Macromol. Symp. **2013**, 324, 11–18 DOI: 10.1002/masy.201200062

Novel Test System for Gas Sensing Materials and Sensors

*K. M. E. Stewart, A. Penlidis**

Summary: A growing interest in gas sensors necessitates the requirement for a test system that is reliable and capable of handling multiple gas analytes at various concentrations. Most test systems currently used do not incorporate some type of standard with which to verify the actual concentrations of the gas analytes being tested, but rather calculate concentrations indirectly. The problem is that the calculated concentrations rarely take into account any loss that may occur across the test system. The test system described herein uses a specialized gas chromatograph (GC) that is capable of detecting down to the ppb range. It can either be used to screen potential sensing materials or to verify the actual concentration being tested for a specific sensor.

Keywords: gas sensors; gas chromatography; polymer sensors

Introduction

Gas sensors represent a growing area of interest. To identify effective sensing materials, a test system must be constructed that is able to determine both the sensitivity and selectivity of a sensing material or sensor. A good test system has the ability to test multiple gases for a variety of sensing materials. By introducing interferents typically present with the desired analyte, very realistic scenarios and conditions may be tested.

A sensing material may be assessed under steady state/equilibrium conditions[1] or in a dynamic fashion.[2] Initial testing of a sensing material is generally done under equilibrium conditions to determine how the sensing material interacts with various analytes.

There are four ways to obtain gaseous analytes with which to test a sensing material. Firstly, gas may be obtained from a gas cylinder.[3] For low concentrations, such as those in the ppm range, pre-made mixtures of an analyte and nitrogen may be available. Secondly, liquid analytes may also be used in permeation tubes that slowly release the analyte vapour into a chamber.[4] Thirdly, gaseous analytes may be acquired through the use of a bubbler.[5] By passing nitrogen, or another carrier gas, through a liquid analyte, vapour is picked up and transported into the test system. Finally, a carrier gas may flow over a solid, in a way similar to the bubbler case, thus picking up vapour.[5] Dilution is achieved by combining the gas containing the analyte with another gas stream containing a carrier gas such as nitrogen.[6] When multiple analytes are tested simultaneously, the concentration of each analyte is usually lowered through dilution.

Most test systems for gas analytes rely on ‘‘calculated’’ values for the concentration and do not take into consideration any loss along the system. This results in no confirmation of the actual concentration of analytes via a standard such as a gas chromatograph. Typically, only temperature and humidity are confirmed using commercially available sensors.[7]

A novel test system has been designed to incorporate an in-line, specialized gas chromatograph (GC) to confirm the

---

Institute for Polymer Research, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1
E-mail: penlidis@uwaterloo.ca

concentration of the analytes used. It is also able to evaluate sensing materials by determining the amount of an analyte sorbed onto the sensing material. Hence, it is possible to reduce the testing time for evaluating full sensors by first screening for the most promising sensing materials for a specific analyte. Such an application is described in,[8] where polyaniline sensing materials doped with nickel oxide and/or aluminum oxide were investigated using this test system for the detection of formaldehyde.

An overview of some sensing materials for different analytes is listed in Table 1. Sensing materials are evaluated based on both their sensitivity and selectivity, where sensitivity is the lowest detectable limit of an analyte and selectivity is the ratio between the sensitivity of the target analyte and a specific interferent. A good sensor will have a low sensitivity and a high selectivity (for example, see the entry for aldehyde dehydrogenase (ALDH) listed in the first row of Table 1). It should also be noted that sensitivity and selectivity requirements are based on the intended application of the sensor.

Test System for Gas Sensing Materials

Before depositing sensing materials onto a sensor, prospective sensing materials can be tested with different gas analytes. By narrowing down the sensing materials to the more promising ones for a specific analyte, less time is taken in the preparation of complete sensors since deposition of sensing materials onto a sensor can be very time consuming.

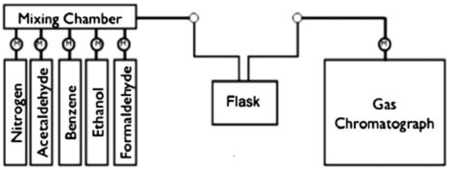

Figure 1.
Sensing material test system, where M represents mass flow controllers.

The test system (see Figure 1) was set up so that the gases would pass through an empty flask en route to the specialized gas chromatograph (GC) to determine the initial concentration of gas. A flask that contained the sensing material, which had been purged with dry nitrogen, subsequently replaced the empty flask, which allowed the sensing material to be saturated with the gas. The difference between the concentrations measured was the amount of analyte that interacted with (and was sorbed by) the sensing material. The GC was used as a reference to determine the concentration of analyte that sorbed.

