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Low-cost, portable open-source gas monitoring device based on chemosensory technology

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Abstract

We report herein the construction of an electronic device to perform the real-time digitalization of the color state of the optical chemosensors used in the detection of dangerous gases. To construct the device, we used open-source modular electronics, such as Arduino and Sparkfun components, as well as free and open-source software (FOSS). The basic principle of the operation of this device is the continuous color measurement of a chemosensor-doped sensing film, whose color changes in the presence of a specific gas. The chemosensor-sensing film can be prepared by using any of the widely available chemosensors for the desired gas. Color measurement is taken by two TCS230 color sensor ICs, reported to the microcontroller, and the results are displayed on an LCD display and pushed through a USB serial port. By using a cyanide optical chemosensor, we demonstrated the operation of the device as a HCN gas detector at low concentrations.

Keywords: color, gas, sensor, chemosensor, monitor, open-source, Arduino

(Some figures may appear in colour only in the online journal)

1. Introduction

Gas detectors have become absolutely necessary nowadays due to increased gas handling and the dangerous nature they involve. Risks related to gases are classified into three main categories: risk of poisoning by toxic gases; risk of explosion by flammable gases; risk of flammability by oxygen enrichment or asphyxiation by oxygen displacement.

This last point is extremely important when working in confined spaces where the release of certain gases can happen. This evidences how even a leakage of harmless gases, such as carbon dioxide, argon, helium, or nitrogen may become dangerous as they can fast displace oxygen by sudden release [1–3].

The human nose can detect the presence of certain amounts of some gases. For instance, hydrogen sulphide at low concentrations can be perceived by humans because of its typical odour of rotten eggs. However at lethally high concentrations of this gas, the human nose is no longer sensitive and, consequently, disaster may follow [4].

These facts demonstrate the importance of using gas detectors. A gas detector is a system designed to detect dangerous gas concentrations, to trigger alarms, and to activate counter measures. Gas sensors are used in industrial production, the automotive industry, medical applications, indoor air quality supervision, or environmental studies [5].

Today's market offers different gas detection technologies. The most widely used are electrochemical [6] and amperometric [7] gas sensors, catalytic bead sensors [8], infrared point sensors [9], ultrasonic gas flow sensors [10], ion-mobility spectrometry [11], photo-ionization detection [12], semiconductor sensors, or open path detectors [13].

These technologies have proven suitable for the detection of a broad spectrum of gases, and are in fact employed in

industrial environments, car parks, basements, etc. However, despite their reliability and efficiency, most of these technologies present major drawbacks, such as lack of selectivity and specificity, which can lead to the generation of false-positives. For instance, electrochemical gas sensors rely on the redox properties of the gas that is to be measured. Electrochemical sensors for HCN, HCl, or NH_3 present cross-sensitivity with H_2S, Cl_2, NO_2, and SO_2 [14], as well as hydrocarbons and organic solvent vapors [15], and other sensors like catalytic bead sensors yield a similar response to all combustible gases.

In the last few decades, optical chemosensors have become a new potential alternative to these electronic gas detectors [16]. Chemosensors detection is based on true specific chemical recognition by generally producing a response in the presence of the desired analyte. Optical chemosensors are the type of chemosensors that have the particularity of producing an optical event in the presence of the species to be detected. The optical event may be colorimetric or fluorometric.

Generally, the chemosensors designed to detect gases are supported on solid materials, such as polymeric or paper films. The gas to be measured undergoes a chemical reaction with chemosensors bleaching that can intensify or modulate their color, or with fluorescent chemosensors that can intensify or cancel their fluorescence. The magnitude of this change is often proportional to the concentration of the gas.

Thus, different research groups have designed chemosensors that are selective or specific towards a broad variety of gases (e.g. gases such as CO [17], CO_2 [18–20], alkylamines and thiols [21], NH_3 [22–24], nitroaromatics [25], NO_x [26, 27], O_2 [28, 29], HCN [30], alcohols [31], aldehydes [32, 33], organophosphates [34–38], and organophosphonates [39]).

However, most reports carried out on these chemosensors have demonstrated their operation in expensive and non-portable optical measurement systems, such as UV–vis spectrophotometers or fluorometers. The scarcity of cheap, specific instrumentation capable of automatically monitoring and logging the color change of chemosensors holds back this trending research from the market and anchors it to laboratory development stages. This gap between the design and synthesis of a chemosensor and its applicability to real cases has been our driving force to build an economic open-source device capable of bridging the gap we find today.

Our device is a hand-sized light-weight prototype suitable for being operated as both a portable device and a fixed constant monitoring system. The purpose of the prototype is to act as an automatic measuring system for chemosensors. Thus, the types of gases that can be measured with our device are unlimited and are determined by the nature of the chemosensor used.

