Gas sensor measurement system capable of sampling volatile organic compounds (VOCs) in wide concentration range

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Abstract

A gas sensor measurement system has been developed by using a vapor-generating bubbler, analyte-diluted delivery lines and a detection chamber. The bubbler with a perforated disk design permits to pick up analyte vapor with fixed efficiency under a carrier flow rate of 0.5–100 sccm. The pickup efficiency was modulated logarithmically by varying the bubbler temperature. The practically controllable range in acetone flux was nearly three orders of magnitude through the variation of the carrier flow rate, and an order of magnitude by the use of the bubble temperature, independently. The generated vapor was diluted efficiently through a cascading two-step process which leads to homogeneous mixing up to the flow ratio of dilution:carrier = 500:0.25, and then delivered into a small-gapped planar detection chamber operated at room temperature. The newly-designed planar chamber induces fast equilibrium and high local concentration on a sensor surface, thus resulting in a short detection time and a higher response magnitude. From measuring chemoresistive responses of carbon black-polymer composites upon exposure to acetone analyte, the measurement system was confirmed to be reliably applicable to a wide concentration range of from 3.7 ppm to 10.7%.
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Keywords: Gas sensor; Measurement system; Bubbler; Carbon black-polymer composite

1. Introduction

Odor sensing systems have attracted much attention due to their potential applications in food quality control, medical diagnosis, and environmental monitoring of pollutants [1,2]. They require high sensitivity, good selectivity, short detection time, and excellent reproducibility for these applications. Vapor detection performance strongly depends on a sampling apparatus which generates and delivers volatile analyte samples into sensing systems as well as excellent sensing properties of the sensors. It is therefore very important for the sampling devices to be designed in such a way that all factors influencing the sensor responses are optimized and kept under control. However, there exist few references readily available in literature except for some general discussions [3].

There are various methods to generate continuously a fixed concentration of volatile analyte from liquid samples instead of preparing gas mixtures in a cylinder with a limited volume [4]: (1) syringe injection of a sample with a known mass or volume into a fixed volume vessel [5]; (2) vapor diffusion from a reservoir through a narrow tube into a flowing stream [6]; (3) permeation of analyte molecules through membranes [7]; and (4) bubbler-based evaporation by passing carrier gas-through a liquid sample [8–10]. Among them, the bubbler method has been utilized extensively in chemical vapor deposition systems as well as sensor measurement systems due to its simple setup. An important point in such bubblers is to achieve a steady, controllable flux of an analyte sample. Common restrictions are the formation of aerosols leading to a higher analyte concentration in the gas phase, and the decrease in pickup efficiency due to the sample depletion around bubble-passing channels. However, these uncertainties are possible to minimize through optimized bubbler design [10], and to be corrected with a system calibration [8].

Recently, simulation studies on flow dynamics were performed to examine the space distribution of analyte molecules within a measurement chamber and its time-dependent evolution

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[11–13]. From these transport phenomena analyses, the geometrical parameters such as chamber volume and shape were found to give a great influence on the gas-sensing characteristics because of the direct correlation of sensor response to the local analyte concentration on the sensor surface rather than to the average value within the chamber. Accordingly, the chamber has to be designed harmoniously with the whole system to achieve the excellent sensing performances. Moreover, the introduction of flow diffusers at the inlet and the outlet resulted in increasing the flow uniformity over the sensors and minimizing the stagnation regions [12].

In this work, we present a bubbler-based sensor measurement system that allows timed flow injection of gaseous volatile organic compounds (VOCs) in a wide analyte concentration range. By using the bubbler with a perforated ceramic disk, the analyte flux could be regulated over a range of almost four orders of magnitude, simply with varying both the flow rate of carrier gas and the bubbler temperature. The generated analytes were efficiently diluted by two-step dilution process, and delivered into a detection chamber. The vapor detection characteristics were improved by using the newly-designed parallelepiped chamber with a small lamina space. The performance of the measurement system was evaluated in terms of the vapor generation efficiency of the bubbler and the time-profiled chemoresistive responses of carbon black-polymer composite sensors.

2. Sensor measurement system

The sensor measurement system consists of three major parts: a vapor-generating bubbler, analyte-diluted delivery lines, and a detection chamber. Each part will be described separately.