Tygon® tubing was used to transport the gas analytes since the gases tested were less likely to sorb onto the inside of the tubing. Although some off gassing from the tubing was observed by the GC, there was no

Table 1.
A Sample of Sensing Materials for Various Analytes

Sensing Material	Analyte	Sensitivity	Selectivity	Reference
Aldehyde Dehydrogenase (ALDH)	Acetaldehyde	0.105 ppm	167	[9]
Flavin-containing Monooxygenase 3 (FCO3)	Trimethyl Amine	0.52 ppm	10.9	[10]
Poly (2,3-dimethyl aniline) (P2,3-DMA)	Heptanol	3000 ppm	1.02	[11]
Poly (2,5-dimethyl aniline) (P2,3-DMA)	Methanol	3000 ppm	1.20	[11]
Poly (dimethyl siloxane) with 2.0% (w/v) Polystyrene (PDMS/PS)	Xylene	10 pg/mL	3.23	[12]
Poly(m-aminobenzene sulfonic acid) Functionalized Single-Wall Carbon Nanotubes	Relative Humidity	10%–70%	–	[13]
Polyaniline doped with 5% NiO and 15% Al_2O_3	Formaldehyde	0.09 ppm	1.86	[8]

change in the area of the peak registered by the GC between the blank and a sample. Therefore, these off gases did not interact with the prospective sensing materials. The mixing chamber was made of glass and contained valves to ensure only the gases being tested entered the mixing chamber. MKS RS-485 mass flow controllers were used to control the flow rate of the gases, which in turn controlled the concentration of the gases being tested.

As an example, the test system was used to determine whether polyaniline and polyaniline doped with nickel oxide and/or aluminum oxide were good sensing materials for formaldehyde at concentrations in the ppb range. This is discussed further under the evaluation of the test system.

Test System for Complete Gas Sensors

Once the more promising sensing materials were determined from the preliminary tests using the system described above, they were deposited onto sensors to be further analyzed. By adding a parallel line to the test chamber, the gas chromatograph (GC) was used as a standard to determine the actual concentration of the gases tested (see Figure 2). The line was split after the mixing chamber, but before the line entered the GC. This split was achieved using an MKS 640A pressure controller (PC) and an MKS 179A mass flow meter (FM) on one side and an MKS RS-485 mass flow controller (MFC) on the other. The pressure on the PC was adjusted so that the FM read the same as the MFC to ensure a 50:50 split of the gases. Therefore, half the gases being tested ran into the chamber, where the sensor resided, and the other half ran into the GC. By allowing each run to reach equilibrium before a signal was taken, the GC was used as a reference to determine the actual concentration of the gases being tested.

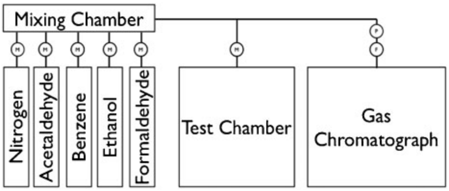

Figure 2.
Modified test system for gas sensors, where M, P, and F represent mass flow controller, pressure controller, and flow meter, respectively.

Gas Chromatograph (GC)

A very sensitive, specialized gas chromatograph (GC) was used to qualitatively and quantitatively identify components in either a liquid or a gas sample. The components of a sample were separated as they flowed through a column, which contained a suitable packing material. The packing material was chosen based on what components were known to be in the sample. As the components of a sample passed through the column, they adsorbed or absorbed (sorbed) onto the packing material at different rates, resulting in each component having its own retention time. Hence, the components of the sample were separated based on their retention times. The retention time indicated qualitatively which components were present in a sample. The data from the GC appeared as peaks on a voltage versus time graph. The areas under the peaks were integrated, and compared to those of a standard with a known concentration, to determine quantitatively the concentration of each component in the sample.[14]

The specialized GC used in this study needed to be able to separate very chemically similar compounds (see Figure 3) and detect very low concentrations (see Figure 4 and 5). The separation was achieved using a Varian CP-Sil 5 CB for formaldehyde with a capillary column of dimensions 60 m × 0.32 mm × 8 μm (CP-Sil 5 CB was the column packing identifier).

