Article

A Paper-Based Ultrasensitive Optical Sensor for the Selective Detection of H₂S Vapors

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Abstract: A selective and inexpensive chemical paper-based sensor for the detection of gaseous H₂S is presented. The triggering of the sensing mechanism is based on an arene-derivative dye which undergoes specific reactions in the presence of H₂S, allowing for colorimetric analysis. The dye is embedded into a porous cellulose matrix. We passively exposed the paper strips to H₂S generated in itu, while the absorbance was monitored via an optic fiber connected to a spectrophotometer. The kinetics of the emerging absorbance at 534 nm constitute the sensor response and maintain a very stable calibration signal in both concentration and time dimensions for quantitative applications. The time and concentration dependence of the calibration function allows the extraction of unusual analytical information that expands the potential comparability with other sensors in the literature, as the limit of detection admissible within a given exposure time. The use of this specific reaction ensures a very high selectivity against saturated vapors of primary interferents and typical volatile compounds, including alkanethiols. The specific performance of the proposed sensor was explicitly compared with other colorimetric alternatives, including standard lead acetate strips. Additionally, the use of a smartphone camera to follow the color change in the sensing reaction was also tested. With this straightforward method, also affordable for miniature photodiode devices, a limit of detection below the ppm scale was reached in both colorimetric approaches.

Keywords: optical gas sensor; chemical sensors; toxic gases; colorimetric probes

1. Introduction

H₂S is a toxic, water-soluble, and flammable gas produced as a byproduct of a wide variety of industrial processes (petroleum and gas natural industries, coal mines, or paper, fertilizer and detergent production) or by the anoxygenic metabolism of some types of bacteria [1]. It is lethal at relatively low concentration levels [2] because it is absorbed by the lungs quickly, causing blood poisoning, headache and nausea, among other symptoms [3]. For instance, it causes loss of consciousness or death by respiratory paralysis by inhalation of 500–1000 ppm for 30 min [4]. Hence, this gas is regulated as toxic and dangerous according to the Occupational Safety and Health Administration (OSHA), that establishes an immediately dangerous to life and health limit of 100 ppm, a construction 8 h limit of 10 ppm, and a peak of up to 50 ppm for 10 min for the general industry (ceiling permissible exposure limit, PEL-C) [5]. Despite this gas having a particular and unpleasant rotten egg smell that can be quickly detected by the human nose [6] with a sensitivity of 5–10 ppb, it cannot serve as a long-term H₂S detector because of olfactory fatigue. Precisely, one of the reasons why this gas is very dangerous is because at very low concentrations humans stop perceiving the smell that it produces due to the saturation of our very own gas detector, the pituitary gland. Therefore, there is a constant requirement to develop portable and real-time quantitative methods for low levels of H₂S in gas streams or the atmosphere.

Additionally, the biological importance of this molecule is the justification of why some of the contemporary research efforts towards the optical detection of H_2S have been focused on solution or living cells [7–10]. Its importance as a biomarker has also been reported [11]. Overall, traditional solution methods [12–28] cope with fluorescence [29–35] and colorimetric sensors based on chromophores [36–44], organometallic complexes [45–48], or nanostructures [49–57], among others [58–64].

From a commercial perspective, the proper adaptation of the above-mentioned solution methods to gas phase sensors would allow the progressive substitution of the traditional gas phase detector tubes based on papers impregnated in metal salts such as lead (II) acetate [65], $CuSO_4$ [66] or $Bi(OH)_3$ [23]. The exploration of these cheaper and more eco-friendly colorimetric paper methodologies has been conducted for some analytes in the past [67–71]. Additionally, the increase in the quality/price ratio of digital cameras built into smartphones may help in the simplification and widening of the operativity of colorimetric sensors [72–84].

Here, we combine both approaches by developing a sensor for gaseous H_2S based on a paper substrate embedded with an arene-dye (bis(7-nitrobenzo[c][1,2,5]oxadiazol-4-yl)sulfane) that serves as spectrophotometric probe. These types of molecules have been exploited as H_2S sensors in solution/biological environments [85–87], but no attempt to exploit its performance in gas phase sensors has been reported. Together with the unusual signal processing that enables us to extract important and general analytical information, the solution-to-gas phase conversion of the chemical probe is the main novelty of the present work and is of direct industrial interest. Besides being employed as a colorimetric probe for the detection of gaseous H_2S using laboratory equipment, the dye was also tested with a smartphone-based colorimetric methodology. Although the dynamic range is higher when the traditional spectrophotometry approach is employed, the limits of detection and quantification are well below the ppm in both cases.

