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New optical paper sensor for in situ measurement of hydrogen sulphide in waters and atmospheres

J. Pla-Tolós, Y. Moliner-Martínez, J. Verdú-Andrés, J. Casanova-Chafer, C. Molins-Legua *, P. Campíns-Falcó

Department of Analytical Chemistry, Faculty of Chemistry, University of Valencia, Doctor Moliner 50, Burjassot, Valencia, Spain

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ABSTRACT

A novel and low-cost colorimetric sensor for the determination of hydrogen sulphide in environmental samples has been developed. This sensor is based on the immobilization of the reagent N,N-Dimethyl-p-phenylenediamine and $FeCl_3$ in paper support, in which the H_2S is adsorbed in order to give rise to the formation of methylene blue as reaction product.

The sensor has been applied to determine H_2S in water and air samples. Two different sampling systems for H_2S caption from the air have been assayed: active and passive sampling. The analytical properties of the different systems have been obtained and compared. The analytical signals, corresponding to the methylene blue, have been obtained measuring the absorbance by conventional reflectance diffuse or using different algorithms for quantifying color intensity. The results obtained with both measurement procedures were comparable, with a detection limit of 1.11 and 1.12 mL m^{-3} for air samples (active and passive), and 0.5 mg L^{-1} for water samples. The developed sensor provides good accuracy and precision (RSD < 12%) and simplifies significantly the analytical measurements because it avoids the need of preparing derivatization reagents, sample handling and allows in situ measurements. The reaction product obtained is highly stable in this support and no provide any blank signal. Under the optimal conditions, the proposed method exhibit excellent visual sensitivity for the naked eye procedure, making the detection of H_2S possible.

1. Introduction

Hydrogen sulphide is a toxic, corrosive, flammable and water-soluble gas, with a characteristic smell of rotten eggs. This gas can be produced from natural sources (volcanic activity or by sulphate-reducing bacteria) or from industrial activities (petroleum extraction, natural gas industries, coal mines, fuel burning, production of detergents and the industrial processes of paper) [1–4]. As a consequence of its toxicity and the risks related with exposure in several occupational settings, the detection of this compound has gained importance within the analytical field [5]. Moreover, although the human olfactory threshold is set close to 10 μL m^{-3} (depending on the individual and the exposure time), there is a maximum sensitivity of, approximately, 100 mL m^{-3} above which or through prolonged exposure, the perception of the gas disappears because the neurotoxic effects overwhelm the olfactory nerves [1,4,6]. The Directive 2009/161/EU – "Indicative Occupational Exposure Limit Values" stablishes values for a reference period of eight-hour time weighted average and for a short term period of 15 min of 5 mL m^{-3} and 10 mL m^{-3}, respectively, for hydrogen sulphide. Moreover, in Table 1 are summarized the occupational exposure limit of H_2S recommended by different organizations.

Therefore, there is a requirement to develop portable and real-time monitoring methods for low levels of H_2S. Chemical sensors are very useful tools which can be employed in a large variety of applications, such as industrial hygiene, emissions monitoring or clinical diagnostics. These sensor-based devices have shown several benefits in terms of high sensitivity, fast response, easy operation and low cost [7]. Some publications have already published different types of sensors to determine this compound in air or water samples [1–4, 7–20].

Optical sensors offer several interesting properties over the other types because they are sensitive and easy to operate [1]. Some of these sensors are based on the changes in the optical properties of reagents immobilized on a solid support when interacts with the analyte. More concretely, colorimetric sensors are especially attractive because they offer some potential advantages, such as the possibility of being visually observed and measured by the naked eye, without the requirements of sophisticated instrumentation [1,3,21]. Thus, some colorimetric sensors have been

* Corresponding author.

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Table 1
Occupational exposure limit values for H_2S proposed by different organizations.

	Permisible limit value (PEL)		Recommended exposure limit (REL)	Immediately dangerous to life or health (IDLH)
	Threshold limit value-time weighted average (TLV-TWA)	Threshold limit value-short term exposure limit (TLV-STEL)		
Occupational safety and health administration (OSHA)				
Permisible limit value (PEL				
Construction industry	10 mL m^{-3}	–	–	–
Maritime	10 mL m^{-3}	–	–	–
General industry	[a]	[a]	–	–
American conference of governmental industrial hygienists (ACGIH)	1 mL m^{-3}	5 mL m^{-3}		
National institute for occupational safety and health (NIOSH)	–	–	10 mL m^{-3} (10 min)	100 mL m^{-3}
Instituto Nacional de Seguridad e Higiene en el Trabajo (INSHT)	5 mL m^{-3}	10 mL m^{-3}	–	–

[a] Exposures shall not exceed 20 mL m^{-3} (ceiling) with the following exception: if no other measurable exposure occurs during the 8-h work shift, exposures may exceed 20 ppm, but not more than 50 mL m^{-3} (peak), for a single time period up to 10 min.

reported for the detection of H_2S in air [2,6,15,17,22–25].

