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Sensors and Actuators B 115 (2006) 28–32
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

A non-invasive ultrasonic gas sensor for binary gas mixtures

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Received 27 January 2005; received in revised form 2 August 2005; accepted 3 August 2005
Available online 29 September 2005

Abstract

A non-invasive gas sensor has been fabricated for quantitative measurement of a specific gas in a binary mixture such as H_2, He, etc. mixed in air, based on time of flight (TOF) measurements of the ultrasonic signal. A test gas with different concentration was mixed in air and its concentration was determined using the observed TOF data and a theoretically derived relation. The results were compared with the actually used values of gas concentration in the mixture, and a good agreement was found between them. The method can find potential use for various applications in different fields, such as chemical industry and medical diagnosis.

Keywords: Gas sensors; Sound velocity in gases; Ultrasonic methods

1. Introduction

Quantitative determination of specific non-reactive gas compositions in a given binary mixture has important applications in several fields such as chemical processing and handling industry, or for online measurement of a specific gas in the given environment. For example, hydrogen is extensively used in industry, and is a potential non-pollutant energy source for near future energy requirements in various fields. However, H_2 gas forms a self-explosive mixture when its concentration exceeds about 4% in air, which is known as the lower explosion limit (LEL) of the gas concentration in air. Therefore, online detection of this gas in the presence of other gases such as oxygen, which form explosive mixtures with it, is a very important safety aspect. For this, among others, Pd thin films, diodes and FET devices have been reported in the literature [1–3], which can detect H_2 gas at 100 ppm level. However, electronic devices (diode or FET type) saturate at about 1000–10,000 ppm, and therefore, are not suitable at higher concentrations near LEL and higher levels. Furthermore, the response time of the electronic devices is 10–50 s, which is relatively large for application of the corrective measures. So a faster and reliable method having good sensitivity around both sides of the LEL is needed for this purpose. Similar difficulties exist with detectors of other gases and a relatively quicker method may be more useful for such applications.

The speed of sound in gases is a function of pressure and density. The density of any gas in turn is a function of the molecular weight of the gas. Therefore, measurement of the speed of sound in gases at a specific pressure and temperature can be used to find molecular weight of a gas or a mixture of gases [4]. For a non-reacting gas mixture, the gas pressure is the sum of all the partial pressures of the component gases and similarly the average density of the gas mixture is the weighted sum of the individual densities. Therefore, measuring sound speed, while keeping other parameters such as pressure and temperature constant, one can measure the gas composition of the sample under observation [4–6]. The speed of sound can be determined by measuring the time of flight (TOF) of sound pulse on passing through a given distance. Alternatively, one can also use a resonating chamber and the gas composition can be determined by measuring the resonant frequency of the resonator, which varies due to the change in velocity of sound with the variation in gas composition [7,8]. The technique has been utilized to find out specific gas concentrations quantitatively, for example, in a binary mixture [7], in air [6], or in other carrier gases [5]. We have fabricated a system based on the above-mentioned technique and measured TOF values for different gas concentrations for gases like H_2, CO_2 and He in air. However, when we calculated the unknown concentrations of a particular gas in

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doi:10.1016/j.snb.2005.08.016

the gaseous mixture by using our TOF data and the formulation as described by Sheen et al. [6], the calculated concentrations of the gas in use were much different from the actual values used in the gas mixture. In order to understand this discrepancy, we derived an explicit relation for the calculation of an unknown concentration of a given gas in a binary mixture. This was then used to calculate the gas concentration from the TOF data. A good agreement of the measured concentration with the actual concentration used was obtained. In the following we give the derivation of our formula and present our observed data along with calculated gas concentrations for different binary gas mixtures.