The GC used a pulsed discharge helium ionization detector (PDHID) which was very sensitive and could detect in the parts

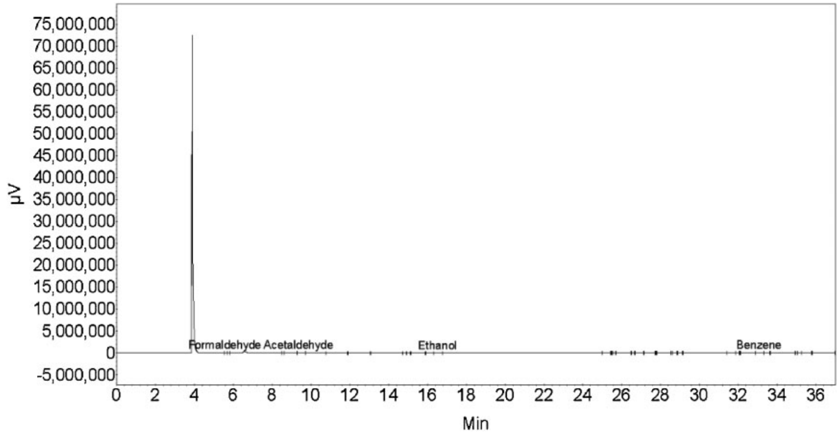

Figure 3.
Chromatogram for all four analytes tested. The large peak around 4 minutes is from the carrier gas, nitrogen.

per billion (ppb) range. Pulsed direct current (DC) discharge caused the helium to ionize. As the helium returned to its natural state, photons were released and ionized the sample as it flowed down the column, producing electrons. These electrons were forced towards the detector and generated a response. This detector was virtually non-destructive to the sample and very sensitive. Because of the sensitivity of the detector, the detector was encased in helium to limit interference from the atmosphere.[15]

The GC's signal-to-noise ratio is defined as the ratio between the signal, in this case the peak, and the noise from the baseline (see Equation 1, where A represents the area under the chromatogram peak for either the signal, the analyte being tested, or the noise from the baseline). At higher concentrations, where the peak is large compared to the baseline, signal-to-noise ratio is not a concern (see Figure 4). For lower concentrations of formaldehyde tested, there was a lower signal-to-noise ratio on the chromatogram (see Figure 5). The noise was measured through the first minute of the chromatogram, where no analyte peaks were present, and compared to the signal, or peak response, for each

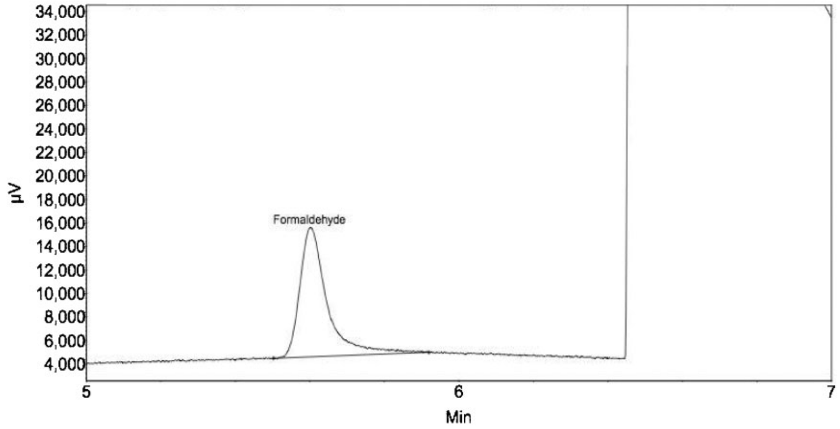

Figure 4.
Chromatogram for formaldehyde at 5.05 ppm.

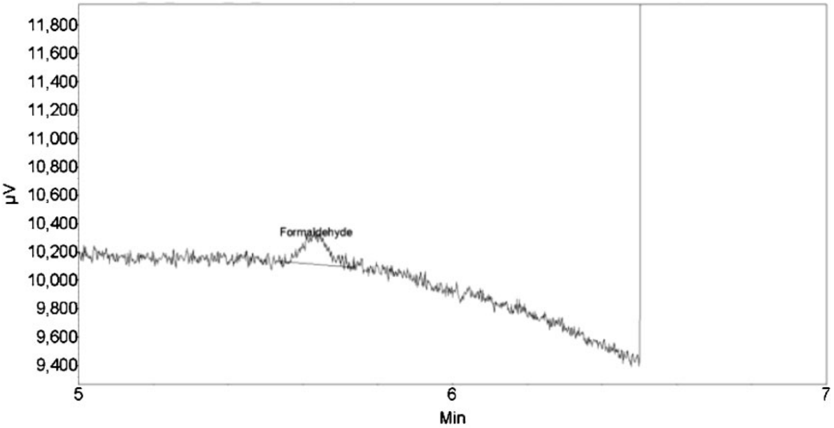

Figure 5.
Chromatogram for formaldehyde at 0.09 ppm.

