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Portable dual-channel gas analyzer for continuous monitoring of carbon dioxide in gas streams

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ABSTRACT

Development, characterization and application of a portable dual-channel analyzer based on gravity driven flow for continuous monitoring of CO_2 in gas streams are presented. The analyzer is constructed from (i) a carrier/stripping solution reservoir, (ii) a diffusion scrubber (DS) in the form of a hollow fiber membrane (HFM) module integrated with a custom-designed flow-through pH-detector cell, and (iii) a waste solution reservoir. The analyzer is designed in such a way that the dilute sodium bicarbonate carrier/stripping solution flows downward by gravity into the lumen side of the hollow fibers in the HFM module which allows efficient contact with the gas stream. Absorption of CO_2 into the carrier solution produces pH changes that constituted the analytical signal. Flat-bottom glass electrode and solid-state IrO_2 electrodes were used as pH detectors in two types of custom-built flow cells, respectively. Under the optimized conditions, the measured pH signal showed Nernstian response to the CO_2 concentration (59.6 and 62.0 mV/log[CO_2] and $r^2 = 0.9992$ and 0.9984 for the glass and IrO_2 pH detectors, respectively) in the gas stream over a wide dynamic range (0.1-100 % CO_2 in balance of nitrogen). Moreover, the presented analyzer based on either detector offered several favorable performance characteristics such as reasonably short response and recovery times; excellent signal stability and reproducibility and high selectivity in the presence of non-ionogenic gases, e.g., CH_4, N_2, O_2, CO, etc. The suggested analyzer was applied successfully in the dual-channel monitoring of CO_2 absorption from CO_2-CH_4 binary feed gas mixtures.

1. Introduction

Due to the essential role of carbon dioxide in our life, in several industries and the greenhouse effect as well as its importance in several experimental setups [1–6], development of analytical devices for the observation of carbon dioxide has been an active area of research. The operating principles of carbon dioxide sensors and their manifold applications in environmental control, biology, biotechnology, medicine and food production and control were reviewed recently [7].

Among various analytical methods, portable analyzers offer the advantage of convenient mobility. However, there are several requirements that should be considered in developing portable analyzers. These include: ease-of-use, light weight (≤10 kg) [8], low power consumption, rugged, no sample preparation, and real time monitoring capability. Several types of gas analyzers have been commercialized for monitoring of important gases such as CO_2, CO, NO_x, H_2S, SO_2, O_2, O_3, THC and VOCs. Commercial gas analyzers based on different detection principles, e.g., non-dispersive infrared, Fourier-transform infrared, Chemiluminescence, UV absorption, UV fluorescence, electrochemical detection, flame ionization, paramagnetic cell, and mass spectrometry have been used successfully in several applications [9–19].

Some of the commercial analyzers are also available as portable devices. Although such commercial and portable gas analyzers provide several attractive features such as high sensitivity, standalone operations, i.e., they do not require consumable reagents for their operations. The portable gas analyzers are still of considerable cost and sometimes of limited linear range.

In addition to the commercialized gas analyzers, considerable efforts have been reported in literature to describe portable gas analyzers based on several detection schemes. Gas analyzers based on colorimetric detection were developed for the determination of several gases such as acetylene [20], ammonia [21,22], nitrogen dioxide [23], and carbon dioxide [24]. Portable analyzers for H_2S [25] and NO [26] employed fluorimetric detection were reported. Electrochemical detection methods [27–29] were also commonly used in developing analyzers for several important gases such as hydrogen fluoride [30], hydrogen chloride [31], CO_2 [32–35], SO_2 [36,37] and volatile alcohols [38]. Other detection principles such as thermometric [39], gravimetric

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[40], and IR [41] were also utilized by different researchers to develop gas analyzers.

Although of the relatively large body of literature aimed at developing gas analyzers, there are only a few reports devoted to the development of portable gas analyzers [20,21,30,33] which were based on a liquid pump and various detection schemes and were mainly limited to low concentration range. It was developed recently in our laboratory a bench-scale gas analyzer for CO_2 based on a carrier solution, diffusion scrubber (DS) and a commercial flow-through cell equipped with glass pH detector [32]. The most obvious way to develop a portable version of such analyzer was to utilize an onboard pump to propel the carrier solution. This approach was excluded to keep the gross weight to a minimum by excluding the weight of the pump and the required battery. Alternatively, a gravity driven flow was proposed in the present work. This approach was encouraged because of previous experience which indicated insensitivity of the analyzer response to CO_2 with considerable variations in the carrier solution flow rate. This implies that a successful portable analyzer can be achieved using a gravity driven flow even though it does not provide a constant flow rate.

The presented analyzer is based on integrating the carrier/stripping solution reservoir which is positioned above the waste solution reservoir using three stainless steel rods in such a way to create adequate space to accommodate the DS (fabricated in the form of a hollow fiber membrane (HFM) module) and the custom built pH-flow cell in between the two reservoirs.