2. Materials and Methods

2.1. Chemicals

Chemicals 4-chloro-7-nitro-1,2,3-benzoxadiazole (NBD-Cl), sodium sulfide hydrated ($Na_2S \cdot xH_2O$), methylamine, 2-mercaptoethanol, 1-butanethiol, hydrochloric acid and other reagents used as interferents or solvents were purchased from Sigma-Aldrich (Madrid, Spain) and used without further purification. The concentrations of hydrated Na_2S solutions were evaluated by titration with standardized HCl.

2.2. Synthesis

2.2.1. Preparation of 7-Nitrobenzo[c][1,2,5]Oxadiazole-4-Thiol (NBD-SH)

Mixed methanolic solutions of Na_2S 1.02 mM and NBD-Cl 0.51 mM were prepared by dropwise addition of Na_2S while stirring. Once mixed, the solutions were kept under agitation for 1 h until a dark purple solution was formed.

2.2.2. Preparation of (bis(7-Nitrobenzo[c][1,2,5]Oxadiazol-4-yl)Sulfane (NBD)$_2$S

Mixed methanolic solutions of NBD-Cl 1.50 mM and Na_2S 0.75 mM were prepared by dropwise addition of Na_2S while stirring. The solutions were kept under agitation for 3 h until a coppery-yellow solution with a precipitate was formed. This precipitate was then separated from the supernatant by means of 10 centrifuge cycles (10 min at 5000 rpm each, 66% yield). The resulting compound was characterized by electrospray ionization mass spectrometry (ESI-MS) and UV-Vis spectroscopy. ESI-MS spectra in positive mode displayed a main parent peak at ~360 m/z that matched with that of the thioether compound (see Figure S1). In diluted methanol solutions, the UV-Vis spectral features resembled those reported by Montoya et al. [85] This characterization constitutes direct proof of the purification of (NBD)$_2$S after the corresponding stoichiometric titration of NBD-Cl. It must be stressed that the procedure developed here constitutes a faster purification route than that described by Montoya et al. [85] Notably, the solution remained stable for at least

1 year, as checked by UV–Vis spectroscopy (see Figure S2 of the Supplementary Materials for details).

2.2.3. Sensor Preparation

The sensor was prepared by adding 100 μL of $(NBD)_2S$ 10 μM in methanol to a 1 cm × 2 cm strip of Whatman's chromatography paper (Whatman, Cat. No: 3001 604, Little Chalfont, UK) and dried in air. The transmittance of the paper was measured to be ~80% at the excitation wavelength, high enough to ensure sensing in absorbance mode. The impregnating solution was diluted enough to avoid the precipitation of the thioether. This paper strip containing the sensing probe was then encapsulated between two glass plates attached to each other (hereafter referred to as the sensor). In this way, the chromatography paper was covered by the glass on both sides, producing a channel into which the gas could easily and homogeneously penetrate. Preliminary tests showed that this design maximized the interaction of the sensing part with the analyte. A scheme and some exemplifying photographs of the basic sensor setup are shown in Figure S3 for the sake of visualization.

2.3. Sensing Experiments and Instrumentation

2.3.1. Mass Spectrometry

Mass spectra were measured using a triple quadrupole system coupled to an Electrospray Source, Thermo Fisher TSQ Quantum Max (Thermo Fisher Scientific, Waltham, MA, USA). Spray voltage and capillary temperature were set at 3000 V and 35 °C, respectively. Full scan positive mode was selected to measure all positive ions generated in a m/z range between 100 and 600. Scan time was set to 1 s and the acquisition time was 2 min.

2.3.2. Spectroscopy

The spectroscopic measurements were carried out by means of a spectrophotometer (Ocean Optics USB4000, Ocean Optics, Orlando, FL, USA), a deuterium/tungsten lamp (DH-2000-BAL for paper sensor experiments and DT-MINI-2-GS for experiments in solution, Ocean Optics), and two 600 nm diameter optical fibers (Ocean Optics) coupled to collimating lenses before and after passing through the sample. The time step was set to 100 ms.

2.3.3. Exposure of $(NBD)_2S$ in Solution to Gaseous H_2S

Test experiments in methanol solutions were performed by bubbling the H_2S of the headspace of a reservoir dragged with a N_2 flow of 0.1 L/min. The flow was controlled by a Bronkhorst F-201FV mass flow controller.