2. Description

2.1. Working principle

The basic principle of this device relies on measuring the visible color of a film containing a chemosensor that is sensitive to the gas that has to be monitored. As indicated above, the chemosensor is selected in such a way that a strong variation in optical properties occurs upon a reaction with toxic gas. The variation in optical properties can increase, decrease, or modulate the absorbed color and/or the emitted fluorescence.

The chemosensor has to be placed on a solid support inside the device's measuring chamber. Then an air current is forced to flow over the sensing film, allowing the chemosensor to react with the gas. The constructed device is sensitive enough to measure the color change of the chemosensor producing an analytical response.

2.2. Construction of the device

2.2.1. Hardware and electronics. The electronic nature of the device is based on a commercial Arduino UNO board [40]. These prototyping platforms are designed around an Atmel ATmega328 [41] microcontroller (μC) that works at 16 MHz. The kit includes all the components required to conceive a stand-alone board. It provides 14 digital input/output pins and six analogue inputs. The processor has a pre-programmed bootloader that allows programmes written in C/C++ to be uploaded from a PC through an on-board integrated future technologies devices international (FTDI) chip (FT232RL), which is responsible for interfacing the Arduino's UART with the USB host.

The pinning of the Arduino is exposed in such a way that the board can be connected to a wide range of add-ons, known by the Arduino community as *shields*. Thus, the μC in our device is connected to a Sparkfun microSD card shield [42] and a Serial-LCD display shield [43] (both open-source) provided by Sparkfun Electronics.

The microSD card shield provides a fast, easy way for storing parameter files and measurement datalogs, which can be later consulted and plotted by the user on a PC. The Serial-LCD display allows the device to communicate with the front-end user without having to use too many valuable I/O Arduino pins (using a parallel LCD means employing a total of I/O 7 pins, while Serial-LCD uses 1).

The device's sensing core is composed of two commercially available RGB color sensors (one as the reference and the other as the sample), which use the TAOS TCS230 [44] color-to-frequency converter ICs. The color measurement is carried on by an array of 16 × 4 photodiodes. Each group is filtered with no, red, green, and blue filters (respectively). The on-board IC provides a signal output of variable frequency which is proportional to the amount of light within the kHz range. The use of RGB photodetectors instead of monochromatic ones allows the device to measure not only chemosensors which bleach or intensify their color absorption, but also chemosensors which shift their color absorption wavelength upon detection of the analyte.

TCS230 is fitted on a breakout board which incorporates an adjustable lens system with a focal length of approximately 25 mm, as well as a UART integrated circuit that interfaces the output of the TCS230 to a string in the ASCII format to provide information as RGB values. The whole board is sold commercially by Sure Electronics as DC-SS501 [45].

The sensing film is previously placed in a closed opaque measurement chamber to avoid any exterior light reflection. Then it is illuminated prior to the measurement by the two