The presented analyzer was developed and mainly characterized as a portable single-channel analyzer for CO_2 which was expanded to a dual-channel version. To the authors best knowledge this is the first report on developing gas analyzer based on a gravity driven flow for the continuous monitoring of CO_2 in gas streams. To achieve reasonable standalone operation, the analyzer was designed with the objective of operating continuously for up to 16 hours and to be less than 10 Kg [8] to realize the simplest, yet powerful, portable gas analyzer for continuous CO_2 monitoring in gas streams.

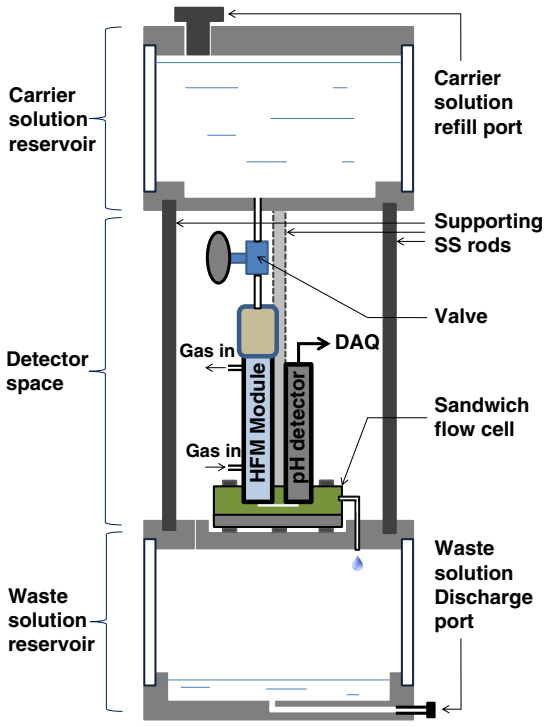

Fig. 1. Conceptual design of the portable CO_2 analyzer showing a single channel flow-through cell equipped with a flat-bottom glass pH electrode.

2. Experimental

2.1. Materials and Reagents

Carbon dioxide (99.99%), nitrogen (99.99%), methane (99.99%), sulfur dioxide standard (1.00 % in N_2) and hydrogen sulfide (2.00 % in N_2) were received from Air products (UAE). Poly(tetrafluoroethylene-co-perfluorinated alkyl vinyl ether) (PFA) Microporous hollow fibers (0.25 mm ID, 0.65 mm OD) were purchased from Entegris (USA). Commercial modules based on polypropylene hollow fibers (Models G542 and G543) were received from Membrana (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). All chemicals used were of the highest available purity. Acrylic tubes of different sizes and Polyethylene round bar, and stainless steel rods and tubes were purchased from the local market. All solutions were prepared using deionized water.

2.2. Instrumentation

A 4-Channel 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 CO_2 (and/or H_2S and SO_2) in a balance of N_2 or CH_4 for calibration and characterization purposes. The MFC-4 utility software (Sable Systems) was used to run a given preset program of concentration steps.

2.3. Construction of the portable Single-Channel CO_2 analyzer

The analyzer consisted of three main components, i.e., (i) carrier/stripping solution reservoir; (ii) diffusion scrubber (DS) in the form of a HFM module integrated with the flow-through cell equipped with a pH detector and (iii) the waste solution reservoir as shown in Fig. 1. Both of the carrier and the waste solution reservoirs have ~1.1-L capacity and were constructed from acrylic cylinder (7.0 cm height, 15.0 cm OD, 14.0 cm ID). The base and the top of each cylinder (25 mm thick discs) were machined from a polyethylene round bar (15.0 cm dia). The carrier/stripping solution reservoir was positioned above the waste solution reservoir by means of three vertical stainless steel (SS) rods (28 cm long) secured tightly in three holes (5.5 mm dia and 10 mm deep) drilled on the top and the base of the waste and the carrier solution reservoirs, respectively as shown in Fig. 1. The carrier reservoir capacity was adequate for continuous flow (~1.0 mL/min) for up to at least 14 hours.

2.3.1. Construction of the diffusion scrubber-detector assembly

The utilized DS were fabricated by potting a bundle of 20 PFA fibers (20 cm long) using thin epoxy at both ends in transparent acrylic tube (20 mm OD, 16 mm ID, 14.0 cm long,) to provide an active fibers length of approximately 12 cm. The fibers were etched at both end (~4 cm) using the chemical etchant to promote the necessary adhesion to the potting epoxy. Stainless steel tubes (3 mm OD, ~2.5 cm in length) served as inlet and outlet for the gas stream to the shell compartment as well as an inlet for the carrier/stripping solution to the lumen compartment. The bottom of the HFM module was kept flat and smooth to minimize the dead volume inside the flow cell. The detailed procedure of the custom fabrication of such HFM modules were previously described [39].

Two types of pH detectors were tested in constructing the present portable CO_2 analyzer, i.e., the flat bottom glass combination cell (Model 450 C, Sensorex, USA) and the solid state electrodeposited IrO_2-pH sensors [42]. Titanium rods (6.3 mm dia, ~20 mm long) served as substrate for the electrodeposited IrO_2 layer. The side wall of the titanium rod was insulated using nail polish to leave the lower disc as the pH sensitive area. Electrical leads were connected to the top of the Ti rods by means of silver epoxy.