2. Basic principles

We obtain here relations for sound velocity of a mixture of a gas (1) in the gas (2) that is typically air. The isentropic speed of sound v in a gas medium is given by

$$v = \left(\frac{\gamma P}{\rho}\right)^{0.5} \tag{1}$$

where $\gamma = (C_p/C_v)$ is the ratio of the specific heats of the gas, with C_p and C_v denoting the molar specific heats at constant pressure and at constant volume, respectively. Here, P is the gas pressure, and ρ the density of the gas. For a given gas, γ may be regarded as constant in a small temperature range. At a fixed pressure P we may write

$$\left(\frac{v_m^2}{v_2^2}\right) = \left(\frac{\gamma_m}{\gamma_2}\right)\left(\frac{\rho_2}{\rho_m}\right) \tag{2}$$

where the suffixes 2 and m attached with respective parameters denote its value for the air and the mixture of an unknown gas and air. If x is the molar concentration of an unknown gas in the mixture with other gas, the parameters ρ_m and γ_m may be written under linear approximation as $\rho_m = x\rho_1 + (1-x)\rho_2$ and $\gamma_m = \{xC_{p1} + (1-x)C_{p2}\}/\{xC_{v1} + (1-x)C_{v2}\}$. Furthermore, if t_2 and t_m denote the time of flight in gas (2) and in the mixture, respectively, we can write $(v_m^2/v_2^2) = (t_2^2/t_m^2)$ for a fixed distance between the transducer and the reflector, and finally by using Eq. (2), we get

$$\left[\left\{\frac{\rho_1-\rho_2}{\rho_2}\right\}\frac{C_{v1}-C_{v2}}{C_{v2}}\right]x^2 + \left[\left\{\frac{\rho_1-\rho_2}{\rho_2}\right\} + \left\{\frac{C_{v1}-C_{v2}}{C_{v2}}\right\} - \left\{\frac{C_{p1}-C_{p2}}{C_{p2}}\right\}\left(\frac{t_m^2}{t_2^2}\right)\right]x + \left\{1 - \left(\frac{t_m^2}{t_2^2}\right)\right\} = 0 \tag{3}$$

This is a quadratic equation in x, and may be solved by using known values of thermal parameters of the gases used from literature [9], and measured values of t_2 and t_m. Of the two solutions obtained for each value of t_m, the one satisfying condition $0 \le x \le 1$ gives the required gas concentration.

The relation given by Eq. (3) may be simplified further, when both of the gases contained in the mixture have the same number of atoms in their molecules. In such a case $C_{v1} = C_{v2}$ and making use Eqs. (2) and (3) gives

$$x = \frac{t_2^2 - t_m^2}{t_2^2 - t_1^2} \tag{4}$$

Furthermore, for low concentration of gas (1) in the mixture Eq. (4) yields an approximate linear relation

$$x = a(t_2 - t_m) \tag{5}$$

where $a = \{(t_m + t_2)/(t_2^2 - t_1^2)\} \approx \{2t_2/(t_2^2 - t_1^2)\}$ may be considered an approximate constant for small value of $(t_2 - t_m)$, compared with the values of t_2 or t_m [10].

3. Experimental

We have used a pulser-receiver model 4400 MX from M/s. Roop Telsonic Ultrasonix (P) Ltd., Mumbai (India), for these measurements. The system can measure TOF with resolution of 10 ns in the 0–5 ms range. The transducer (500 kHz) is excited in pulse mode, and it also detects the echo of the reflected signal. The difference between the starting time of the pulse and that of the echo gives the TOF of the to and fro path traveled by the signal. The transducer is fixed in a test chamber having gas inlet and outlet connections, and with a provision to adjust the distance between the transducer and the reflector. The temperature of the test chamber was maintained by using a water jacket, as shown schematically in Fig. 1. The test gas such as H_2 was mixed with the air and passed through the test chamber. Flow rates of hydrogen and air were determined by using a mass flow controller (MFC) and a rota-meter, respectively. TOF data were recorded for samples of clean air as well as for the mixtures having known concentration of hydrogen, helium or carbon dioxide. Fig. 2 shows a plot of the observed TOF as a function of H_2 gas concentration in air, whereas Figs. 3 and 4 show similar plots for He and CO_2 gas mixtures in air. It may be noted that the distance between the transducer and the reflector was slightly different for the data in these three figures.

