49 each measurement of the calibration (Figure S1). The mean resolution in the range
50 studied was found to be 6 ppm.
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 The stability of the sensing membranes, both short-term and long-term, is a very
2 important issue for any real application. Stability was studied by means of an inter-day
3 study, using the same sensor for 8 days ($n = 15$ per day). The inter-day standard
4 deviation was 1.50%, which is in agreement with our previous stability studies of the α -
5 naphtholphthalein membrane, where more than one-year long-term stability of the
6 indicator membrane was demonstrated with no special storage conditions [20].
7
8
9

10
11 Reversible operation, quick response time and high photostability are the essential
12 criteria for practical applications of optical sensors. To investigate reversibility and
13 response time, the sensing membranes were exposed to alternating atmospheres of pure
14 CO₂ and pure nitrogen as shown in Figure 3.
15
16
17
18
19

20 **Figure 3**

21
22 The response time between 10% and 90% of the maximum signal was 1.3 s, while the
23 recovery time from 90% to 10% was 2.5 s. In both cases, the signal change was fully
24 reversible and hysteresis was not observed during the measurements. The obtained
25 values are better than in previous studies [24], which is probably due to the inclusion of
26 ionic liquids, as we observed that they produce a significant improvement in recovery
27 and response times and increase the sensor's lifetime [20].
28
29
30
31
32
33

34 As usual with sensors based on acid-base transduction, the presence of acid gases
35 produces interference. That is the case with acid gases such as SO₂ and HCl, which have
36 a strong interference, as expected. Nevertheless, gases such as CH₄ and O₂ do not
37 produce any change in the signal when in contact with the sensor.
38
39
40
41

42 It is also well known that temperature and humidity influence the response of these
43 solid CO₂ gas sensors [25], especially at high values of both parameters. This problem
44 can be solved by knowing the dependence of both variables on the sensor signal in order
45 to introduce correction factors.
46
47
48
49

50 To check the influence of temperature, the prototype was put inside a thermal chamber,
51 and calibrations at different temperatures were conducted. Figure 5 shows a decrease in
52 sensitivity while the temperature increases, which is attributed to the reverse
53 dependence of the CO₂ solubility in the pH indicator membrane on temperature [26].
54 Each curve in Figure 4 can be linearly fitted. The slope m and y-intercept y_0 of these
55 fittings can be related to the temperature in the form:
56
57
58
59
60
61

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

$$m = -7.99 \cdot 10^{-3} \cdot T + 0.245 \quad (R^2 = 0.988) \quad (\text{eq.2})$$

$$y_0 = -60.145 \cdot T + 16192 \quad (R^2 = 0.976) \quad (\text{eq.3})$$

Thus, the correction of the temperature drift in the response of the sensitive membrane is programmed into the microprocessor unit.

Figure 4

The influence of the relative humidity was studied at room temperature (25°C) in a range between 10 and 90%. The results obtained are presented in Figure 5. As can be seen, the relative humidity has a strong influence on the response of the instrument, which must be corrected by including a humidity sensor in the portable device.

Figure 5

Table 1 shows the comparison of our proposed prototype and different optical CO₂ sensing devices found in the literature.

Depositing the pH indicator on the photodetector improves the results in terms of detection limits and recovery and response times. The main difference with respect to previous studies [23, 24] lies in the composition of the membrane: a different polymer that makes it possible to prepare it in water along with a surfactant to improve the surface tension of the cocktail; a phase transfer agent to improve the stability of the membrane [27]; and the addition of an ionic liquid that increases the lifetime while reducing the response and recovery times [20].

A comparison of response times of the proposed sensor and the dedicated instruments found in the bibliography [23, 24] shows that the detection limits are very similar in all cases. Only when HPTS is used as indicator is the response time somewhat higher than with the rest [32]. The sensor to determine CO₂ in a multianalyte platform [11, 28] has accuracy values of 30 and 50 ppm, respectively, which are considerably higher than those found with our prototype.