2.3.4. Exposure of the Paper Sensor to Gaseous H_2S

Exposure to the gas was performed in a passive sampling manner at room temperature for 2 min. Specifically, the sensor was fixed to one of the walls of a 4.5 mL quartz cuvette, keeping it out of contact with the analyte that was placed in the lower part. Gaseous H_2S was prepared in situ by the addition of HCl to Na_2S aqueous solutions. HCl concentration was always 20-fold higher than that of Na_2S, to ensure the excess HCl for the reaction to be completed. The amount of Na_2S solution was selected according to the volume of the head space to provide the desired H_2S concentration in the sampling volume. The generated gas would subsequently interact with the sensor. Additionally, similar experiments were carried out by generating H_2S via the reaction $FeS + 2HCl \rightarrow FeCl_2 + H_2S$.

2.3.5. Camera-Based Color Recognition

Pictures of the sensors were taken in raw image format with a resolution of 20 megapixels using the camera of a regular smartphone (Xiaomi M1805E10A). Constant and uniform artificial light was used for all pictures, with a white chromatography paper strip placed besides the sensor as a reference for the comparative analysis of the pictures and to con-

trol for possible light fluctuations. Pictures were then processed using Adobe Photoshop CS6 (Adobe Inc., San Jose, CA, USA) without applying any color or exposure corrections. The color information for each of the sensor exposures was extracted using the major color spaces, namely CIELAB, RGB, HSB and CMYK. The analysis of the pictures revealed that the best characterization of our sensors corresponded to the *a** parameter in the CIELAB color space, which accounts for the green-to-red palette.

3. Results and Discussion

The sensing mechanism for the detection of H_2S using $(NBD)_2S$ as a colorimetric probe is based on the formation of its synthesis precursor NBD-SH, which displays an intense absorption band centered at 534 nm, as depicted in Figure 1. Figure 1a shows the chemical reaction pathway for the formation of $(NBD)_2S$ from NBD-Cl, and the corresponding solution UV-Vis spectra of the isolated species. According to Montoya et al. [85], NBD-Cl and other derivatives suffer a standard nucleophilic bimolecular $S_{N2}Ar$ addition from thiol-containing species via formation of a Meisenheimer complex. The resulting thiol, NBD-SH, proceeds to the formation of the thioether $(NBD)_2S$ under excess of NBD-Cl. The $(NBD)_2S$ probe is insensitive towards thiol attack because of its electrophilicity. However, H_2S remains nucleophilic enough to attack the ipso carbon of the thioether and regenerate the thiol. The UV-Vis spectra of the compounds involved in the reaction (see Figure 1a) are shown in Figure 1b. NBD-Cl shows its maximum absorbance peak at 337 nm. The spectral shapes of these bands are close to those reported by Montoya et al. [85], while the maxima of the absorption peaks at 543 nm for (NBD)SH and 406 nm for $(NBD)_2S$ are slightly different from these prior results due to hydrogen bonding and polarity differences provoked by solvent effects.
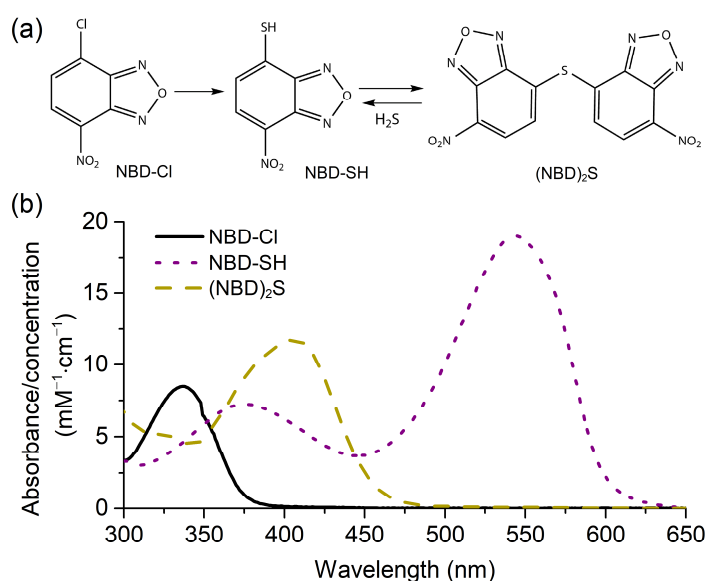

Figure 1. (**a**) Chemical reaction pathway of NBD derivatives involved in the sensing mechanism, namely NBD-Cl, NBD-SH and $(NBD)_2S$. (**b**) UV−Vis spectra of NBD-Cl, NBD-SH and $(NBD)_2S$ in diluted methanol solution.