analyte. A signal-to-noise ratio of more than 3 is an indicator of good performance.

$$signal - to - noise = \frac{A_{Signal}}{A_{Noise}} \qquad (1)$$

The limit of detection, or detection limit, is the lowest signal that can be detected, which is not buried in the noise of the baseline, and is calculated from the signal-to-noise ratio. Generally, a signal-to-noise ratio of 3 is used to find the limit of detection. This ensures that the signal is not lost within the noise of the baseline exhibited by the sensor; however, the signal may still be present and detectable (discernible). The limit of detection for formaldehyde for the gas chromatograph used was 0.05 ppm, which was calculated from a signal-to-noise ratio of 3 (see Equation 2 and Equation 3).

$$A_{Signal} = 3 \times A_{Noise} \qquad (2)$$

$$Detection\ Limit = \frac{A_{Signal} \times [Analyte]_{Concentration\ of\ Standard}}{A_{Concentration\ of\ Standard}} \qquad (3)$$

Although it was possible to see a signal even at a concentration less than 0.05 ppm, since the signal is considered to be buried in the noise, caution must be exercised. In both Figure 6 and 7, the chromatograms show the residual concentration (of formaldehyde) not sorbed by the polymer. The peak (signal) shown in Figure 6 is 0.05 ppm, which is 3 times the signal of the noise. Therefore, the peak is not buried in the noise and can be easily distinguished. On the other hand, in Figure 7, the peak (signal) (corresponding to a concentration of 0.03 ppm) is only 2 times the noise signal and thus, overall, the signal-to-noise ratio is below 3. The signal, in this case, is harder to see since its amplitude (or height) is not much greater (stronger) than the noise of the baseline. Although the signal can still be discerned (or seen) in Figure 7, it is considered to be buried within the noise for all practical purposes.

Evaluation of the Test System

As an example, the test system was used to determine the effectiveness of polyaniline and polyaniline doped with nickel oxide and/or aluminum oxide as sensing materials for the detection of very low concentrations (ppb range) of formaldehyde.[8] Formaldehyde, along with acetaldehyde, benzene and ethanol, which were chosen as interferents since they typically appear in mixtures with formaldehyde, were all certified standards from Praxair with a concentration of approximately 5 ppm in

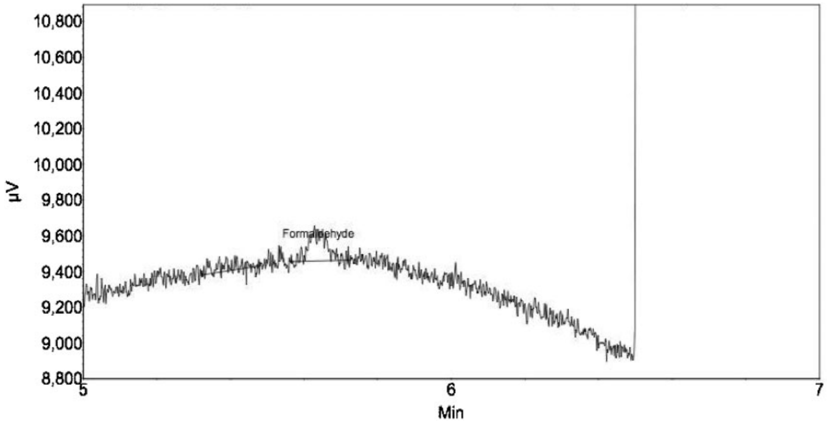

Figure 6.
Chromatogram of polyaniline doped with 15% NiO for formaldehyde at a concentration of 0.05 ppm.

nitrogen. The gases were diluted with 5.0 grade nitrogen to get down to concentrations as low as 90 ppb.

When mixing the gases, the calculated concentration did not match the actual concentration measured by the gas chromatograph. For example, using the ideal gas law and related dilutions, the calculated concentration of benzene of a 50% benzene and 50% nitrogen mixture, with the same initial pressure, was 2.55 ppm; however, the actual concentration of benzene was measured at 3.19 ppm. The change in tubing diameter along the test system caused drops in pressure and created areas in the system where the concentration of the gases built up before continuing along the test system. This was the case for all of the gases tested. Therefore, had the GC not been used as a confirmation of the concentration, incorrect data would have been recorded.