3.2 Application to indoor atmosphere

1 To check the applicability of the instrument to study indoor CO₂ concentration,
2 continuous monitoring was carried out in twelve secondary schools, with the prior
3 permission of the Provincial Delegation of Education of Granada (Spain). Ten
4 secondary schools and two training centres in the region of Granada participated in this
5 study (see Table 2, which presents the characteristics of the different classrooms). The
6 measurements were made on different days, with experimental values of pressure and
7 temperature between 1000 and 1028 hPA, and 15 and 20 °C, respectively. The data was
8 collected in a similar way in all the buildings where the study was conducted: both the
9 portable device and the commercial sensor were placed on the teacher's table. Both
10 instruments were left in the secondary schools during the morning from 8:00 h (before
11 the students arrived) until 14:30 h, and from 16:30 h to 21:00 h. In the two training
12 centres, the instruments only measured from 16:30 h. to 21:00 h in the afternoon, the
13 hours when they were in operation. Figure 6 presents an example of the data registered
14 with the portable and the commercial devices over 5 hours of classes in one classroom.
15 As can be seen, both curves show the same trend, which is to be expected in a densely
16 occupied closed classroom with a low ventilation rate [29]. A low indoor environmental
17 quality (IEQ) is observed with CO₂ levels above 2000 ppm throughout the period.
18
19
20
21
22
23
24
25
26
27
28
29
30

31 **Figure 6**

32 *Calibration*

33
34
35
36
37 In order to check whether the experimental values obtained with our prototype and the
38 reference instrument are equivalent, a simple linear regression was performed. The
39 results obtained partially support this hypothesis (see Figure S1 and Table S1), with R²
40 close to 1 (0.902). However, the obtained p-value associated with the independent term
41 is significantly different from zero, the desired value. On average, the developed
42 prototype measures a value only slightly lower than the commercial unit (15 units
43 lower). The fact that the correlation coefficient is close to 1 suggests that the partial lack
44 of adjustment is due to some influential value, as the graph shows. As an alternative
45 analysis to the regression conducted, we applied a Wilcoxon-Mann-Whitney test to
46 verify if the values obtained by both devices are equally distributed, in that the
47 measurements from one are not significantly greater or lesser than those from the other.
48 This was confirmed by the Wilcoxon-Mann-Whitney test (W=3034, p=0.770), hence
49 there is no displacement bias. Additionally, in order to establish whether the dispersion
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 of the means of the prototype and the commercial device are equivalent, the Moses test
2 was carried out ($S= 143$; p -value = 0.1348). In conclusion, the hypothesis that both
3 dispersions are equal cannot be rejected.
4

5 6 *Contrast of means by school*

7
8 From the measurements obtained with the prototype, a test was done to look for
9 statistically significant differences among the CO₂ average values observed per hour in
10 the different secondary schools. Firstly, we checked for differences between the
11 measurements made during the morning and the afternoon, depending on the
12 measurement schedules. To that end, the t-Student test was used to verify the hypothesis
13 of normality (Shapiro-Wilk test) and homoscedasticity (Test of Equality of Variances,
14 Levene's). The results obtained from the application of the Shapiro-Wilk test in the
15 morning and in the afternoon were $W=0.935$ and $W=0.948$, and $p=0.002$ and $p=0.603$,
16 respectively. Levene's test recorded $F=0.403$, $df=1$ and $p=0.528$. From the results, it can
17 be concluded that there is no normality in the measurements in the morning. This is
18 possibly due to the fact that the measurements were taken during opening hours, when
19 the CO₂ values are not affected by the personnel in the classroom.
20
21
22
23
24
25
26
27
28
29
30

31 In any case, the hypothesis that CO₂ measurements are equivalent in the morning and
32 the afternoon can be rejected. Therefore, a separate analysis should be made of the data
33 taken in the morning and in the afternoon.
34
35
36

37 38 *Analysis of differences by school*

39
40 The calibration of the proposed system was carried out including situational variables:
41 classroom volume, number of occupants and time of day. The calibration graph for both
42 devices including situation variables is presented in Figure S2. The prototype provides
43 values equivalent to the commercial device regardless of the classroom volume, number
44 of occupants and time of measurement. In fact, the correlation coefficient that
45 accompanies the values of the prototype regression is close to 1, as would be expected
46 in a calibration (see Supplementary Information). Additionally, an estimation of the
47 increase in CO₂ levels was made as a function of the time, classroom volume and
48 number of occupants (Figure S3).
49
50
51
52
53
54
55
56

57 There is an increase that only lessens during recess, at 11:00 h, probably due to
58 classroom ventilation. The small decrease observed at 21:00 h may be due to the smaller
59
60
61
62
63
64
65