The formation of NBD-SH in solution from isolated $(NBD)_2S$ (32.5 μM) in the presence of bubbled H_2S at 750 ppm is shown in Figure 2a over a time period of 90 s. The absorbance of NBD-SH at 543 nm grows upon exposure to H_2S, with an isosbestic point at 448 nm and a shift of the peak at 406 nm towards blue, which is clearly indicative of the formation of the thiol from the thioether. This last peak possesses contributions from the two involved species, denoting a partial consumption of $(NBD)_2S$ due to its relative excess. The sensing reaction is easily detected with the naked eye by the appearance of a purple solution provoked by the electron delocalization in the deprotonated S^- group within the

aromatic moiety. The operativity of this set of coupled reactions has already been tested in solution; therefore, a question arises about its transferability to solid detectors.
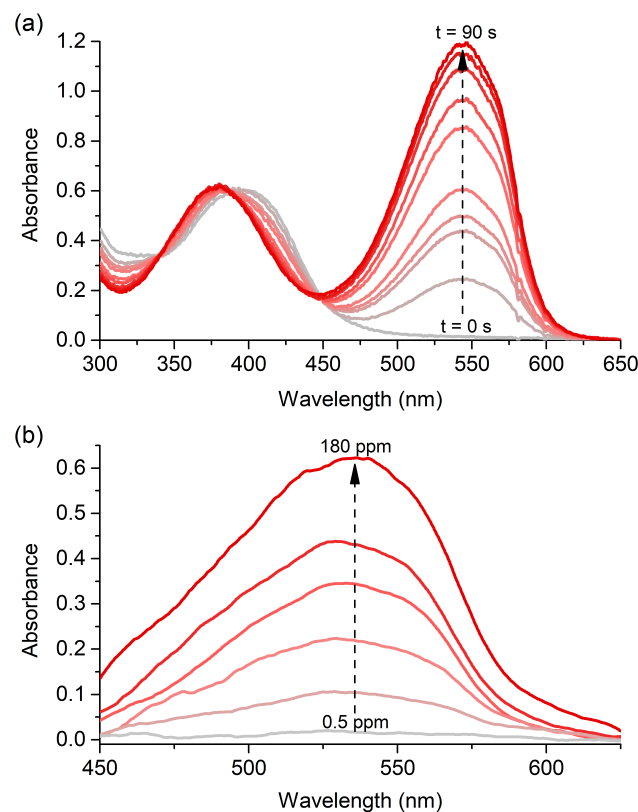

Figure 2. (**a**) Time-dependent response of the colorimetric probe. Exposure of a 32.5 μM (NBD)$_2$S methanol solution to 750 ppm of H$_2$S (bubbled in a N$_2$ stream) in the 0–90 s range. (**b**) Spectral response of the embedded paper strip under an exposure of 15 min to H$_2$S atmospheres of different concentrations in the 0–180 ppm range.

Hence, to alleviate the doubts concerning its applicability in solid-state gas sensors, paper strips embedded in (NBD)$_2$S were exposed to low and moderate concentrations of H$_2$S gas for 15 min. As can be seen in Figure 2b, the formation of NBD-SH can be monitored by UV−Vis spectrophotometry, from a band centered at ∼534 nm. The absorbance of this band increases with the concentration of the gas, allowing its use for quantification purposes. The shift and broadening of the thiol band can be ascribed to the infiltration into a porous substrate. We conclude that it is feasible to use a paper-based (NBD)$_2$S probe to detect H$_2$S, even in the absence of any solvent. The direct reaction between (NBD)$_2$S and H$_2$S is ensured because of the porosity of the cellulose and the reaction time is maximized by the partial encapsulation of the strip (see methods above).

The highly specific reaction that takes place during the sensing process ensures the selectivity of the system. In Figure 3, this selectivity is demonstrated against a set of volatile compounds, including commonly used solvents, thiols, inorganic and organic acid and basic vapors, together with organic reductive compounds such as formaldehyde. We measured the absorbance of the sensor during its exposure to saturated vapors of these compounds and compared their corresponding signal with that produced by a reference atmosphere containing 50 ppm H$_2$S. Although in all cases the gas concentration of the interferent was substantially higher than that of H$_2$S, exposure to the latter always led to the greatest changes in absorbance. Of all the selected potential interferents, only 2-mercaptoethanol, formaldehyde and 1-butanethiol produced clearly measurable changes in the sensor. This change was, however, 125-, 4900- and 9600-fold smaller, respectively, than that induced by H$_2$S, at the same concentration. Additionally, we confirmed