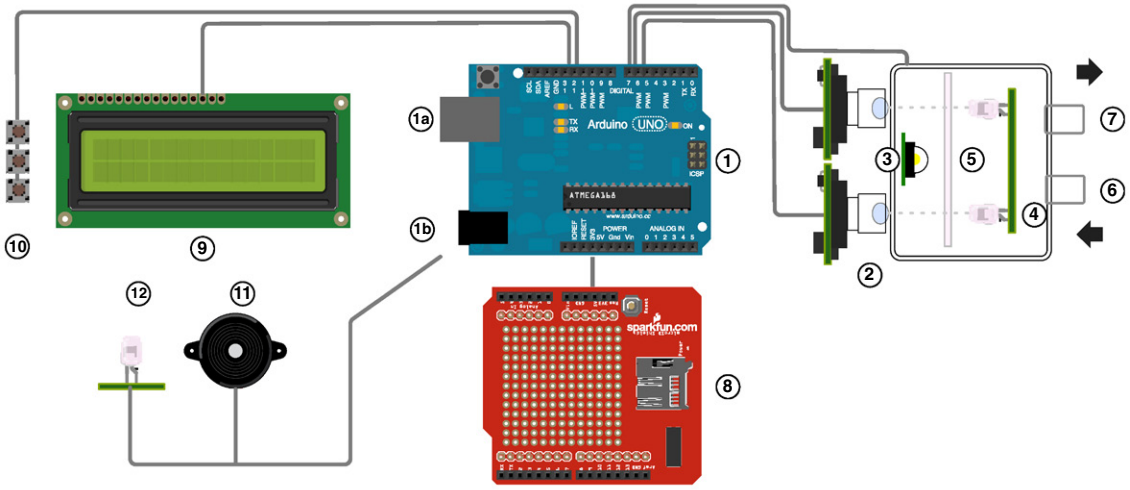
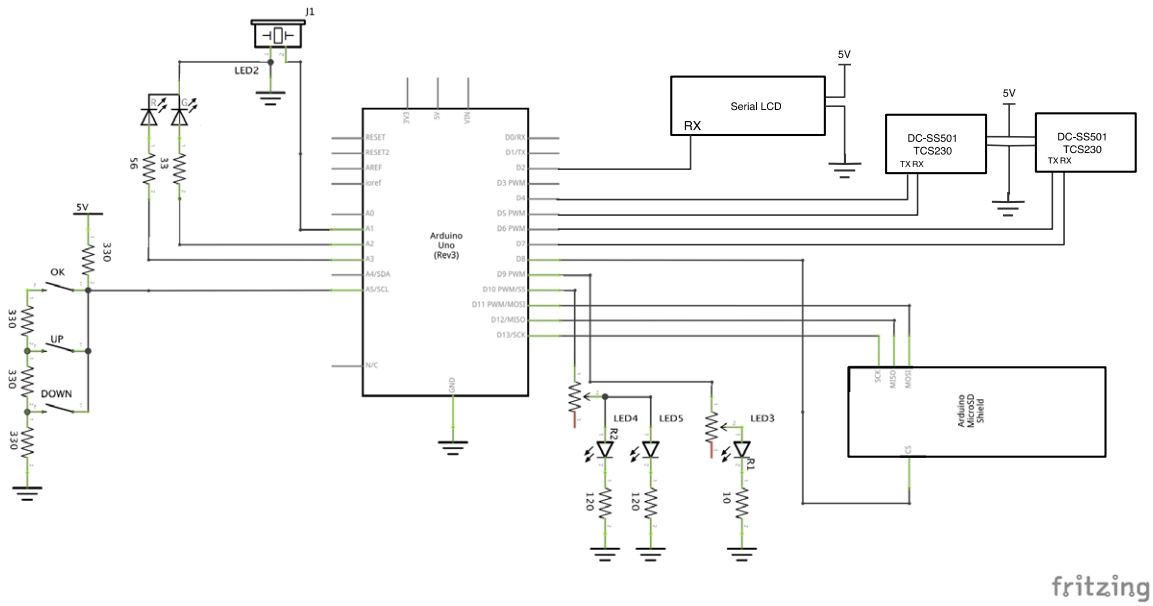


Figure 1. Schematic representation of the connections between the different modules. (**1**) Arduino Uno board. (**1a**) USB communication port. (**1b**) Power connector. (**2**) TAOS TCS230 color sensors. (**3**) Reflection illumination. (**4**) Transmission illumination. (**5**) Sensing film. (**6**) Air inlet raccord. (7) Air outlet raccord. (**8**) microSD card module (*shield*). (**9**) Serial LCD display module. (**10**) Navigation push buttons. (**11**) Acoustic buzzer. (**12**) Visual LED indicator.



Scheme 1. Electronic scheme of the complete device. The buzzer, RGB LEDs, and push buttons are driven by the Arduino analogical ports A1, A2-A3, and A5, respectively. The RX pin of the Serial LCD is connected to the Arduino's digital pin D2. The color sensors TCS230 are controlled via SPI through digital pins D4-D5 and D6-D7. The microSD shield is connected via SPI to the MOSI, MISO and SCK pins of the Arduino (D11-D13, respectively). Pins D9 and D10 control the transmission and reflection of the illumination modes.

sets of 5700 K light-emitting diodes, arranged in such a way that color can be measured by transmission or reflectance, depending on the solid support chosen. The response time of each color sensor is approximately 500 ms, allowing color measurements every 1 s.

A buzzer and a red LED are also integrated to alert the user when detection reaches a certain value.

The system is controlled by the user, who employs three push buttons (OK, up, and down) that allow the user to navigate through the device menu. A schematic representation of all the connections is shown in figure 1. An electronic scheme is shown in scheme 1.

2.2.2. Enclosure. The complete electronics are fitted in a 400 × 62 × 56 mm metallic box, except for the lighting system, which is placed in the separate measuring chamber (see figure 2). Three function buttons and the LCD display are integrated into the enclosure. Two holes in the back of the box allow the power adaptor and the USB communication cable to be connected.

2.2.3. Measuring chamber. The measuring chamber is a PVC cylinder (60 × 45 mm) with two metallic raccords (25 × 10 mm) that provides the air inlet and outlet (see figure 3). Inside the chamber, there is a pair of white LEDs (5700 K,