1 number of measurements taken at that time. Considering average values, the value of
2 the increase produced in the concentration of CO₂ is about 240 concentration units per
3 hour. Special consideration must be given to the disparity of measurements per school,
4 which are presumably due to the difference in the quality of the window closures. Table
5 3 summarizes the results obtained regarding the amount of CO₂ gas measured with our
6 prototype and the commercial system, specifying the observation time (time of
7 measurement) for each school.
8
9
10
11
12

13 **4. Conclusion**

14 A simple, low-cost, portable device for CO₂ gas monitoring in indoor environments has
15 been presented. The proposed instrument is based on an optical sensor using a water
16 solution of a pH indicator, α -naphtholtalein. The chemistry used in previous designs
17 was simplified by eliminating the need to use a different sensing area containing the
18 platinum complex (PtOEP) luminophore. Instead, an LED emitting at the same
19 wavelength was used and the sensor membrane was directly placed on the top surface of
20 the colour detector. Thus, a simple, portable, electronic device based on a low-cost, low-
21 power SoC microcontroller with integrated Wi-Fi was designed. The system includes
22 temperature and humidity sensors for drift correction. The information collected about
23 the CO₂ is automatically logged and can be accessed in real time via a webpage or
24 smartphone application. This portable instrument was applied to determine the
25 concentration of CO₂ gas in several secondary schools, taking measurements
26 simultaneously with a commercially available device. The results were statistically
27 compared, concluding that there are no significant differences between the results found
28 with both devices. The application of this methodology to evaluate air quality in the
29 secondary school classrooms showed that in 5 out of the 12 schools studied,
30 approximately 42% have CO₂ values above 2000 ppm, which are above the normal
31 values established for this gas for health reasons. In conclusion, the results obtained are
32 very promising, indicating that the developed device could compete with classic
33 commercially available portable instruments.
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52

53 **Acknowledgements**

54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

This study was supported by projects from the Spanish MINECO (CTQ2013-44545-R and CTQ2016-78754-C2-1-R). The project was partially supported by European Regional Development Funds (ERDF).

Conflict of interest

The authors declare that there are no conflicts of interest with regard to this study.

References

1. I. Annesi-Maesano, N. Baiz, S. Banerjee, P. Rudnai, S. Rive, Indoor Air Quality and Sources in Schools and Related Health Effects, *J.Toxicol.Environ.Health, Part B*, *16* (2013), 491-550.
2. W. Wardencki, R. J. Katulski, J. Stefanski, J. Namiesnik, The state of the art in the field of non-stationary instruments for the determination and monitoring of atmospheric pollutants, *Crit.Rev.Anal.Chem.*, *38* (2008), 259-268.
3. G. R. McKercher, J. A. Salmond, J. K. Vanos, Characteristics and applications of small, portable gaseous air pollution monitors, *Environ.Pollut.(Oxford, U.K.)*, *223* (2017), 102-110.
4. J. Y. Kim, C. H. Chu, S. M. Shin, ISSAQ: an integrated sensing systems for real-time indoor air quality monitoring, *IEEE Sens.J.*, *14* (2014), 4230-4244.
5. A. Kumar, G. P. Hancke, Energy efficient environment monitoring system based on the IEEE 802.15.4 standard for low cost requirements, *IEEE Sens.J.*, *14* (2014), 2557-2566.
6. K. S. E. Phala, A. Kumar, G. P. Hancke, Air quality monitoring system based on ISO/IEC/IEEE 21451 standards, *IEEE Sens.J.*, *16* (2016), 5037-5045.
7. M. Marc, M. Tobiszewski, B. Zabiegala, M. d. I. Guardia, J. Namiesnik, Current air quality analytics and monitoring: A review, *Anal.Chim.Acta*, *853* (2015), 116-126.
8. A. S. Ali, Z. Zanzinger, D. Debose, B. Stephens, Open Source Building Science Sensors (OSBSS): A low-cost Arduino-based platform for long-term indoor environmental data collection, *Building and Environment*, *100* (2016), 114-126.
9. S. Abraham, X. Li, A Cost-effective Wireless Sensor Network System for Indoor Air Quality Monitoring Applications, *Procedia Computer Science*, *34* (2014), 165-171.
10. E. Arens, H. Zhang, C. Huizenga, Partial- and whole-body thermal sensation and comfortGÇöPart II: Non-uniform environmental conditions, *J.Therm.Biol.*, *31* (2006), 60-66.
11. M. Karami, G. V. McMorro, L. Wang, Continuous monitoring of indoor environmental quality using an Arduino-based data acquisition system, *Journal of Building Engineering*, *19* (2018), 412-419.