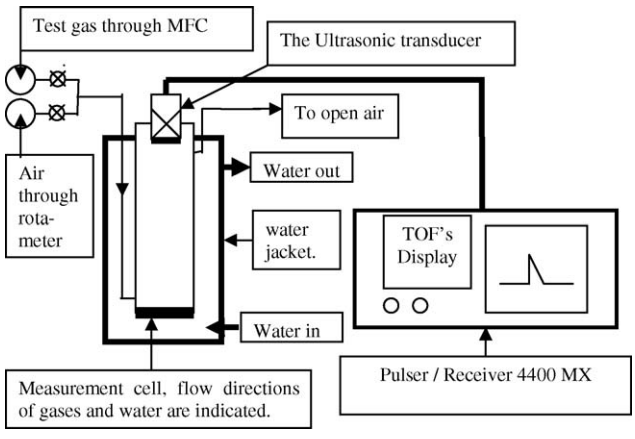

Fig. 1. Schematic diagram of the set up used for measurement of unknown concentrations of test gases in a binary gas mixture.

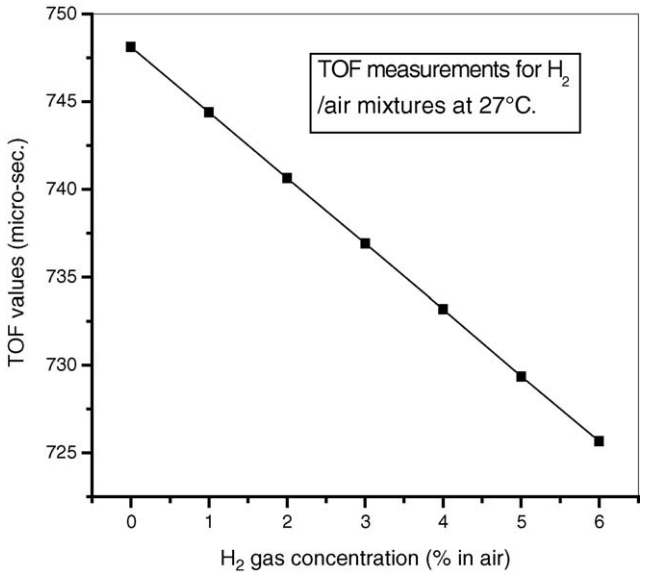

Fig. 2. Dependence of measured TOF on the H_2 gas concentration in air.

4. Results and discussion

Since hydrogen as well as major constituents of air, consist of diatomic molecules, we have used Eq. (4) for determination of hydrogen concentration in air. For this purpose, TOF for the pure air t_2 was directly determined, whereas TOF for the hydrogen gas t_1 was calculated by using the reported values of velocity of sound in air and hydrogen. The observed values of t_m for different mixtures of H_2 in air were then used to calculate the H_2 gas concentration. As seen from Table 1, the results were found to be in good agreement with the actual hydrogen concentration flowing through the test chamber. We have also calculated gas concentrations by using observed TOF values and the theoretical expressions given by Sheen et al. [6] and these results are also shown in Table 1. It is seen that the gas concentrations calculated by using the formula of Sheen et al. [6] are about five times less than the corresponding experimental values. The gas concentrations obtained by using Eq. (4) are within 7% of the experimental values, i.e., within the error margins of the rotameter and mass flow controller (MFC) used. It may be seen from Fig. 2 that the H_2 gas concentration and corresponding TOF values are linearly related with each other. This is in agreement with Eq. (5), which is valid for low gas concentrations. We may add that the TOF measured for a particular concentration was found to be independent of the total flow rate in the range 100–2000 sccm. This was due to the fact that the measured TOF values were comprised of both the forward and the reflected signal travel time in the cell, during these measurements. The response time of the sensor was seen to be governed by the time needed for hydrogen or other test gases to flow from MFC to the test chamber. Some measurements were also carried out by keeping the test chamber (with one wall open to minimize the diffusion time) in a large container of 50 l capacity. Hydrogen gas from a small container (0.5 l capacity) was mixed with air in the large container by opening a valve. The response on the system was found to be less than the measurement limit of 2 s.