that dry N_2 did not produce any change in the sensor, and no influence of the air humidity was observed when we exposed the paper strips to humidity generated by water reservoirs or dry N_2. We observed that the sensors deteriorated within a week after their fabrication. However, the long-term stability of $(NBD)_2S$ in solution (at least up to a year) and the easy procedure for the preparation of the embedded paper strips would allow for the straightforward fabrication of sensors immediately prior to their use in the required environment.
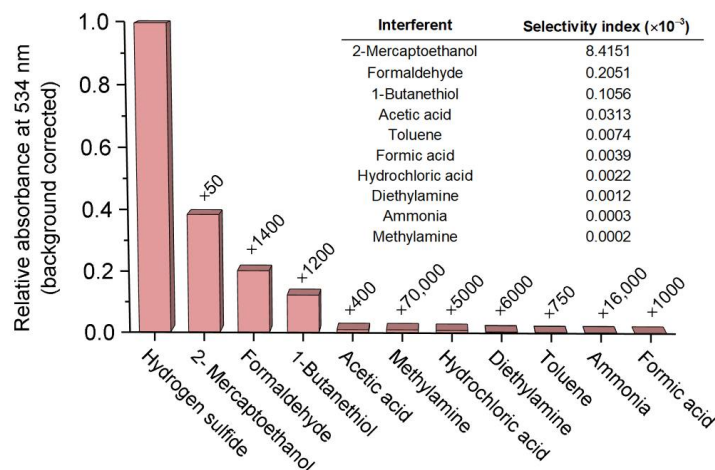

Interferent	Selectivity index ($\times 10^{-3}$)
2-Mercaptoethanol	8.4151
Formaldehyde	0.2051
1-Butanethiol	0.1056
Acetic acid	0.0313
Toluene	0.0074
Formic acid	0.0039
Hydrochloric acid	0.0022
Diethylamine	0.0012
Ammonia	0.0003
Methylamine	0.0002

Figure 3. Effects of various saturated vapors on the absorbance at 534 nm of the paper strip containing $(NBD)_2S$. H_2S was considered as a reference with a concentration of 50 ppm. The relative concentrations of the interferents are denoted on top of each bar. The inset chart shows the selectivity index for each vapor as defined in the text.

To quantify the sensor selectivity, we evaluated the selectivity index $K_{I/A}$, defined as the signal-to-concentration ratio for the interferent gas divided by that of the target analyte (H_2S) after a 15 min exposure. The values of $K_{I/A}$ for each interferent are included as an inset chart in Figure 3. The very low values obtained in all cases further confirm the high selectivity of the sensor and indicate that, despite the high relative concentration of the interferents, the exposure to H_2S was responsible for a distinctive and intense modification of the spectral properties of the colorimetric probe.

We analyzed the temporal variations in the sensor responses to increasing concentrations of H_2S gas in the 0–250 ppm concentration range by monitoring the background-corrected absorption at the wavelength of maximum change (534 nm) ΔA_{534}. The temporal evolution of the signal $S = \Delta A_{534} - A_{700}$ is provided in Figure 4a for a set of H_2S concentrations in the above-mentioned range. It should be noted that the background signal at 700 nm was subtracted from that at 534 nm to account for changes in the baseline due to detector drifts. The sigmoidal-shaped sensing kinetics were fitted to non-linear ad hoc functions of the form:

$$S(c,t) = A_\infty(c)|\tan h[k(c)t/2]|, \tag{1}$$

where A_∞ is the saturation value of the signal at a certain analyte concentration, c, which is ensured by the hyperbolic tangent function that contains the time (t) dependence. k is the parameter that defines the curvature of the S-shaped curve at short times. The fitting data are plotted as continuous red lines in Figure 4a. This functionality was selected after a hard trial-and-error procedure, and, as a result, the fitted parameters are simple functions of the H_2S concentration c. Specifically, for time units in min and c in ppm, $A_\infty(c) = 0.06449 \cdot c^{0.43644}$ ($R^2 = 0.99420$) and $k(c) = 0.17738 + 0.00163 \cdot c$ ($R^2 = 0.99985$), which enables a wide dynamic range with a lower limit of about 0.05 ppm and short sampling times (see below). These coefficients are shown in Figure S4 of the Supplementary Materials. The fit provides an average coefficient of determination of $\langle R^2 \rangle = 0.99982$ in