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
12. A. Galuszka, Z. M. Migaszewski, J. Namiesnik, Moving your laboratories to the field. Advantages and limitations of the use of field portable instruments in environmental sample analysis, *Environmental Research*, *140* (2015), 593-603.
 13. WHO Regional Office for Europe Air Quality Guidelines for Europe; 2nd ed. ed.; Copenhagen, 2000; Vol. European Series, No. 91.
 14. E. T. Gall, T. Cheung, I. Luhung, S. Schiavon, W. W. Nazaroff, Real-time monitoring of personal exposures to carbon dioxide, *Building and Environment*, *104* (2016), 59-67.
 15. A. Singh, Y. Pandey, A. Kumar, M. K. Singh, A. Kumar, S. C. Mukhopadhyay, Ventilation Monitoring and Control System for High Rise Historical Buildings, *IEEE Sens.J.*, *17* (15-11-2017), 7533-7541.
 16. P. Spachos, D. Hatzinakos, Real-Time Indoor Carbon Dioxide Monitoring Through Cognitive Wireless Sensor Networks, *IEEE Sens.J.*, *16* (15-1-2016), 506-514.
 17. A. Al-Hemoud, L. Al-Awadi, M. Al-Rashidi, K. A. Rahman, A. Al-Khayat, W. Behbehani, Comparison of indoor air quality in schools: Urban vs. Industrial 'oil & gas' zones in Kuwait, *Building and Environment*, *122* (2017), 50-60.
 18. Y. You, C. Niu, J. Zhou, Y. Liu, Z. Bai, J. Zhang, F. He, N. Zhang, Measurement of air exchange rates in different indoor environments using continuous CO₂ sensors, *Journal of Environmental Sciences*, *24* (2012), 657-664.
 19. M. D. Fernandez-Ramos, M. L. Aguayo-Lopez, I. M. Perez de Vargas Sansalvador, L. F. Capitan-Vallvey, Ionic liquids on optical sensors for gaseous carbon dioxide, *Anal.Bioanal.Chem.*, *410* (2018), 5931-5939.
 20. M. D. Fernandez-Ramos, M. L. Aguayo-Lopez, I. M. Perez de Vargas Sansalvador, L. F. Capitan-Vallvey, Ionic liquids on optical sensors for gaseous carbon dioxide, *Anal.Bioanal.Chem.*, *410* (2018), 5931-5939.
 21. A. M. Quintana-Suarez, D. Sanchez-Rodriguez, I. Alonso-Gonzalez, B. J. Alonso-Hernandez, A Low Cost Wireless Acoustic Sensor for Ambient Assisted Living Systems, *Applied Sciences*, *7* (2017).
 22. A. Maier, A. Sharp, Y. Vagapov. Comparative analysis and practical implementation of the ESP32 microcontroller module for the internet of things. 2017 Internet Technologies and Applications. 143-148. 12-9-2017.
 23. M. A. Carvajal, I. M. Perez de Vargas Sansalvador, A. J. Palma, M. D. Fernandez-Ramos, L. F. Capitan-Vallvey, Hand-held optical instrument for CO₂ in gas phase based on sensing film coating optoelectronic elements, *Sens.Actuators B*, *B144* (2010), 232-238.
 24. I. M. Perez de Vargas Sansalvador, C. Fay, T. Phelan, M. D. Fernandez-Ramos, L. F. Capitan-Vallvey, D. Diamond, F. Benito-Lopez, A new light emitting diode-light emitting diode portable carbon dioxide gas sensor based on an interchangeable membrane system for industrial applications, *Anal.Chim.Acta*, *699* (2011), 216-222.
 25. A. Mills, Q. Chang, N. McMurray, Equilibrium Studies on Colorimetric Plastic Film Sensors for Carbon Dioxide, *Anal.Chem.*, *64* (1992), 1383-1389.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