Screening tests were used to determine both the sensitivity and selectivity of each sensing material (eight in total) towards formaldehyde. Sensitivity is a quantitative value defined as the concentration of analyte sorbed onto the sensing material divided by the total concentration of the analyte (see Equation 4 and Equation 5). The residual amount of analyte is the

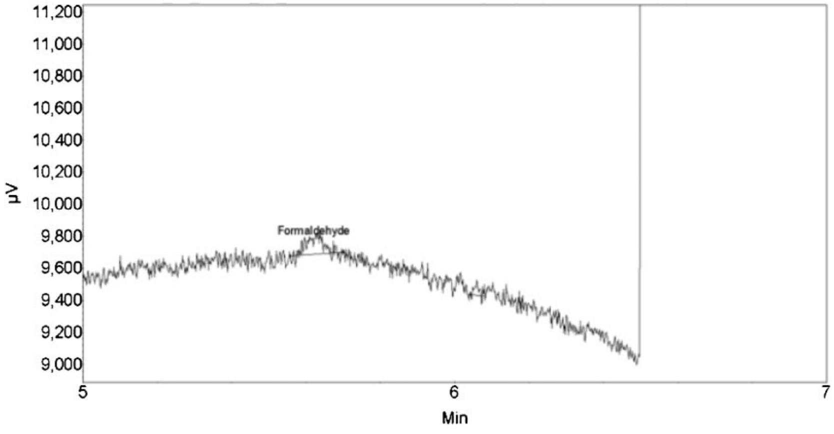

Figure 7.
Chromatogram of polyaniline for formaldehyde at a concentration of 0.03 ppm.

concentration measured by the GC after the analyte has interacted with the sensing material. The larger the signal, the more sensitive a sensor is, especially when low concentrations of an analyte are tested. A sensing material is deemed sensitive when the sensitivity is greater than 0.45.

$$[Analyte]_{Sorbed} = [Analyet]_{Total} - [Analyte]_{Residual} \quad (4)$$

$$Sensitivity = \frac{[Analyte]_{Sorbed}}{[Analyte]_{Total}} \quad (5)$$

Selectivity, on the other hand, is a qualitative indicator that measures difference in sensitivities. A ratio is taken between the concentration of two analytes that sorb onto the polymer (see Equation 6). The higher concentration is taken as the numerator (Gas 1). If the ratio is larger than 1.75, then the sensing material is selective towards Gas 1 (the target analyte), when Gas 2 is present as an interferent.

$$Selectivity = \frac{[Gas\,1]}{[Gas\,2]} \quad (6)$$

The gas analytes were tested both individually and simultaneously at various concentrations for each of the eight potential formaldehyde sensing materials. Two materials stood out as promising sensing materials for formaldehyde. At high concentrations, above 1 ppm, polyaniline doped with 5% nickel oxide and 15% aluminum oxide had high selectivity towards formaldehyde (selectivity values greater than 1.75), but was unable to detect formaldehyde at 90 ppb, and thus did not have the desired sensitivity (see Table 2). At low concentrations, below 1 ppm (and down to 90 ppb), polyaniline doped with 15% nickel oxide had the sensitivity, but not the selectivity desired (see again Table 2). Since these were the two most promising sensing materials for formaldehyde, they were chosen to be deposited. By using the test system to screen the sensing materials, it was possible to reduce the number of sensing materials to be deposited from eight down to two. This significantly reduced the time, effort, and cost required to construct sensors for further testing.

Selectivity changes as more gases are simultaneously tested (see Table 3). Despite a decrease in concentration, when single gases are tested as opposed to quaternary gas mixtures, the selectivity values may increase or decrease, depending on the analyte. For instance, the selectivity of polyaniline doped with 5% nickel oxide and 15% aluminum oxide towards formaldehyde for both acetaldehyde and benzene increased as more gases were added to the mixture. Therefore, as more desirable analytes, for the sensing material, were added, less acetaldehyde and benzene were sorbed. The opposite is true for ethanol,

Table 2.
Selectivity of Polyaniline (PANI) Materials Towards Formaldehyde with Respect to Each Interferent.