the considered time and concentration ranges. Such agreement allows us to confidently extrapolate important analytical information, as explained in the next paragraph.
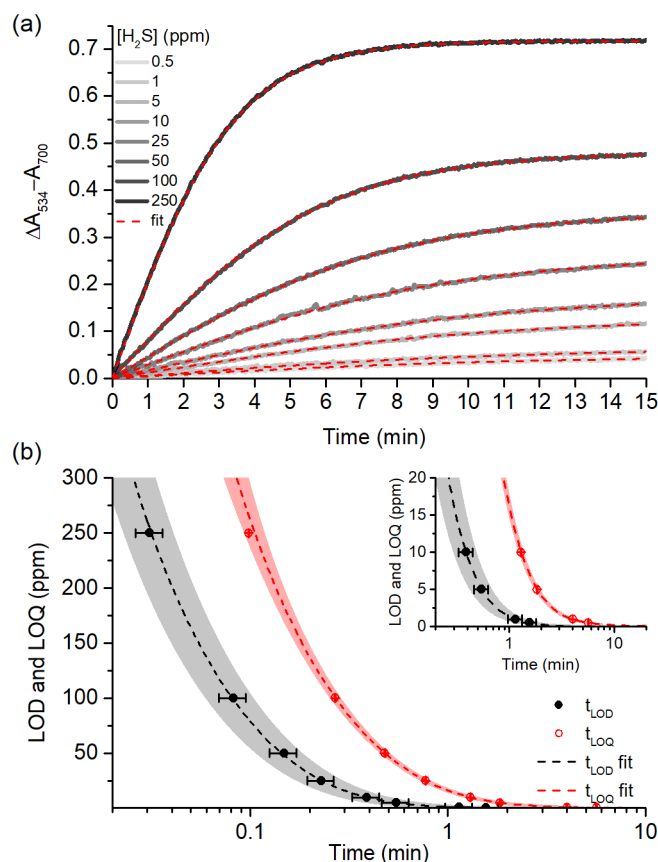

Figure 4. (**a**) Kinetics for the colorimetric signal $S(t)$ (see text for details) of the sensor as a function of the H_2S concentration in the passive sampling experiment. Grayscale lines indicate the experimental data, while red dashed lines correspond to the sigmoidal fits described in the text (see Equation (1)). (**b**) Semilog plots of the experimental LOD ($S/N = 3$) and LOQ ($S/N = 10$) values for different exposure times (symbols). Dashed lines correspond to the analytical inversion of Equation (1). Shaded regions correspond to the error limits obtained from the fitting function, and the error bars stand for the experimental error ($\pm 1\ \sigma$) of triplicate experiments. Inset shows the low concentration region.

　　　The signal evolves with time; therefore, we have first calculated the steady-state or "asymptotic" limits of detection (LOD_∞) and quantification (LOQ_∞) as $A_\infty = \alpha N$ where $\alpha = 3$ ($A_\infty = LOD_\infty$) or 10 ($A_\infty = LOQ_\infty$), and N is the instrumental noise extracted from the arithmetic mean of ten blank experiments. Statistical errors are evaluated by error propagation. These parameters provide information about the minimum detectable and quantifiable concentrations at a time $t \rightarrow \infty$. The resulting values are $LOD_\infty = 5.4 \pm 1.5$ ppb and $LOQ_\infty = 86 \pm 23$ ppb. From the root of the fitting function, the more useful parameters LOD_t and LOQ_t can also be evaluated. They are defined as the minimum detectable and quantifiable concentration within a period of t min. These obtained values are $LOD_{15} = 0.008 \pm 0.002$ ppm and $LOQ_{15} = 0.12 \pm 0.03$ ppm for an exposition time of 15 min, and $LOD_{10} = 0.012 \pm 0.003$ ppm and $LOQ_{10} = 0.19 \pm 0.04$ ppm for 10 min exposures. This last value is well above the PEL-C. Finally, the time required to obtain a signal equal to αN at each concentration is extracted from both the experiments and the analytical inversion of Equation (1). The results are plotted in Figure 4b. The shaded regions indicate the limits extracted from the error propagation of the analytical inversion of Equation (1). Both LOD and LOQ decrease quasi-exponentially with the exposition time.

　　　A comparative study with both colorimetric commercial methods and results published in the scientific literature for the detection of gaseous H_2S postulates our sensor

as a feasible alternative in the field. Most contributions reported sensors with relatively high LOD (see, for instance, refs [21,30]), with no calibration or selectivity data in some cases [88], here we focus on some examples of colorimetric approaches with the lowest LODs found in the literature. Sen et al. [38] reported a "limit of detection" of 50 ppb upon 15 min exposure, which is more than six-fold higher than our measured value. For their part, Tanaka et al. [40] provided an $LOD_{60} = 19$ ppb, also much higher than our predicted value according to the extrapolation in Figure 4b. Our results are also favorable against naked-eye sensors based on $Bi(OH)_3$ [23] and some fluorescence methods [31]. The proposed chemical probe is free of heavy metal compounds, which plays right into our approach against other reported methods. This is the case of the interesting work by Silveira da Petrucci and Cardoso [35], in which a Hg-based fluorescent probe is employed in a paper-based method with $LOD_1 = 3$ ppb, estimated out of the linear calibration region.

