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A cost-efficient and portable sulfide device with in situ integrating gas-permeable porous tube isolation and long path absorbance detection

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ABSTRACT

A cost-efficient and portable device for detecting sulfide at submicromolar level was fabricated by in situ integrating gas-permeable porous tube isolation and long path absorbance detection. The device consisted of a pair of petri dish, having a diametrically strung porous membrane tube in the top cover. The ends of the tube were terminated by a light emitting diode and a photodiode via plugging acrylic optical fiber into the light input/output of tees. Sulfide put in the bottom dish was liberated by addition of diluted acid through a port on the cover. The liberated hydrogen sulfide diffused into the porous membrane tube and reacted with alkaline nitroprusside acceptor in the tube. The color change in the long path porous membrane tube cell was real-time monitored in the transmission mode. The device responded linearly to sulfide concentration over the range of 0.5–150.0 μmol/L with relative standard deviations less than 5% in all cases. The limits of detection for sulfide were within the range 0.2–1.5 μmol/L in aqueous standard and newborn calf serum. The device was successfully applied to the determination of sulfide in human serum samples.

1. Introduction

The recognition of hydrogen sulfide (H_2S) as the third most important gasotransmitter after nitric oxide and carbon monoxide introduces a new era for sulfide biology; this has been demonstrated with exponentially increasing attention to its in vivo actions [1–3]. Hydrogen sulfide is endogenously generated during 3-mercaptopyruvate sulfurtransferase mediating cysteine metabolism [4], and cystathionine-γ-lyase and cystathionine-β-synthasemediating transsulfuration processes [5]. Endogenous sulfide has been reported modulating a variety of the physiological and pathological processes, such as gastrointestinal tract [6], brain [7], kidney [8] and vasculature [9], as well as playing pivotal physiological functions in regulating inflammation [10], blood pressure [11], metabolic syndrome [12], energy production [13] and oxidative stress [14]. The level of endogenous sulfide closely associates with the diseases, such as cardiovascular [11,15], inflammation [10,16], Down's syndrome [17], and Alzheimer [18].

To better understand the physiological and pathological functions of sulfide, efficient methods for accurate and reliable measuring biological sulfide are desirable [19,20]. The diverse chemistries of sulfide detection methods result in orders of magnitude differences in measured physiological sulfide levels with many reports around 10–100 μmol/L in blood [21–27]. A major challenge in sulfide detection is to evade from the interference of similar reactivity of bio-thiols and other nucleophiles, and the effect from sample matrix. One of the most common strategies used to address this challenge is to isolate sulfide from the sample matrix through precipitation, distillation or evaporation prior to detection [24–27]. The conversion of sulfide to ZnS via precipitation by zinc acetate and subsequently dissolution the produced ZnS precipitate under acidic conditions is currently the most widely used. This sample pretreatment is complicated, time-consuming, cannot allow real-time, on-field, and point of care detection of sulfide. Table S1 summarizes the analytical performance of the previously reported methods for sulfide detection.

UV–vis absorption spectrometry is a well established technique prominent in many fields. The sensitivity for absorption detection can be significantly increased, up to two orders of magnitude, by using long path cell (liquid core waveguides) [28] as the measured absorbance is linearly related to the path length. The successful marriage of long path absorbance detection with gas-permeable isolation [29–31] promised the method having the features of sensitivity and selectivity, and has been explored for the detection

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of some gases and volatile analytes, e.g. O_3 and NO_2 [29], CO_2 [30], and cyanide [31]. The previous work of Dasgupta and Peterson showed that water-filled porous polytetrafluoroethylene (PTFE) and polypropylene (PPE) tube behaved as a similar function like liquid core waveguides and could conduct light over several cm [32]. This finding can help to sharply reduce the cost of modestly long path spectroscopy compared to commercial liquid core waveguides based on Teflon AF, currently the most expensive commercially available polymer (greater in cost per unit weight than gold).

Here we reported a cost-efficient and portable device for sulfide measurement by integrating gas-permeable porous tube isolation and long path absorbance detection. Sulfide was isolated from complex sample matrices by converting it to volatile H_2S. The liberated H_2S evaporated and permeated into the porous membrane tube reaction cell, and was then trapped by an alkaline nitroprusside acceptor pre-added to the tube. The reaction of sulfide with alkaline nitroprusside caused a color change that can be monitored in real-time. The device was cost-efficient, portable, fast, and specific for detection of sulfide. The practicability of the device was evaluated by determining sulfide in human serum samples.