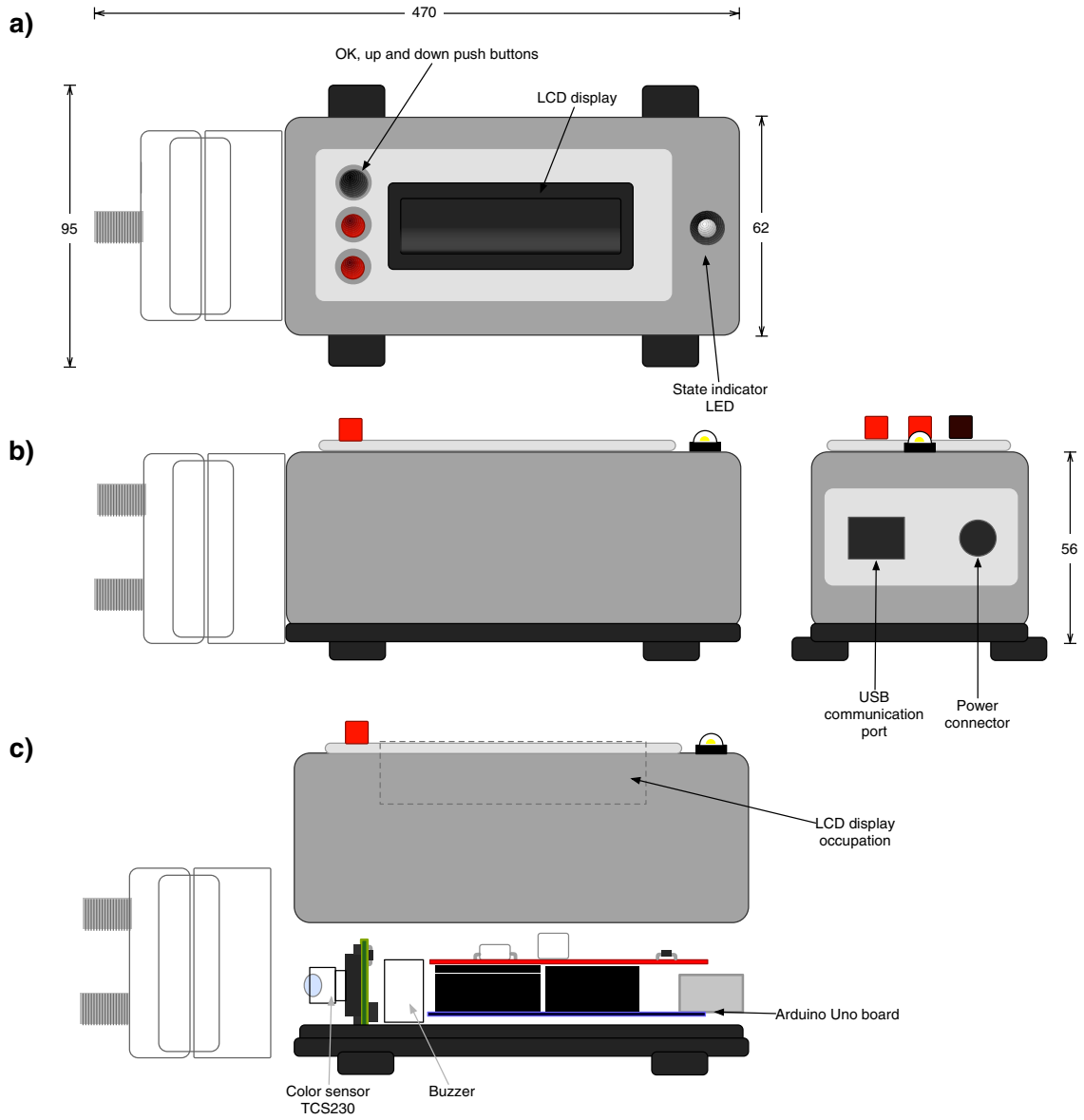


Figure 2. Schematic representation of the device's enclosure. Sizes are given in mm. (**a**) Top view. (**b**) Side and rear views. (**c**) Side view of the opened enclosure. Dashed line indicates the occupation of the LCD display.

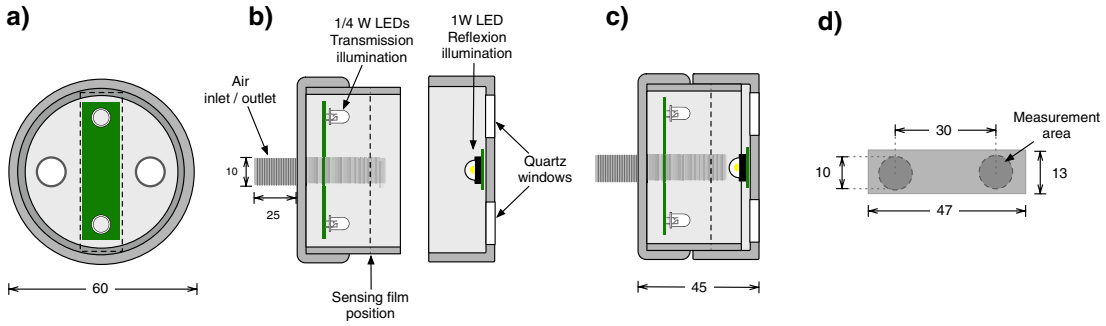


Figure 3. Schematic representation of the measurement chamber and its size (given in mm). (**a**) Front view of inside the chamber. The dashed lines determine the sensing film position. (**b**) Side view of the opened chamber. (**c**) Side view of the closed chamber. (**d**) Sizes required for the sensing film. The gray areas determine the measurement areas where the chemosensor must be located.