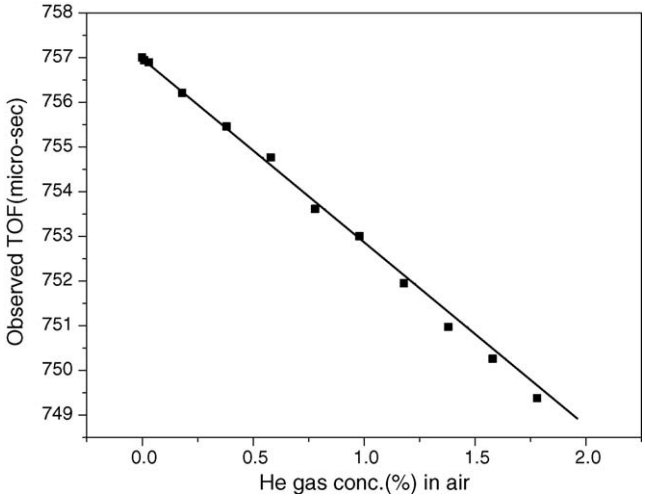

Fig. 3. Dependence of TOF on the He gas concentration in air. Data points indicate TOF values observed for experimentally chosen gas concentrations, whereas the smooth curve is drawn through the calculated values of gas concentration corresponding to these TOF values by using Eq. (3).

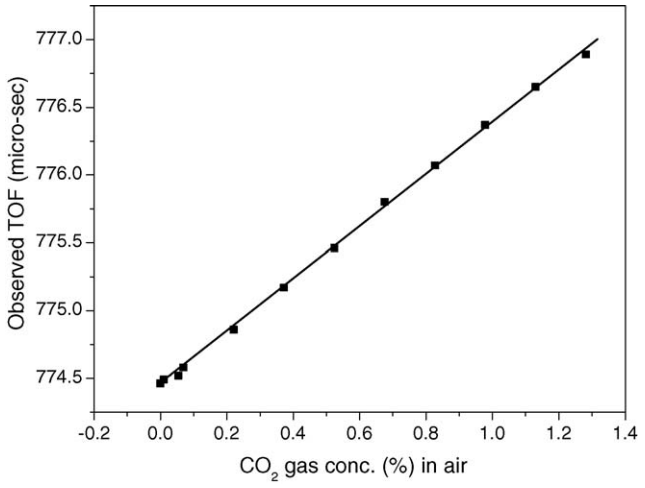

Fig. 4. Dependence of TOF on the CO_2 gas concentrations in air. Data points indicate experimental values of gas concentration in air. The smooth curve is drawn through corresponding calculated values of gas concentration obtained by using Eq. (3), and observed TOF values.

The sensor was also evaluated for measurement of helium and CO_2 concentrations in air. Figs. 3 and 4 show the measured

Table 1
Observed TOF for various H_2 concentrations in air and corresponding values calculated by using different equations

H_2 in air (%) from MFC	Observed TOF (μs)	Calculated value of H_2 in air using formula of Sheen et al. [6] (%)	Calculated value of H_2 in air using Eq. (4) of present work (%)
0	748.120	0.0	0.0
1	744.380	0.18	1.07
2	740.640	0.36	2.14
3	736.920	0.55	3.19
4	733.180	0.73	4.25
5	729.360	0.93	5.32
6	725.680	1.11	6.35

dependence of TOF on the concentration for these gases. Theoretical results obtained by using the measured TOF values and Eq. (3), are also shown in these figures. A good agreement is observed between the experimentally used concentrations and the theoretically calculated values. It may be noted that for calculation of gas concentrations in these cases, Eq. (3) is necessary, as the number of atoms in the molecules of these gases are different from that of the air. It is seen that at low concentrations, these gases also show an approximately linear relation between the gas concentration and the TOF. It may be added that the TOF for CO_2 increases with increase in the gas concentration (in contrast to helium and hydrogen) as it has larger molecular weight than air.