26. M. D. Marazuela, M. C. Moreno-Bondi, G. Orellana, Enhanced performance of a fiber-optic luminescence CO₂ sensor using carbonic anhydrase, *Sens.Actuators B*, 29 (1995), 126-131.
27. M. L. Aguayo-Lopez, L. F. Capitan-Vallvey, M. D. Fernandez-Ramos, Optical sensor for carbon dioxide gas determination, characterization and improvements, *Talanta*, 126 (2014), 196-201.
28. G. Marques, R. Pitarma, An Indoor Monitoring System for Ambient Assisted Living Based on Internet of Things Architecture, *Int.J.Environ.Res.Public Health*, 13 (2016).
29. A. Ortiz Perez, B. Bierer, L. Scholz, J. Wöllenstein, S. Palzer, A Wireless Gas Sensor Network to Monitor Indoor Environmental Quality in Schools, 18 (2018).
30. J. Hodgkinson, R. Smith, W. O. Ho, J. R. Saffell, R. P. Tatam, Non-dispersive infra-red (NDIR) measurement of carbon dioxide at 4.2 μm in a compact and optically efficient sensor, *Sensors and Actuators B: Chemical*, 186 (2013), 580-588.
31. D. Zhao, D. Miller, X. Xian, F. Tsow, E. S. Forzani, A novel real-time carbon dioxide analyzer for health and environmental applications, *Sensors and Actuators B: Chemical*, 195 (2014), 171-176.
32. S.S. Hung, H.-C. Chang, I.-N. Chang, A Portable Array-Type Optical Fiber Sensing Instrument for Real-Time Gas Detection, *Sensors*, 16 (2016), 2087.

Table 1. Comparison of performance of proposed instrument for CO₂ with literature.

Instrument type	Sensing membrane	Dynamic Range (%)	LOD (%)	t ₉₀ -t ₁₀ (s)	Remarks	Ref.
Dedicated	PtOEP/PVCD- αNTTLN /EC	0-100	-	31-117	Coated photodetector-coated LED	[23]
Dedicated	α-naphtholphthalein /EC	<100	0.0066	11 - 55	PEDD technique	[24]
Dedicated	NDIR	-	0.0004	-	Dual element detector	[30]
Dedicated	m-cresol purple/ hydrophobic membrane	0.005- 11.5	-	0.1-	LED-photodiode	[31]
Multianalyte Platform	K-30	0-1	-	-	Platform VOLTTRON	[11]
Multianalyte Platform	T6615 CO ₂	0-0.5	-	120	IoT system	[28]
Multianalyte Platform	HPTS	2-5	-	48-76	Optical Fiber sensing array	[32]
Dedicated	α-naphtholphthalein / HPMC/IL	0.005-0.5	0.005	1.3 – 2.5 s	PEDD technique	Current study

αNTTLN: α-naphtholphthalein; PtOEP: Platinum octaethylporphyrin complex; PVCD: poly(vinylidene chloride-co-vinyl chloride); EC: ethyl cellulose; PEDD: paired emitter-detector diode; NDIR: non-dispersive infra-red; **HPTS: 1-hydroxy-3,6,8-pyrene trisulfonic acid trisodium salt**; HPMC: hydroxypropylmethylcellulose; IL: ionic liquid;

Table 2. Characteristic of classrooms under study.

High school center	Classroom dimensions (m)	Volume (m³)	Number of students
1	7.69×8.01×2.88	177.86	32.0
2	10.38×6.31×3.19	209.29	28.0
3	7.73×7.828×2.94	178.04	26.0
4	8.67×6.69×3.73	216.79	31.0
5	8.20×7.09×4.33	251.87	28.0
6	12.18×4.40×3.32	178.00	17.0
7	9.20×5.29×3.19	155.25	29.0
8	8.50×6.79×3.10	179.48	25.0
9	6.28×9.20×3.00	174.00	12.0
10	7.35×7.66×3.18	179.05	32.0
11	8.40×7.02×2.91	171.64	34.0
12	17.50×6.62×2.90	335.96	43.0

Table 3. Comparison of average results found with the proposed prototype and with the commercial device

High School	[CO ₂] prototype (ppm)	[CO ₂] commercial (ppm)	t	P	N
1	824 ± 247	1020 ± 177	-1.71	0.11	7
2	1350 ± 4923	1552 ± 459	-0.74	0.50	6
3	1259 ± 257	1142 ± 264	0.80	0.50	6
4	2600 ± 486	2580 ± 460	0.07	0.94	6
5	1125 ± 362	1035 ± 449	0.41	0.70	7
6	1366 ± 469	1513 ± 499	-0.60	0.60	7
7	2423 ± 646	2668 ± 630	-0.70	0.52	6
8	2182 ± 1228	2102 ± 1169	0.07	0.95	7
9	2625 ± 1024	2723 ± 796	-0.20	0.85	6
10	3133 ± 872	3025 ± 834	0.22	0.83	6
11	4255 ± 361	4252 ± 434	0.01	0.99	6
12	5311 ± 1053	5419 ± 1767	-0.13	0.90	6

Figure captions

Figure 1. Block scheme of the portable device.