¼W, $\Delta V \approx 3.5$ V) used as illumination in the transmission mode, and a white LED (5700 K, 1 W, $\Delta V \approx 3.5$ V) used for the reflection mode. In between the two sets of LEDs, there is a slot for placing the sensing film. This chamber also has two quartz windows through which measurements can be taken.

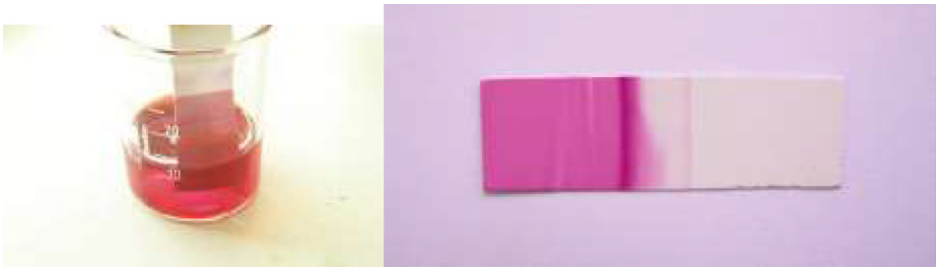
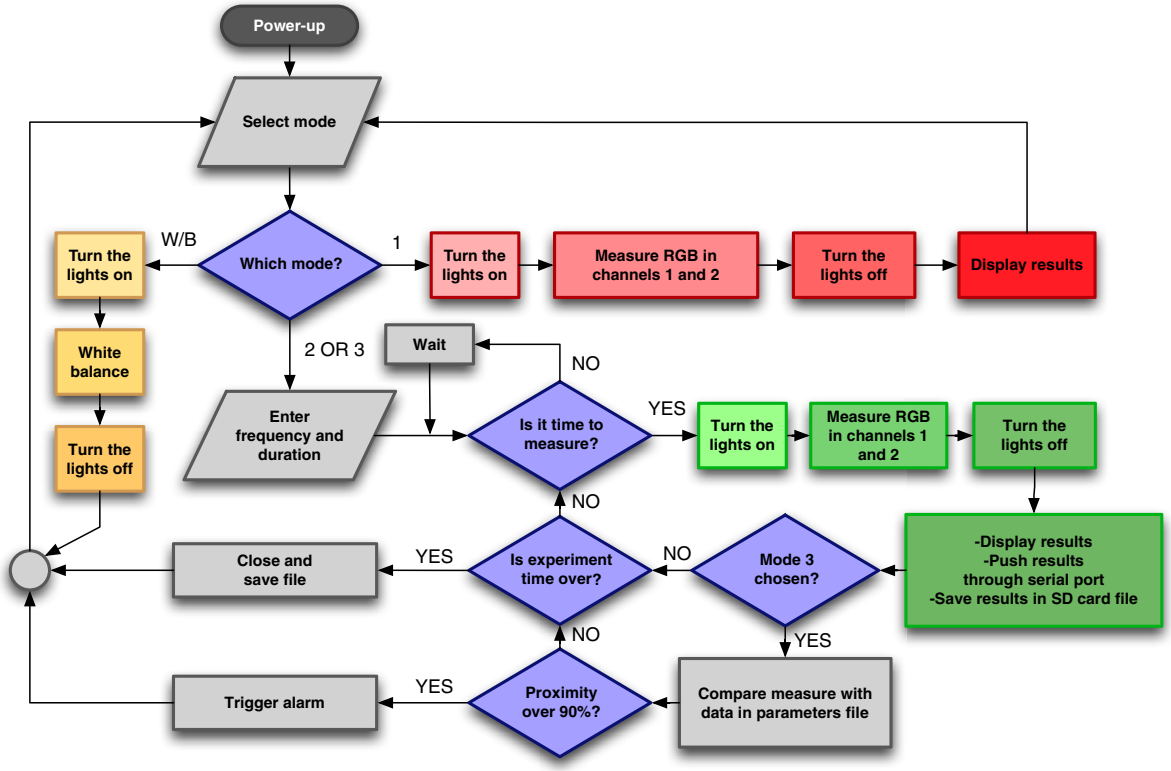


Figure 4. Preparation of the sensing film through probe adsorption on aminated silica sheets.



Scheme 2. Flow chart for the device's software operation.

An external air pump can be connected to the air inlet to force air to flow through the measuring chamber if closed system measurements need to be done, but the pump is not required in open-air measurements.