On the other hand, comparison with commercial tubes is not an easy task because, in most cases, companies do not provide measuring times. Some stroke tubes based on heavy metals are reported to have $LOQ_2 = 2$ ppm (lead acetate based, Sensidyne, LP) [65] or $LOQ_3 = 0.1$ ppm (tubes based on $HgCl_2$, Rae Systems, Inc. (San Jose, CA, USA) [89], close to our values of $LOQ_2 = 0.16 \pm 0.03$ ppm and $LOQ_3 = 0.12 \pm 0.03$ ppm. The company Gastec has developed metal-free colorimetric tubes for the detection of H_2S, ranging from 0.2 to 4000 ppm. The most effective (hydrogen sulfide 4HT, Gastec Corporation, Fukayanaka, Japan) [66] has an $LOD_3 = 0.05$ ppm, also comparable to the evaluated $LOD_3 = 0.05 \pm 0.01$ ppm for our paper strips. In relation with the classical use of lead (II) acetate, it must be mentioned that the original version of lead acetate paper tapes gave LODs of 5–10 ppm, considerably higher than the value provided here. Although it has been recognized that these classical tapes, besides being ecologically questionable, are strongly dependent on ambient humidity [90] (which is not the case with our sensor), some improvements on the use of this compound are still underway on the scientific community. For instance, one colorimetric approach led to an LOD of 400 ppb [44]. Additionally, some complex instrumental refinements available in the market provide upgraded performance with respect to our colorimetric approach. As an example, the proposal reported by Innov Analysis Systems (Issoudun, France) [91] with an $LOD_{0.33} = 5$ ppm compares favorably against our value of 13.6 ppm. However, it must be noted that several compounds, such as mercaptans, are strong interferents for the detection systems behind many of these commercial tubes. In contrast with our proposal, this may limit their usability in certain atmospheres and needs to be carefully considered when comparing and selecting appropriate detectors for each scenario.

In principle, the calibration of the absorbance kinetics provided by Equation (1) enables the quantification of the H_2S concentration by measuring the signal at any time or the kinetics over a (narrow) period. This calibration also encompassed the long-time behavior through A_∞. The precision and accuracy of the calibration was assessed with three blind experiments covering a wide concentration range. The results obtained with the fit of the kinetics over 15 min to Equation (1) were 4047 ± 3, $11{,}577 \pm 6$ and $153{,}339 \pm 34$ ppb. In comparison with the concentrations obtained with the A_∞ values, the absolute errors are recurrently higher in this case, although the average least significant difference between both calibration methods is 0.6 ppm. It can be concluded that Equation (1) provides an adequate calibration function because it allows the extraction of the H_2S concentration faster than that obtained via A_∞, although both methods are equally usable on the condition that the H_2S concentrations were high enough to ensure a fast saturation value. Additionally, we have performed a set of three experiments in which the H_2S vapors were produced in situ by the reaction of FeS with HCl. Given the difficulties to obtain H_2S samples produced naturally, meaning without human intent, we deemed it appropriate to include this second source of H_2S in our analysis. Besides being of educational interest, it is also of importance in the oil and natural gas industry because of the common formation of sulfide scales [92]. The target H_2S concentrations in our experiments span the 5–280 ppm range. The difference between the nominal and the calculated concentration

after 2 min exposure led to an average absolute deviation of $\langle \Delta_m \rangle$ = 0.6 ppm. Experimental results are shown in Figure S5. These tests validate our sensor against another (dry) H_2S source and demonstrate its analytical robustness. Finally, it should be mentioned that the consistency between both generation methods constitutes a double check of the humidity-independent kinetics provided by the specific reaction driving the sensing mechanism. To emphasize the negligible effect of humidity conditions, the effect of water vapors on the sensor absorbance is included in Figure S5.

