



Portable analyzer for continuous monitoring of sulfur dioxide in gas stream based on amperometric detection and stabilized gravity-driven flow



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ABSTRACT

The construction, optimization and application are described for a portable gas analyzer which gives real-time measurement of sulfur dioxide in a gas stream. The SO₂ is absorbed from the analyte gas stream into a gravity-driven carrier solution flowing through a diffusion scrubber (DS), in the form of a bundle of polymeric hollow fibers. The sulfite ions in the carrier solution are detected by anodic amperometry at a novel carbon nanotube (CNT) electrode polarized at 0.35 V vs Ag/AgCl reference electrode. A novel compact design is the result of integrating the DS with the amperometric detector and yields a light weight portable analyzer (900 g) with a small footprint. The optimized analyzer has favorable performance characteristics such as (i) good sensitivity (LOD = 4 ppm, S/N = 3), (ii) wide linear dynamic range up to 5000 ppm, (iii) reasonably fast response time (t_{95%}, 4.1 min), (iv) excellent signal stability and repeatability (RSD = 1.3%), and (v) continuous standalone operation for 6 h. The interfering effect of H₂S is avoided by removing H₂S using a prior guard column. The analyzer can successfully monitor the removal of SO₂ from SO₂-N₂ gas mixtures and in determining sulfite in foodstuffs.

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1. Introduction

Sulfur dioxide (SO₂) is a main air pollutant which is released to the atmosphere by several sources [1–4] and is associated with several environmental [5–7] and health problems [1,8–11]. Also, SO₂ and other sulfating agents (sodium and potassium sulfite, bisulfite and metabisulfite) are widely used as preservatives or antioxidants in the food industry [12,13]. Although sulfites are regulated food additives, some individuals are sensitive to them and develop allergy-like symptoms [14–16].

The paramount importance of SO₂ and sulfite measurements has been a motive for numerous research groups to develop various analytical methods to determine the concentration of SO₂ in air [17–20] and sulfites in food and beverages [13,21–23]. Also, SO₂ analyzers, mainly based on the pulsed UV fluorescence and nondispersive infrared (NDIR), are commercially available [24]. Although such analyzers provide the advantages of high sensitivity and the

standalone operation, i.e., they do not require the consumption of reagents, they are usually costly. Similar to SO₂ gas analyzers, several SO₂ gas sensors were reported which can provide direct monitoring of SO₂ but they suffer from at least one major limitation, e.g., long response and/or recovery times [25–27], major interference [28], need for special fabrication [29], and limited linearity or signal instability [30–33] or combination thereof.

To fill the gap between the high cost of the commercial analyzers and the limitations of the previously reported SO₂ gas sensors, we reported previously a simple and low cost bench-scale analyzer for continuous monitoring of SO₂ in gas streams. That analyzer was based on a diffusion scrubber (DS) in the form of a hollow fiber membrane module (HFM) and commercial pH and conductometric flow-through detectors, respectively, placed downstream [34]. These two detectors were first selected because SO₂ molecules impart significant acidity to the carrier solution and hence the pH drop or the conductivity increase was conveniently measured using the commercially available pH and conductivity detectors, respectively.

The third possible way for detecting the dissolved SO₂ in carrier solution is by anodic amperometry. Compared to the previous detectors [34], amperometric detector should provide

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additional advantages such as (i) linear response compared to the logarithmic pH response, (ii) more selective response compared to the non-selective pH and the conductivity detectors, (iii) cheaper/disposable custom fabricated electrodes compared to the commercial flat-bottom pH-glass electrodes and the flow-through conductivity detectors and (iv) more flexibility to efficiently integrate the custom-built detector with other parts to produce more compact analyzer.

A careful literature search for amperometric methods revealed that SO₂ oxidation could be achieved either at bare solid electrodes (i.e., platinum, gold and glassy carbon) or at modified electrodes. However, our initial attempts to use bare Pt, Au and GC electrodes as working electrodes in the anodic amperometric detection of sulfite proved that they are not appropriate since the obtained current–time (*i*–*t*) response curves were neither stable nor reproducible. This observation was in agreement with the literature reports using solid bare electrode [35]. It was reported that such unsatisfactory response commonly obtained at bare solid electrodes for sulfur containing compounds would be attributed to the strong adsorption of reactants, stable intermediates and/or reaction products on the electrode surface which leads to fouling of the catalytic sites [35,36]. Moreover, the involved mechanism of the oxidation process of sulfite, in particular, could play a role in such observed behavior [37].

Unlike bare solid electrodes, the development of chemically modified electrodes for amperometric detection of sulfite ions in various samples attracted much interest in the past two decades. The studied modifiers included multi-wall carbon nanotubes/polymer/Au nanoparticles [38], carbon nanotubes/ferrocene/chitosan composite [39], Prussian blue [40], Prussian blue analogs [41], metal porphyrin complexes [42], pentacyanonitrosylferrate [43], PVP/Pd/IrO₂ [44], nickel powder [45], and silver [46]. Regardless of the used modifier, it was noticed that all the reported data for sulfite determination were limited to cyclic voltammetry, flow injection analysis or to amperometric *i*–*t* curves with relatively short recording time (i.e., 10 min or less). Moreover, the limited stability of the current signal for the reported electrodes apparently cannot suit the intended requirement for reliable amperometric detector to construct an analyzer for continuous monitoring of SO₂.