The overall dimensions of this device are 470 × 95 × 74 mm, which means that it is a portable device that can be placed in sensitive areas. The device power can be supplied with a 9 V battery or with a power adapter that provides 9 V and 200 mA. The overall cost of the prototype was around $95.

2.2.4. Software. The software of the device was programmed in *pseudo*-C++, according to the language that the Arduino IDE uses.

2.2.4.1. Normal operation mode. After power-up, the device prompts a mode of operation (scheme 2). The user should carry then a white balance calibration that employs a blank film (Mode #4). After the white balance has been done, the device returns to the main menu. Then the film has to be replaced with the sensing film.

At this point, any of the other three modes of measurement can be selected.

Mode #1: Single measure: the device returns the RGB values for the samples in the measuring chamber, and prints them on the LCD display.

Mode #2: Measurement versus *t*: the device returns the RGB values to frequency during a period of time specified by the user. These parameters are prompted after the measure versus *t* mode has been selected. These values are stored in the SD card and pushed at the same time through the serial port to be analyzed by a computer in real time.

Mode #3: Detection: the device performs the same way as in the Measure versus *t* mode, but after each measure, the software compares the obtained RGB values with those stored in the 'parameters.txt' file on the microSD card. The stored values can be the corresponding color for the sensing film, when the concentration of a specific gas reaches a dangerous

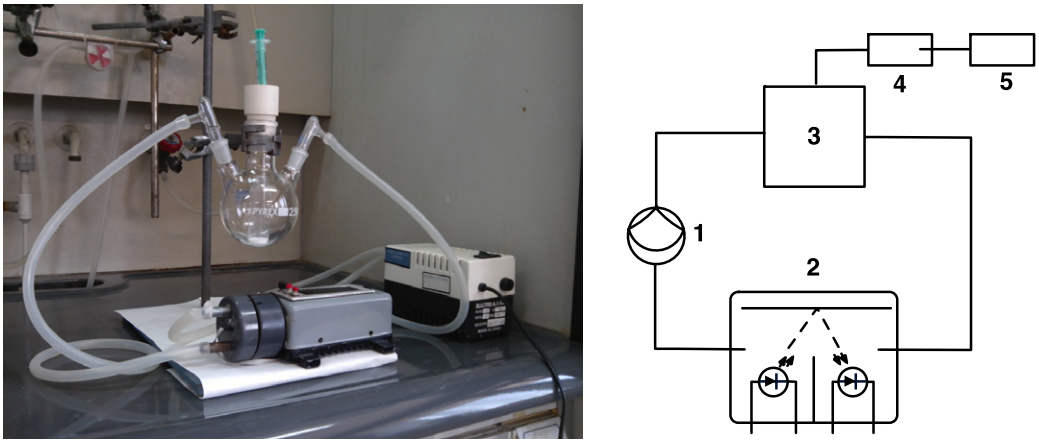
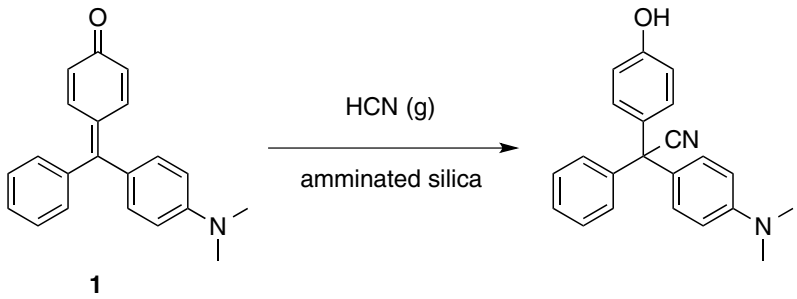


Figure 5. (Left) Photograph of the entire system. (Right) Diagram of the system: (1) diaphragm pump, (2) measuring chamber, (3) 1 L flask, (4) septum, (5) syringe.



Scheme 3. Structure of compound **1** and its chemical reaction with hydrogen cyanide gas.

concentration value. If the measured RGB values pass the threshold (default at 90% similitude), a detection event is triggered. The device acoustically warns about a dangerous atmosphere.

3. Results and discussion

As stated before, the constructed prototype can monitor the state of any chemosensor as long as it produces significant color changes upon reaction with its analyte. In a recent publication, our group demonstrated the performance of chemical compound **1** as a hydrogen cyanide chromogenic chemosensor [30] (see scheme 3). When supported on aminated silica plates, this chemosensor can react with HCN gas in a nucleophilic reaction driven by the CN^- anion.

Chemosensor **1**, initially mallow-pink in color, bleaches proportionally to the amount of HCN present in the air. By way of an example, an atmosphere contaminated with 60 ppm of HCN can completely bleach 2.5 μmol $\cdot$ cm^{-2} of compound **1**, producing an easily detectable color change to the naked eye.