2.1. Vapor-generating bubbler

A bubbler was utilized to vaporize liquid VOCs for the gas-sensing measurements. Fig. 1a displays a photograph of the bubbler used in this work. Dry air as a carrier gas enters into the bottom of a sample-containing vessel through the right inlet pipe, and then takes away the analyte vapor upward. For distributing the carrier gas over a maximized contact area to the samples, the perforated ceramic disc with an identical size to the inner diameter of the sample vessel was utilized as a bubble-forming component. Compared with other conventional bubblers with a dip tube or leg, the perforated structure is a more favorable design to allow uniform and efficient generation of analyte vapors due to its capability of providing multiple and small bubbles [10].

Fig. 1b represents main features of our bubbler relevant to the vapor generation process, schematically. The output flow rate of analyte vapor, F_s, can be described with the bubbler equation [14]:

$$F_s = \left(\frac{P_{th}}{P_o - P_{th}} \right) F_c = \alpha F_c \tag{1}$$

where F_c is the carrier flow rate in standard cubic centimeter per minute (sccm) and α is the vapor pickup efficiency defined as the relative ratio of the output sample flow rate to the carrier flow. P_o is the outlet pressure in the bubbler headspace above the

liquid sample, and P_{th} the thermodynamic vapor pressure of the analyte sample. These parameters were obtained under the standard conditions of $T = 0\,°C$ and $P = 1$ atm. When the carrier gas is completely saturated with analyte vapor, the P_{th} becomes the saturated vapor pressure, P_s, which can be calculated from the empirical Antoine equation [15]. The P_s value is strongly dependent on the temperature of a sample-containing vessel controlled by a thermostat bath. Actually, the output sample flow rate was calculated from the α value determined under both a constant carrier flow rate and a fixed bubbler temperature.

2.2. Analyte delivery system

The generated analyte vapor was delivered into a detection chamber. The delivery system is composed of valves, stainless steel tubing and four mass flow controllers (MFCs; 5850E, Brooks Instrument), as shown in Fig. 2. The carrier flow was controlled by setting the flow rate of MFC 1 (10 sccm maximum flow) or MFC 2 (100 sccm maximum flow). The output flow was mixed with the first dilution flow, F_{d1}, and then further diluted by the main dilution flow, F_{d2}, regulated by MFCs 3 and 4 with a 1000 sccm maximum flow, respectively. Different dilutions were achieved by varying the relative ratio of the carrier flow, F_c, to the total dilution flow, $F_d = F_{d1} + F_{d2}$. The resultant analyte concentration, $C_{analyte}$, in parts per million (ppm) was calculated from the pre-determined pickup efficiency and the dilution ratio:

$$C_{analyte}\,(ppm) = \frac{10^6 F_s}{F_d + F_c + F_s} = \frac{10^6 \alpha}{(F_d/F_c) + 1 + \alpha} \tag{2}$$

Three VOC analytes of acetone, methanol, and benzene were sampled by varying both the carrier flow rate in the range of 0.5–100 sccm and the bubbler temperature of −30 to 30 °C. Most measurements were performed with the dilution flow rates of $F_{d1} = 50$ and $F_{d2} = 450$ or 950 sccm. An analyte sample was injected by switching the first-diluted flow from the house exhaust line into the detection chamber through the three-way valve (TV in Fig. 2). The pulsing was terminated by reversing the procedure after a typical duration time of 2 min. The main dilution flow was maintained for an enough time to arrive at a steady sensor baseline, while the pre-diluted flow was allowed to stabilize for at least 1 min prior to the analyte pulsing. Since the sensor could response to the increase in total flow rate at the moment of analyte pulsing, it was confirmed with the blank measurements under the same conditions. In fact, the variations were negligible for most sensors probably due to the relative small change in total flow rate.

2.3. Detection chamber and data acquisition

An incipient detection chamber has a large volume of about 400 cm³, and is essentially a hollowed glass cylinder with rounded surfaces at the two end faces. Inlet and outlet pipes are connected to the center of the rounded surface along the axial direction. For improving sensor response characteristics, a new parallelepiped chamber was fabricated to have a laminate flow channel with a small gap of 3 mm. Fig. 3a shows an external