Figure 2. Screen captures of the created dashboard using Cayenne platform accessed via (a) webpage and (b) the Android application.

Figure 3. Response and recovery times of the developed portable device with alternate atmospheres of CO₂ from 0% to 100%.

Figure 4. Thermal dependence of the sensing membrane from 5 to 35 °C.

Figure 5. Influence of humidity on the response of the instrument.

Figure 6. Example of CO₂ measurements in one morning during a class session in a high school classroom.

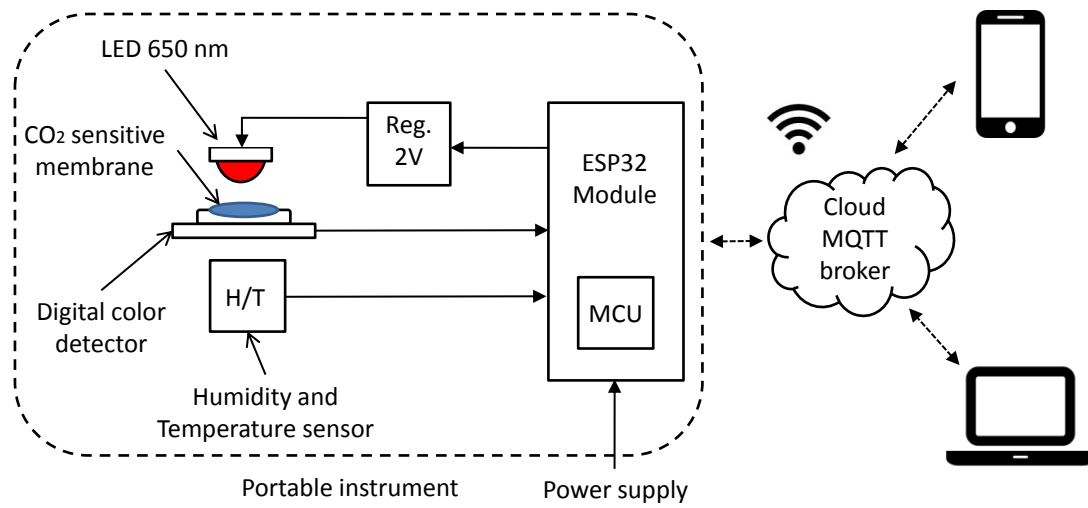
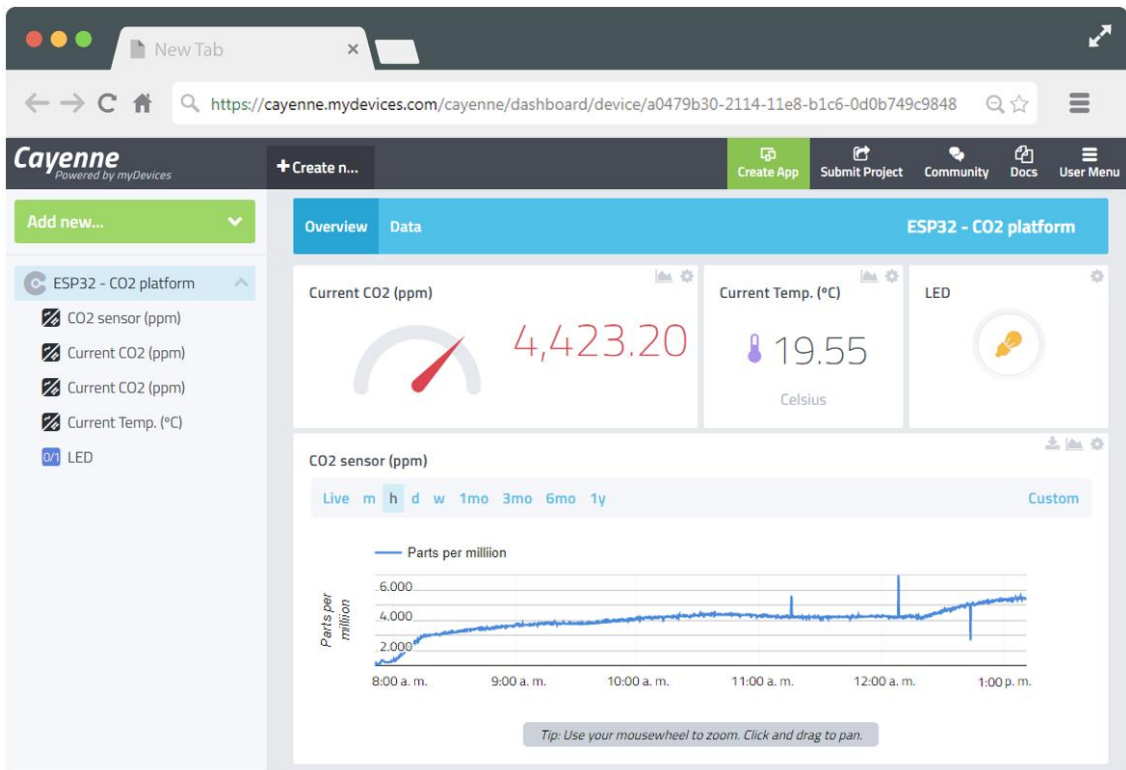
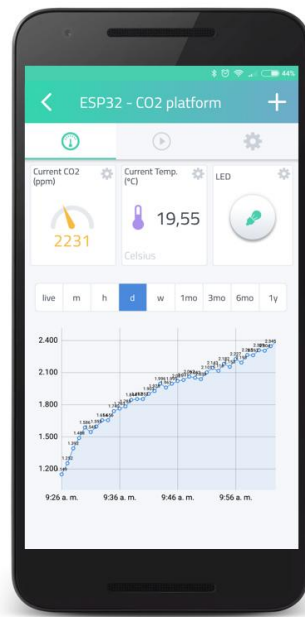