Due to the importance of the detection and monitoring of this toxic gas, we decided that it was appropriate to use the sensing system of **1** with HCN to test our sensing device.

3.1. Preparation of the sensing film of **1***:*

Aminated silica plates (Merck Millipore Silica 60-NH_2) were cut in adequate dimensions (20 $\times$ 30 mm). One of the strips was stored for performing the white balance of the device. The rest of the strips were dipped up to 15 mm in 10^{-3} *M* acetonitrile solutions of chemosensor **1** for 5 s allowing the other half of the strip to remain white for its use as blank reference (see figure 4). After this period, the strips were dried in an oven at 40 °C for 2 min.

3.2. Assembling of the monitoring system

The testing of the device was performed using a closed system which allowed an efficient control of the gas flow over the film. For that, the measuring chamber was connected to an air pump and a three-necked 1 L round bottom flask. In a closed system, the air pump was necessary to force the air flow through the system, which was adjusted to 100 L h^{-1}. The round bottom flask was used to determine the size of the test atmosphere and to allow injection of different amounts of gas through a septum. HCN(g) of known concentration was generated separately from KCN and sulfuric acid following standard procedures. The three parts of the system were connected in series with 8 mm silicone tubing. Any possible absorption of HCN(g) by the silicone tubing was not considered. Thus, the experimental setup was assembled as observed in figure 5.

3.3. White balancing

After turning on the device, the user has to white balance the device. For that, the measuring chamber has to be loaded with

Figure 6. (Left) The sensing film placed in the measurement chamber. (Right) Assembled device and menu operation for the measurement versus time.

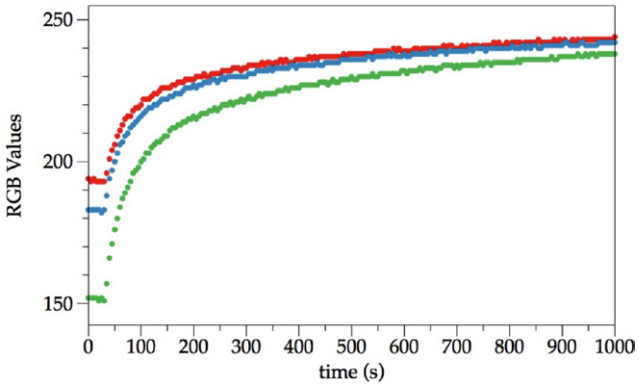


Figure 7. A typical graph of the RGB values versus time after contaminating the system with 14 ppm of HCN gas. The measurement was performed in the reflection mode.

a white strip. Then, in the menu, the white balance option is selected. The film is illuminated and the TCS230 sensors perform the balancing operation with the observed color.

3.4. HCN(g) detection experiments

After the white balance operation, the previously prepared sensing film containing compound **1** is placed in the measuring chamber with a reflection-mode geometry. The 'Measurement versus time' mode is selected and the measurement is chosen to be performed every 5 s. After pressing the start button, the device started to measure the color of the chemosensor (see figure 6). The initial values of RGB(194, 152, 193) and RGB(255, 255, 255) were observed for the left and right channels, respectively, agreeing with the expected mallow-pink color of the chemosensor **1** and the white reference, respectively. Both channels showed a minor deviation of the color values (>1%) during a test period of 12 h.

In a typical experiment, different volumes (i.e. 40 ppm) of HCN(g) were injected into the system after 30 s of measurement. What was observed then was an immediate increase of the three RGB following first-order kinetics. The resulting color values tend to a common RGB value within 240–255, which matches with the white color of the silica strip, indicating that the expected bleaching of the chemosensor **1** has occurred.

Figure 7 shows the typical response of the device after the addition of 14 ppm of HCN gas to simulate a HCN leakage. The addition of HCN to the system took place 30 s after the measurements began. Immediate changes in the RGB values, starting from R: 193, G: 152, B: 183 (mallow-pink), were observed and moved towards a common value of 240–255 (white). These last values agree with the expected decoloration of the chemosensor **1** after reaction with the hydrogen cyanide gas.

Although in this specific example a monochromatic photodetector could also be used, the bleaching of **1** can be treated easily if the RGB values are translated to the CIE *xyY* color space. In this case, there is no color change, but a change in the color luminance. Thus, the measurement of the *Y* value (luminance) of the CIE *xyY* color space is then the most indicative parameter in this case (for the conversion between RGB and CIE 1931, please refer to [46] or [47]). For other chemosensors (i.e. those shifting their color wavelength instead of bleaching or intensifying it) may be appropriate for measuring hue changes instead of luminance.