2. Experimental

2.1. Chemicals and materials

All chemicals were of analytical grade; water was produced from a Molgene 1810b ultrapure water system (Chongqiong Mole, China). Sodium sulfide hydrate ($Na_2S \cdot 9H_2O$) was prepared from Tianjin Fuchen Chemical Reagent Factory, China. Sodium nitroprusside was obtained from Shanghai Shanpu Chemical Reagent Factory, China. The preparation for the solutions was detailed and is presented in the Supporting information. Newborn calf serum (sterile filtered, No. 20111025) was purchased from Lanzhou National Hyclone Bio-engineering Co., Ltd., China. Acrylic optical fiber (2 mm diameter) was purchased from Nanjing Chunhui Science and Technology Industrial Co. Ltd., China.

2.2. Device construction

Fig. 1 schematically depicts the device construction. It consisted of a pair of petri dishes (35 mm diameter), a 35 mm length porous polypropylene membrane tube (PPMT, Accurel PP, 1.8 mm i.d., 0.45 mm wall) functioned as an optical cell, a 535 nm light emitting diode (LED, C503B-GAN-CB0C0891, 5 mm diameter, www.cree.com) and a TSL257 light to voltage converter (monolithic integrated photodiode-operational amplifier combination, www.taosinc.com). Two holes were drilled on opposite sides of top cover of petri dish. The PPMT was diametrically strung across the holes by means of tees (2 mm diameter), which were push-fit into the PPMT ends. The dome part of the LED was removed down to a height of 0.5 mm from the chip, polished, and glued with a 1 cm length of acrylic optical fiber (OF, 2 mm diameter) by epoxy. This LED was functioned as the light source by inserting the optical fiber into one tee. The LED was driven by a supply voltage of 5.0 V (PS-303DF power supply, Longwei Instrument Co. Ltd., Shenzhen, China) with series connection of a 100 Ω dropping resistor to limit the current at 22.3 mA. This arrangement proved to providing considerable immunity against temperature-induced light intensity changes [33]. The light transmitted through the tube was detected with the TSL257 light to voltage converter, which was connected to another tee by using acrylic optical fiber (1 cm length, 2 mm diameter). The output data was acquired with a 12-bit resolution data acquisition card (USB 1208LS, www.measurementcomputing.com) using a 1 s time constant RC filter and recorded with a personal computer. Fig. S1 shows the schematic diagram of the circuit for the device.

2.3. Instrument operation

Sulfide aqueous standard or serum was pipetted into the dish and the cover of the device was closed. Nitroprusside alkaline acceptor (effective volume about 28 μL) was filled in the PPMT through the inlet of the reagent using a syringe. The dark signal (I_d) was acquired with LED off. The LED was turned on ($t=0$), the average signal during 30 s was taken as I_0. At 30 s, 1.0 mL of diluted phosphoric acid was introduced into the dish through the port to

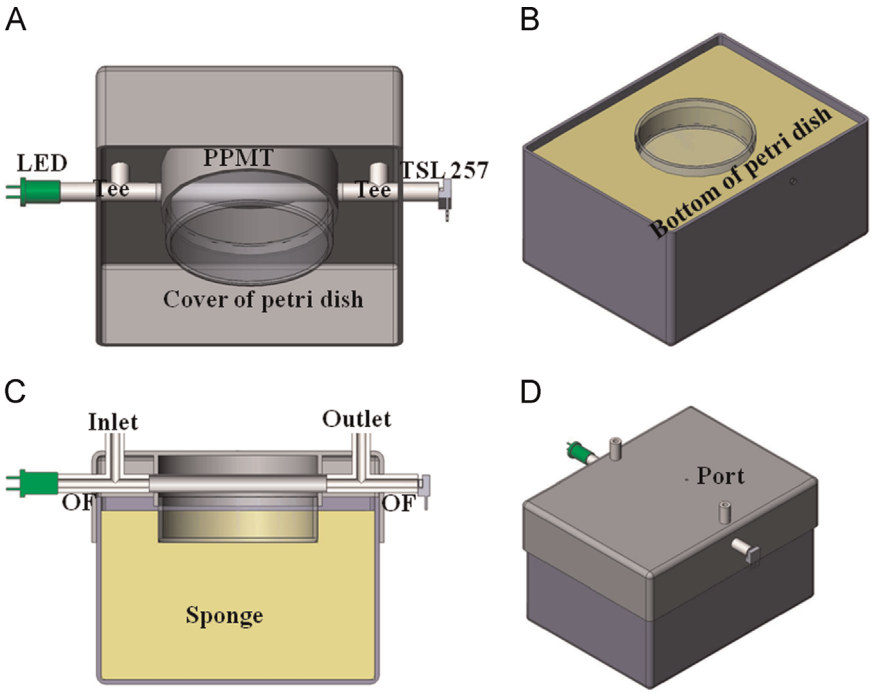

Fig. 1. Schematic diagram of sulfide measuring device. (A) Top cover of the device; (B) bottom of the device; (C) section view of the device; (D) integral exterior of the device. LED: light emitting diode; TSL257: TSL257 light-to-voltage converter; PPMT: porous polypropylene membrane tube; and OF: optical fiber.