On the other hand, paper-based devices have suffered a rapid growth in the analytical chemistry community. As a result, several publications which use paper as a substrate have been published [26–30]. This expansion can be due the intrinsic characteristics of paper, which is an inexpensive material with a large range of thickness, porosity and chemical structure. Furthermore, depending on the type of paper substrate, it can offer different and interesting properties, such as gas permeability, high mechanical flexibility and the possibility to be impregnated with liquids through capillary action, to hold and retain liquids, to be colored and printed, and to be chemically functionalized [27].

Additionally, the current evolution in smartphones and tablets opens up a wide range of interesting alternatives for the development of new analytical tools, because these devices are equipped with several gadgets, such as high resolution cameras, powerful processors or high storage capacity, among other features [31,32]. Free image-editor applications can also be a very useful alternative to scientific equipment [33]. Moreover, the connectivity of mobile phones to internet allows to share data easily and providing real-time results at the point of need [31].

The present work pretends (I) to combine the advantages of paper-based sensors and mobile phone devices to develop a useful analytical method to determine hydrogen sulphide in water and air samples, (II) to compare the analytical properties of different measuring procedures, (III) to control the amount of H_2S in real samples using the proposed sensor. The formation of the methylene blue has been chosen as a colorimetric reaction because it is widely used for the determination of dissolved sulphide in water since its introduction by Fischer in 1883 [5]. This method involves the reaction of this compound with N,N-Dimethyl-p-phenylenediamine in presence of Fe (III) ions, giving rise to a characteristic blue coloration with a maximum at 670 nm, corresponding to the production of the heterocyclic thiazine dye [5]. This reaction is shown in Fig. 1.

The proposed method allows sampling and measuring without any sample treatment, providing an excellent alternative to the conventional analytical approaches for H_2S. These features make this sensor a potentially powerful tool for monitoring hydrogen sulphide in air and water samples.

2. Materials and methods

2.1. Instruments

Absorption spectra were recorded using a Cary 60 UV–vis spectrophotometer (Agilent Technologies, United States) equipped with a diffuse reflection probe from Harrick Scientific Products (United States). The diffuse reflection accessory has an integral video camera in order to select the sample area to be analyzed by providing a visual image. Spectra were recorded from 200 to 800 cm^{-1}. For data processing, CaryWinUV software from Agilent Technologies was used. Ricoh Aficio MP2550 PCL6 multifunctional printer (Ricoh, Japan) was employed to scan the colored sensor. The LG Optimus L5 II smartphone (LG, South Korea) was used to take photos of the sensors. The images were analyzed by the free image editor software GIMP. Grade 41 whatman filter papers ashless (GE Healthcare Life Sciences, United Kingdom) were used as a support for the reagents. An Apex personal sampling pump (Casella, United Kingdom) and Swinnex filter-holder (Merk Millipore, Germany) were used in active sampling. Flow rate was measured using a Multicon KS external flow calibrator (Dräger, Germany). Dilution bottles (2 l) (Supelco, United States) and magnetic stirrer (450 W) (Stuart Scientific, United Kingdom) were used to create the atmosphere of hydrogen sulphide. Dräger-Tube for hydrogen sulphide 0.5/a and Dräger accuro pump (Dräger, Germany) were used to quantify hydrogen sulphide in air samples.

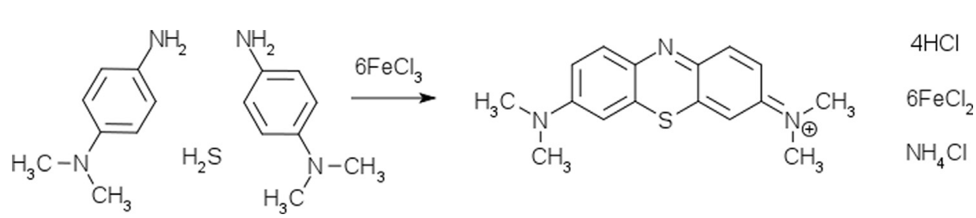

Fig. 1. Reaction between hydrogen sulphide, N,N-dimethyl-p-phenylenediamine and Fe (III) to form the methylene blue.