3.5. Limits of detection

If using the 'Detection mode' (Mode #3), software searches for changes in the luminance of the color bigger than a specified threshold value. In further experiments, using mode #3 and a threshold of 10% (figure 8), we reached a LoD for HCN(g) of 0.2 ppm in a period of 10 min, 10-fold lower than

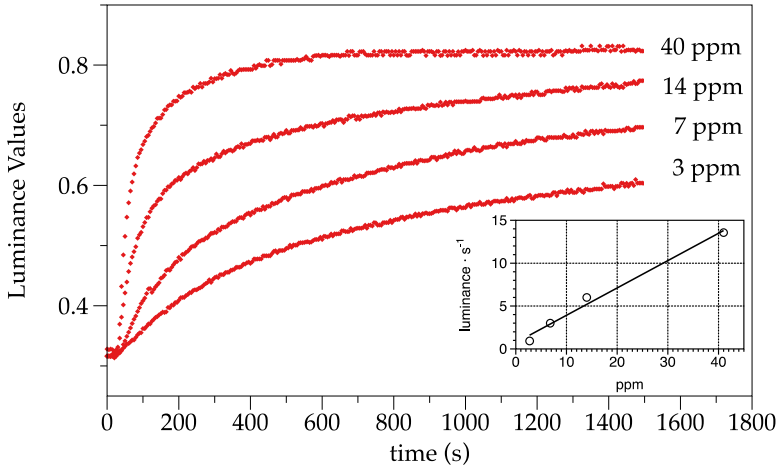
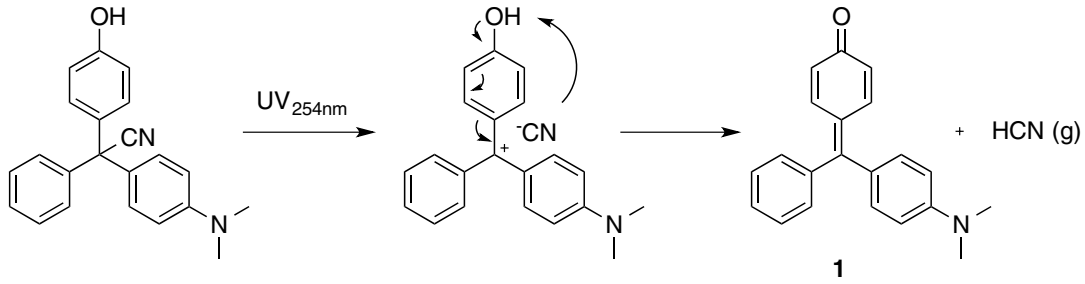


Figure 8. The luminance (*Y*, in the CIE *xyY* color space) plot versus time after contaminating the system with 3, 7, 14, and 40 ppm_v of HCN gas. The measurement was performed in the reflection mode. The inset shows the linear relationship between the concentration and initial reaction rates.



Scheme 4. Photoionic dissociation reaction observed in a leucocyanide derivative of compound **1** after irradiation with UV light (254 nm, 50 W) for 5 min.

those reported for similar compounds when analyzed with the naked eye.

The obtained limit of detection is far below the dangerous concentration for HCN. As stated by the USA National Institute of Occupational Health and Safety (NIOSH), an average population can tolerate HCN in a concentration of 50 ppm for 30–60 min without subsequent effects (ILDH, immediate danger to life and health) with a permissible exposure level (PEL) of 10 ppm [48].

The threshold value, together with the initial and final color values of the sensing film are specified in a text file stored in the microSD card.

3.6. Reversibility

The chemical reaction of compound **1** with HCN forms a colorless leucocyanide. Leucocyanides are known to be able to suffer photoionic dissociation under illumination with ultraviolet light [49]. See scheme 4.

Thus, in order to test the reversibility of this system, we placed already used sensing films under a 50 W 254 nm handheld lamp for a period of 5 min inside a fume-hood. During this period, an immediate coloration of the side of the film where the compound **1** was initially placed was observed. The sensing film was placed back inside the measuring chamber, and simple color measurements (Mode #1) indicated that the regeneration of the chemosensor was complete, as the RGB values matched those of the original film. Repeating this experiment with several films it was observed that the regeneration of the chemosensor is typically achieved within a deviation of 8%.

4. Conclusions

Optical chemosensors have been demonstrated as an interesting alternative for dangerous gas detection thanks to their selectivity and specificity. Notwithstanding, accessible instrumentation for the automatic measurement of a chemosensor state is still rare and expensive. In the present paper, we used modular electronics to build a low-cost and easy-to-construct device capable of detecting dangerous gases after measuring the color of a sensing dye.

By way of an example, we demonstrated the detection capabilities of our device in combination with a specific chemosensor at low concentrations of HCN gas.

We believe that the construction of similar devices is a very important step in the chemosensing field as it helps chemosensor designers to jump to the real application arena. Perhaps more importantly, the use of the FOSS approach brings safety instrumentation nearer to those who most need it.

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