Polymer	Acetaldehyde	Benzene	Ethanol
PANI doped with 5% NiO and 15% Al_2O_3	1.79	2.11	1.86
PANI doped with 15% NiO	1.40	1.60	1.63

Table 3.
Selectivity of Polyaniline Doped with 5% Nickel Oxide and 15% Aluminum Oxide Towards Formaldehyde with Respect to Each Interferent.

Mixture	Approximate Concentration of Each Analyte	Acetaldehyde	Benzene	Ethanol
Single	5 ppm	1.79	2.11	1.86
Binary	2.5 ppm	2.02	2.69	1.55
Quaternary	1 ppm	2.79	14.56	1.28

since it was more attractive to the sensing material. As more gases were simultaneously tested, formaldehyde's selectivity with respect to ethanol decreased, even though less ethanol was available to bind to active (sensing) sites on the sensing material. As a result, ethanol was either able to get to an active site first or/and it bound to another analyte, such as formaldehyde, that had already taken an active site through hydrogen bonding.

The different trends observed in Table 3, as the number of analytes in the gas mixture increased, were the result of the analytes interacting with one another, as well as competing for potential active sites. If there were no interactions between the analytes, then the higher concentrations would result in lower selectivity with respect to formaldehyde due to more analytes competing for active sites on the sensing material. Therefore, when the gases are mixed, as in a more realistic environment, they interact with one another, and thus the sensitivity and selectivity of a sensing material is affected.

Conclusion

Overall, the use of a specialized gas chromatograph (GC) allowed both the ability to screen potential sensing materials, as well as determine the actual gas concentration when sensors were tested. By employing the GC in preliminary testing to screen the potential sensing materials for formaldehyde, it was possible to reduce the deposition of eight sensing materials down to two. This significantly reduced the time, effort, and cost required for depositing the sensing materials and constructing sensors. Without using the GC as a standard to determine the actual concentration, the concentration of the analytes tested would have been inaccurately calculated. Therefore the detection limits of the sensor would also have been inaccurate. The test system described improved the reliability of the data acquired.

[1] D. L. McCorkle, R. J. Warmack, S. V. Patel, T. Mlsna, S. R. Hunter, T. L. Ferrell, *Sens. Actuat. B-Chem.* **2005**, *107*, 892.

[2] S. V. Patel, S. T. Hobson, S. Cemalovic, T. E. Mlsna, *Talanta* **2008**, *76*, 872.

[3] R. Knake, P. Jacquinot, A. W. E. Hodgson, P. C. Hauser, *Anal. Chim. Acta.* **2005**, *549*, 1.

[4] S. Virji, R. B. Kaner, B. H. Weiller, *Chem. Mater.* **2005**, *17*, 1256.

[5] T. E. Mlsna, S. Cemalovic, M. Warburton, S. T. Hobson, D. A. Mlsna, S. V. Patel, *Sens. Actuat. B-Chem.* **2006**, *116*, 192.

[6] H. Dahnke, G. Von Basum, K. Kleinermanns, P. Hering, M. Mürtz, *Appl. Phys. B-Lasers O.* **2002**, *75*, 311.

[7] S. V. Patel, T. E. Mlsna, B. Fruhberger, E. Klaassen, S. Cemalovic, D. R. Baselt, *Sens. Actuat. B-Chem.* **2003**, *96*, 541.

[8] K. M. E. Stewart, N. T. McManus, E. Abdel-Rahman, A. Penlidis, *J. Macromol. Sci. A.* **2012**, *49*, 1.

[9] K. Mitsubayashi, H. Amagai, H. Watanabe, Y. Nakayama, *Sens. Actuat. B-Chem* **2003**, *95*, 303.

[10] K. Mitsubayashi, Y. Hashimoto, *IEEE Sens. J.* **2002**, *2*(3), 133.

[11] A. A. Athwale, M. V. Kulkarni, *Sens. Actuat. B-Chem* **2000**, *67*, 173.

[12] T. Endo, Y. Yenagida, T. Hatsuzawa, *Sens. Actuat B-Chem* **2007**, *125*, 589.

[13] T. Zhang, S. Mubeen, E. Bekyarova, B. Y. Yoo, R. C. Haddon, N. V. Myung, M. A. Deshusses, *Nanotech.* **2007**, *18*, 165504.

[14] R. L. Grob, E. F. Barry, "*Modern Practice of Gas Chromatography*", 4th ed. J. Wiley & Sons, USA **2004**, p. 25.

[15] "*Pulsed Discharge Helium Ionization Detector (PDHID): User Information*", Agilent Technologies, USA **2006**, p. 8.