We have also checked the stability of the system with respect to time. For room air, with nominal flow rates in the range 0–2000 sccm, the TOF data were recorded every 10 s, for a total duration of 30 min. For a typical TOF value of 750 μs, the variation in the above data was found to be within 200 ns. This corresponds to gas concentration measurement accuracy of 0.05% for both hydrogen and helium and 0.1% for CO_2. Typical time needed for acquiring a TOF data is nearly 2 ms. Therefore the sensor may be used for determination of change in gas concentration at short time intervals.

As a specific application of this technique, we analyzed the samples taken from human exhalation, and measured the CO_2 content for different people. The exhalation from the mouth (nose closed during exhalation) at normal breathing rates was connected to the measurement cell (volume 60 cc), whose temperature was maintained at 27 °C. This temperature was selected, because during the measurements the ambient air temperature was around this value. It is known that the exhaled gas mixture contains several gases other than N_2, O_2, and CO_2. But except the moisture, they exist in very small and so negligible quantities. The exhaled air is nearly saturated with moisture and measured relative humidity of the laboratory air was 65–70%. This difference in the moisture content was taken into account for determining the CO_2 concentration from the measured TOF data. We noticed that only a single out-breathing was enough to fill the cell, as may be seen from Table 2 giving data on TOF with respect to the human out-breathing cycle for two persons. It can be seen from this table that the shift in TOF for person no. 1 and 2 was 8.2 and 9.8 μs, respectively. For calculation of CO_2 concentration given in this table the following values of parameters for CO_2 and air were used; $\rho_1 = 44$ g/mol, $\rho_2 = 29$ g/mol, $C_{v1} = 29.0$ J/(K mol), $C_{v2} = 21.0$ J/(K mol), $\gamma_1 = 1.29$, and $\gamma_2 = 1.41$. The measured CO_2 content in exhaled air for person no. 1 and 2 were found to be 3.91 and 4.56%, respectively. These values are well comparable to the reported CO_2 content in the exhaled air.

Table 2
Observed TOF for the room air and for the exhaled air of two persons during normal breathing

No. of cycles (exhalations)	Observed TOF (μs)		Calculated CO_2 concentration using Eq. (4) of this work	
	Person no. 1	Person no. 2	Person no. 1	Person no. 2
0	770.00	770.00		
1	778.22	779.86		
2	778.20	779.84	3.91	4.56
3	778.24	779.84	(%)	(%)
4	778.22	779.82		
5	778.24	779.86		

The method is suitable for finding unknown concentration of any non-reacting gas in combination with any other known gas. It may be noted that a larger gap between the transducer and the reflector increases the TOF and therefore, the sensor resolution. However, due to large attenuation coefficients of many gases, this distance may not be arbitrarily increased. Furthermore, it may be noted that in this method we use the ratio of two TOFs, i.e., (t_m^2/t_2^2), for the calculation of unknown gas concentration in the sample, and therefore, accuracy in time measurement on the absolute scale is not necessary.

5. Conclusions

We have used the pulse echo method to find the unknown concentration of non-interacting gases such as H_2, He and CO_2 in a binary mixture. The method has an advantage of reliability and the sensor has a long life. Theoretical relations for calculation of gas concentration in mixtures have been obtained. The sensor is found to be suitable for determination of CO_2 concentration in human exhaled air.

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Biographies

J.C. Vyas, post graduated in physics from the University of Rajasthan, Jaipur, and PhD from Bombay University, Mumbai. He joined BARC in 1980, and over the years worked on fabrication of space quality Si solar cells,

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V.R. Katti, did his MSc (physics) from Bombay University, Mumbai. Initially in BARC he worked for the development of night vision devices like image converter tubes and image intensifiers for military applications. He also worked on development of space quality silicon solar cells. Presently he is working on the development of gas sensing devices for H_2S, ammonia and hydrogen, etc.

S.K. Gupta, joined BARC in 1975 and is presently Head of Thin Films Devices Section in TPPED. Over the years, he has worked on space quality silicon solar cells, high temperature superconductor thin films and single crystals, gas sensors and thermoelectric materials. He has carried out extensive studies on vortex dynamics in superconductors. He is a member of the National Academy of Sciences, India.

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