Figure 1



(a)



(b)

Figure 2

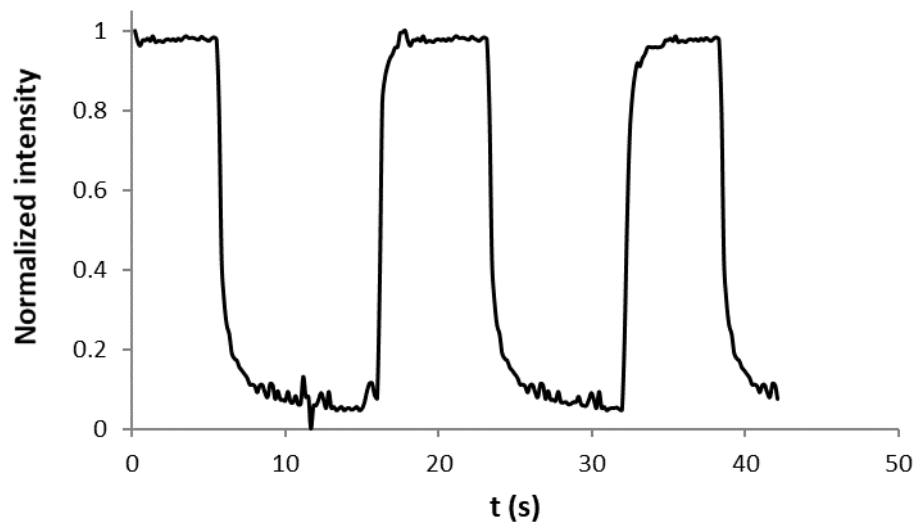


Figure 3

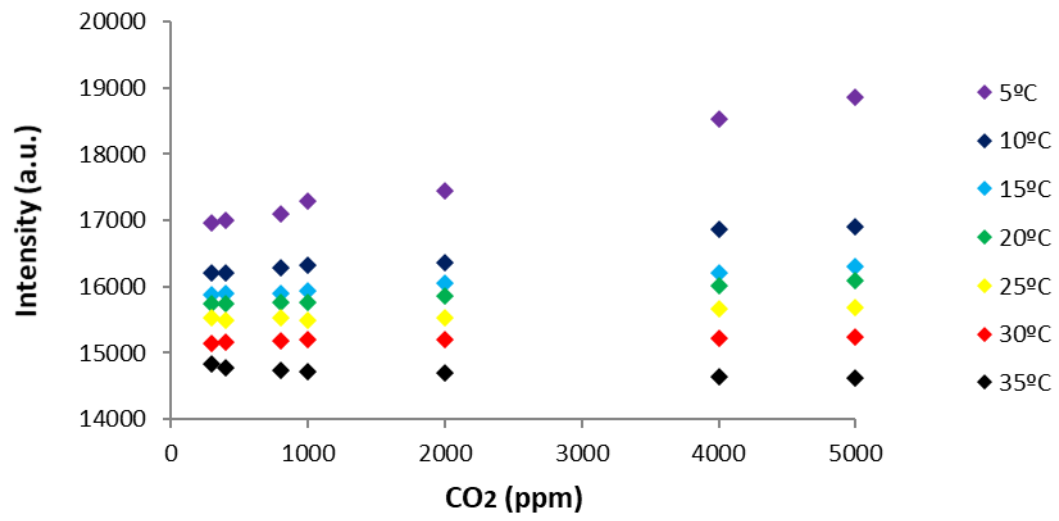


Figure 4

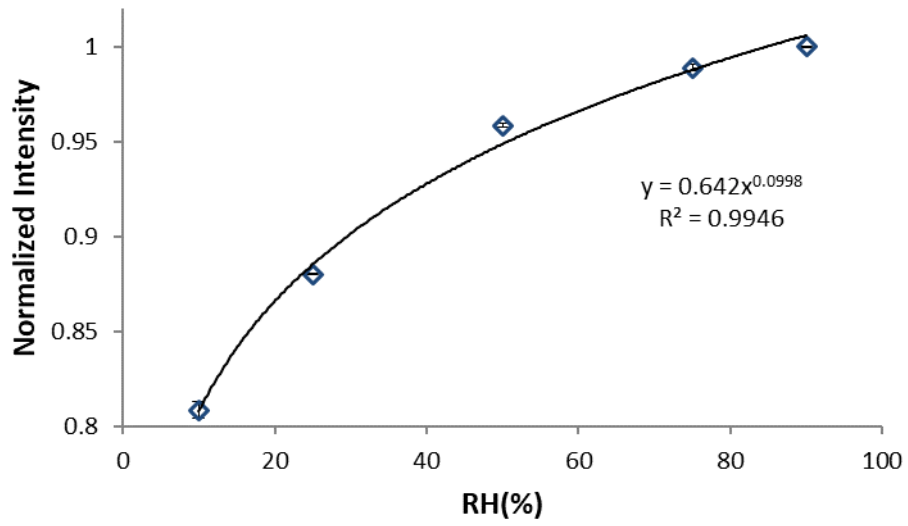


Figure 5

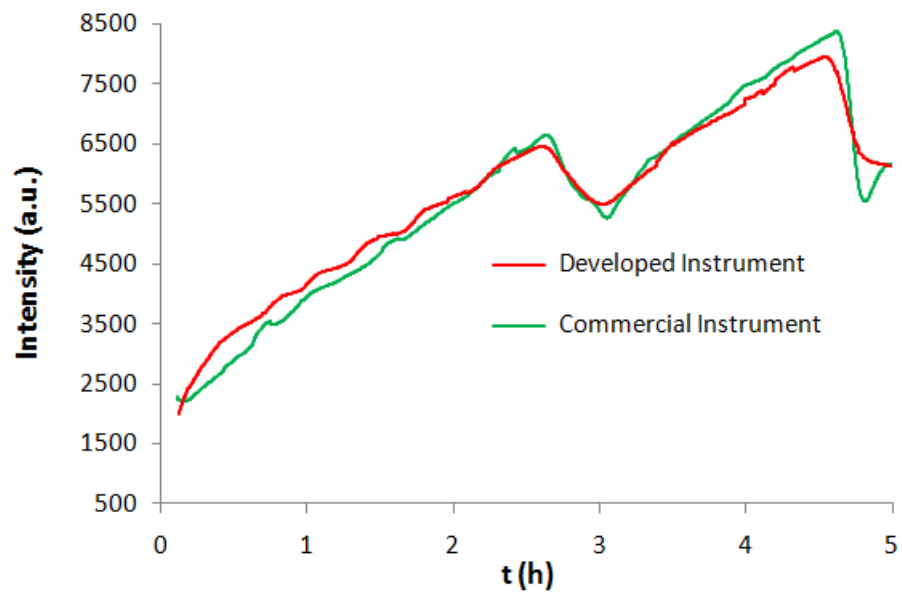


Figure 6

Author Agreement

This study was supported by projects from the Spanish MINECO (CTQ2013-44545-R and CTQ2016-78754-C2-1-R). The project was partially supported by European Regional Development Funds (ERDF).

Supplementary Material

[Click here to download Supplementary Material: Supplementary Material.docx](#)