Therefore, the ambitious objectives of the present work were (i) to evaluate the bulk carbon nanotubes (CNT) as potential candidate to construct stable and reliable electrodes for direct amperometric detection of sulfite ions, (ii) to integrate the bench-scale SO₂ analyzer into a compact/portable version (weight <1.0 Kg) based on a stabilized gravity-driven flow and an integrated amperometric detector, (iii) to optimize the construction and evaluate the analytical performance of the analyzer, (iv) to extend the application of the SO₂ gas analyzer to the determination of sulfites in food-stuffs, and (v) to provide the advantages of the low cost, simplicity, reliability and standalone operation for at least 6 h.

2. Experimental

2.1. Reagents and materials

Sulfur dioxide standard (20,000 ppm in N₂), nitrogen (99.99%), carbon dioxide (99.99%), and hydrogen sulfide (5.00% in N₂) gas cylinders were received from AIR PRODUCTS (United Arab Emirates). Short Multi-Wall Carbon Nanotubes (outer diameter <8 nm, length 0.5–2.0 μm, and purity >95 wt.%) were received from CheapTubes (www.cheaptubes.com). Graphite rods (Ultra “F” Purity, 0.242” dia × 4” long) were received from Alfa Aesar (USA). Poly(tetrafluoroethylene-co-perfluorinated alkyl vinyl ether) (PFA) Microporous hollow fibers (0.25 mm ID, 0.65 mm OD) were

purchased from Entegris (USA). Two-part low viscosity epoxy was received from Buehler (Resin No. 20-8140-128, Hardener No. 20-8142-064). A chemical etchant (FluoroEtch) was received from Acton Technology (USA). Polyester (PE) membranes of various pore diameters were received from STERLITECH (www.sterlitech.com). Polycarbonate rods (different diameters), and clear polycarbonate tubes (6.4 mm ID and 9.5 mm OD) were received from Plastics International (www.plasticsintl.com). Transparent acrylic sheets (18 mm thick) were received from Sign Trade (United Arab Emirates). All chemicals used were of the highest available purity.

2.2. Instrumentation

A 4-CH computer controlled gas mixer (Model MFC-4, Sable Systems, USA) was used to control four Mass flow controllers (Sierra Instruments, Inc. USA) to prepare variable concentrations of SO₂ (and other interfering gases) in the gas stream for calibration and characterization purposes. The MFC-4 utility software (Sable Systems) was used to run different gas programs. Amperometric measurements were conducted using EmStat2 potentiostat (Palm Instruments BV, The Netherlands). PSTrace software was used for data collection and storage.

2.3. Fabrication of the CNT amperometric electrode

A graphite rod (6.2 mm dia) was cut into pieces (15 mm each). A 2-mm dia hole (~6 mm deep) was drilled in the center in one side. A brass rod (2 mm dia, 3 cm long) was inserted in the hole and sealed with silver epoxy which cured at 120 °C. The other end of the graphite rod was polished using a fine emery paper into a smooth and slightly domed shape. Polycarbonate (PC) tube (6.4 mm ID and 9.5 mm OD) was cut into pieces (25 mm each) and a circular groove (~0.8 mm width, ~2 mm depth) was drilled in the circular cross section of the tube wall in one end of the tube as shown in Fig. 1(b). The groove was filled with a quick epoxy (Fevicol blue) and the desired membrane was carefully mounted on the top of the epoxy and left for couple of minutes. When the epoxy was partially set, the membrane was slightly pressed against a flat surface to ensure full contact between the membrane and the epoxy and to fully anchor the epoxy inside the groove. The anchored epoxy inside the groove proved efficient in preventing peeling off the epoxy along with the attached membrane from the PC tube-wall side. The excess membrane was trimmed using a sharp blade to provide a perfectly circular electrode tip. The required amount of the CNT was added inside the tube and the graphite electrode was inserted inside the PC tube to sandwich the CNT between the membrane and the domed tip of the graphite rod as shown in Fig. 1(g). Quick epoxy was added to seal the graphite rod inside the tube and slight hand pressure was applied during epoxy curing to ensure that the graphite-domed tip permanently stretched the membrane to ensure reproducible electrode geometry and performance.

2.4. Construction of the integrated diffusion scrubber and the amperometric flow-through cell

The required number of the PFA fibers of specified length are etched using fluoretech [50] and potted at both ends with thin epoxy within two 30-mm long PC tubes (6.4 mm ID and 9.5 mm OD), respectively, and was allowed to set at room temperature for 24 h. Approximately 5 mm of the polycarbonate tubes were cut using a sharp cutter to expose the open lumen side of the hollow fibers. The detailed steps of potting the PFA fibers are shown in Fig. S-1.

The integrated diffusion scrubber and the amperometric flow-through cell (IC) were constructed from two polycarbonate discs (55 mm dia each). The upper disc (25 mm height) housed the flow-through amperometric cell and also served as inlet and outlet for

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