　　　　Finally, camera-based color recognition was also assessed as a simple colorimetric alternative for the detection of H_2S. Among the major color spaces, CIELAB offered the best results. CIELAB, or $L^*a^*b^*$, is a robust 3D color-space that maps the visible spectrum in terms of three coordinates, namely, L^* which represents the luminosity (with values ranging 0–100); a^*, which accounts for the green-to-red palette (negative for green and positive for red); and b^*, which collects information about the blue-to-yellow coordinate (negative for blue and positive for yellow). In Figure 5, we show the variation of the a^* coordinate as a function of the H_2S concentration. This parameter was obtained from photographs of the embedded paper strips taken after an exposure of 15 min to H_2S. It is quite apparent that saturation is reached above ~1.5 ppm, but a linear region (R^2 = 0.99070) can be found between 0 and 1.5 ppm. Although the operation and dynamics ranges were smaller than those obtained with spectroscopy, the LOD_{15} and LOQ_{15} (obtained as $\alpha \sigma_b / m$, where σ_b is the standard deviation of the intercept and m is the slope of the calibration line) were 106 ± 4 ppb and 355 ± 14 ppb, respectively, values that are still competitive with commercial tubes and only ~three-fold higher than those obtained with the traditional spectrophotometer-based colorimetric approach. Multiple linear regression was also tested, employing n = 7 points of the three $L^*a^*b^*$ coordinates and H_2S concentration as the dependent variable. This led to an equation of the form $[H_2S] = -1.6779 + 0.0076 \cdot L^* + 0.2547 \cdot a^* + 0.0499 \cdot b^*$, with R^2 = 0.98895. The randomness of the residual patterns shown in Figure S5 indicates the suitability of the model. The LOD was evaluated to be 109 ± 2 ppb according to Bro et al. [93] from the calibration line between predicted and nominal H_2S concentrations (R^2 = 0.99832, see Figure S7). This option was, however, set aside because of its relative smaller coefficient of determination and the inherent statistical difficulty in the evaluation of the LOD/LOQs and reliable associated errors within partial least-squares fits.
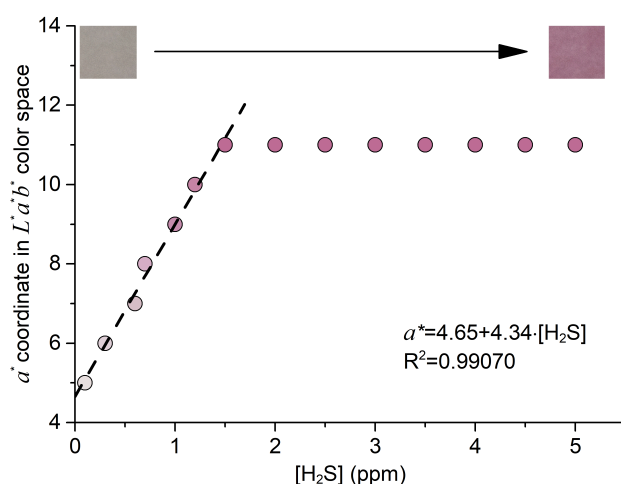

Figure 5. Colorimetric response of the paper strips mapped in the a^* coordinate of the CIELAB color-space. The color of the dots corresponds to the extracted color of the sensor at each concentration. Calibration line in the low-concentration region is added as a dashed line. The linear calibration curve and coefficient of determination are also typed in the graph. Photographs of the unexposed paper (left) and color-saturated sensor (right) are included for the sake of visualization. Values were obtained as the nearest integer of the average of three independent experiments.

Both the *a** parameter analysis and the multiple linear regression obtained from all three *L**a*b* coordinates show that, within their limitations, any smartphone camera can be used to quantify the color change produced by our sensor. Photodetectors inside digital cameras work in a similar way as those implemented in any regular spectrophotometer and; despite their spectral resolution being lower, they can be used for color measurements. With digital cameras incorporated in every smartphone, these present clear advantages in terms of availability and affordability in comparison with regular spectrophotometers. An exhaustive comparison between both methods is beyond the scope of this work, but we consider camera-based color recognition to be a plausible alternative to spectrophotometers in those cases where the required spectral range allows for it. In our case, the combination of the proposed paper-based sensor with smartphone-assisted color measurement could result in a portable, straightforward, and inexpensive system for the detection of gaseous H_2S.

4. Conclusions

We present a simple experimental procedure for the construction of a disposable and selective paper-based sensor for the spectroscopic quantification of H_2S vapors. The method exploits the specific bimolecular nucleophilic aromatic substitution of arene-derivative dyes that can be easily transferred to a solid support to obtain a gas detector. The colorimetric signal of the device upon its exposure to H_2S led to particular and selective spectral changes whose temporal evolution could be evaluated either with UV–Vis spectroscopy or image processing. Although the concentration and temporal ranges for the quantification in each optical method differ substantially, we were able to use the compiled data as input in calibration procedures, which allowed for the temporal detection and quantification of H_2S with low LOD/LOQs. The results obtained from UV–Vis spectroscopy enabled us to reach better LOD/LOQs than most commercial methods based on poisonous transition metal salts such as lead or mercury. In addition, we have demonstrated that it is possible to perform a direct calibration at low H_2S concentrations through the color extraction of digital pictures taken with a regular smartphone, broadening the potential range of use of our disposable sensor.

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