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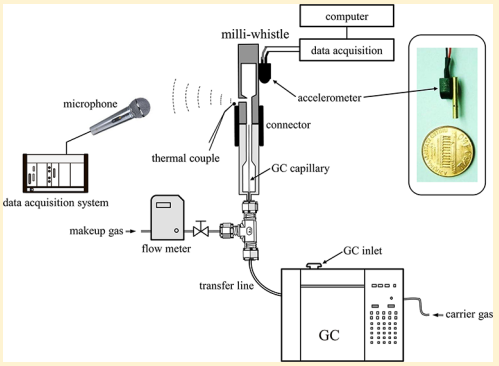
Use of an Accelerometer and a Microphone as Gas Detectors in the Online Quantitative Detection of Hydrogen Released from Ammonia Borane by Gas Chromatography

Yi-San He,[†] Kuan-Fu Chen,[†] Chien-Hung Lin,[†] Min-Tsung Lin,[‡] Chien-Chung Chen,*[,‡] and Cheng-Huang Lin*[,†]

[†]Department of Chemistry, National Taiwan Normal University, 88 Sec. 4, Tingchow Road, Taipei 11677, Taiwan

[‡]Graduate Institute of Biomedical Materials and Tissue Engineering, Taipei Medical University, 250 Wu-Hsing St., Taipei, Taiwan

ABSTRACT: The use of an accelerometer as a gas detector in gas chromatography (GC) is described for the first time. A milli-whistle was connected to the outlet of the GC capillary. When the eluted and GC carrier gases pass through the capillary and milli-whistle, a sound is produced. After a fast Fourier transform (FFT), the sound wave generated from the milli-whistle is picked up by a microphone and the resulting vibration of the milli-whistle body can be recorded by an accelerometer. The release of hydrogen gas, as the result of thermal energy, from ammonia borane (NH_3BH_3), which has been suggested as a storage medium for hydrogen, was selected as the model sample. The findings show that the frequencies generated, either by sound or by the vibration from the whistle body, were identical. The concentration levels of the released hydrogen gas can be determined online, based on the frequency changes. Ammonia borane was placed in a brass reservoir, heated continually, and the released hydrogen gas was directly injected into the GC inlet at 0.5 min intervals, using a home-built electromagnetic pulse injector. The concentration of hydrogen for each injection can be calculated immediately. When the ammonia borane was encapsulated within a polycarbonate (PC) microtube array membrane, the temperature required for the release of hydrogen can be decreased, which would make such a material more convenient for use. The findings indicate that 1.0 mg of ammonia borane can produce hydrogen in the range of 1.0−1.25 mL, in the temperature range of 85−115 °C.



A variety of different detectors based on different mechanisms, such as flame ionization, thermal conductivity, electron capture, and surface acoustic wave, are currently used in gas chromatography (GC). Undoubtedly the most popular and well-developed method is the use of a mass spectrometer. Each has a unique advantage and disadvantage regarding sensitivity, precision, and simplicity of use. In our previous study, we reported on the development of a novel type of GC detector based on a milli-whistle.[1] The milli-whistle was connected to the outlet of the GC capillary and the GC eluants and carrier gas passing through the capillary together produces a sound as they pass through the milli-whistle. When the molecular weights of the GC eluants are lower than the carrier gas, the frequencies observed are higher than that of the carrier gas, whereas GC eluants with molecular weights higher than carrier gas would produce lower frequencies. Since it is possible to control the temperature of a GC oven and the flow rate of the carrier gas very precisely, a sound wave generated from the milli-whistle and after applying a Fast Fourier transform using a LabVIEW (Laboratory Virtual Instrumentation Engineering Workbench) built-in program, a specific frequency can be observed. In terms of sensitivity, this detector is superior to that for a regular thermal conductivity detector and is very useful in analyzing gases, irrespective of whether they are organic, inorganic, or rare gases. Qualitative analyses can be performed based on retention times corresponding to various GC elutes, while the concentration levels of the analytes can be determined based on frequency changes relative to the fundamental frequency produced by the carrier gas.

Many methods for the storage of hydrogen are being developed and currently in use.[2−9] One of them, ammonia borane (AB), with the formula NH_3BH_3,[10−13] has attracted attention as a source of hydrogen fuel and has been proposed as a hydrogen storage medium because it can be made to release hydrogen on heating, is more hydrogen-dense than liquid hydrogen, and can be stored at normal temperatures and pressures relatively safely.[14] We recently developed a novel hydrogen storage and delivery device. On the basis of a novel substrate of microtube array membrane (MTAM),[15,16] a microcomposite of AB/PC MTAM was recently prepared by encapsulating AB within a polycarbonate (PC) MTAM via coaxial electrospinning with the intention of being a lightweight and effective hydrogen storage and carrier device. Although many types of hydrogen detectors can be used for estimating the efficiency of the release of a gas from various types of

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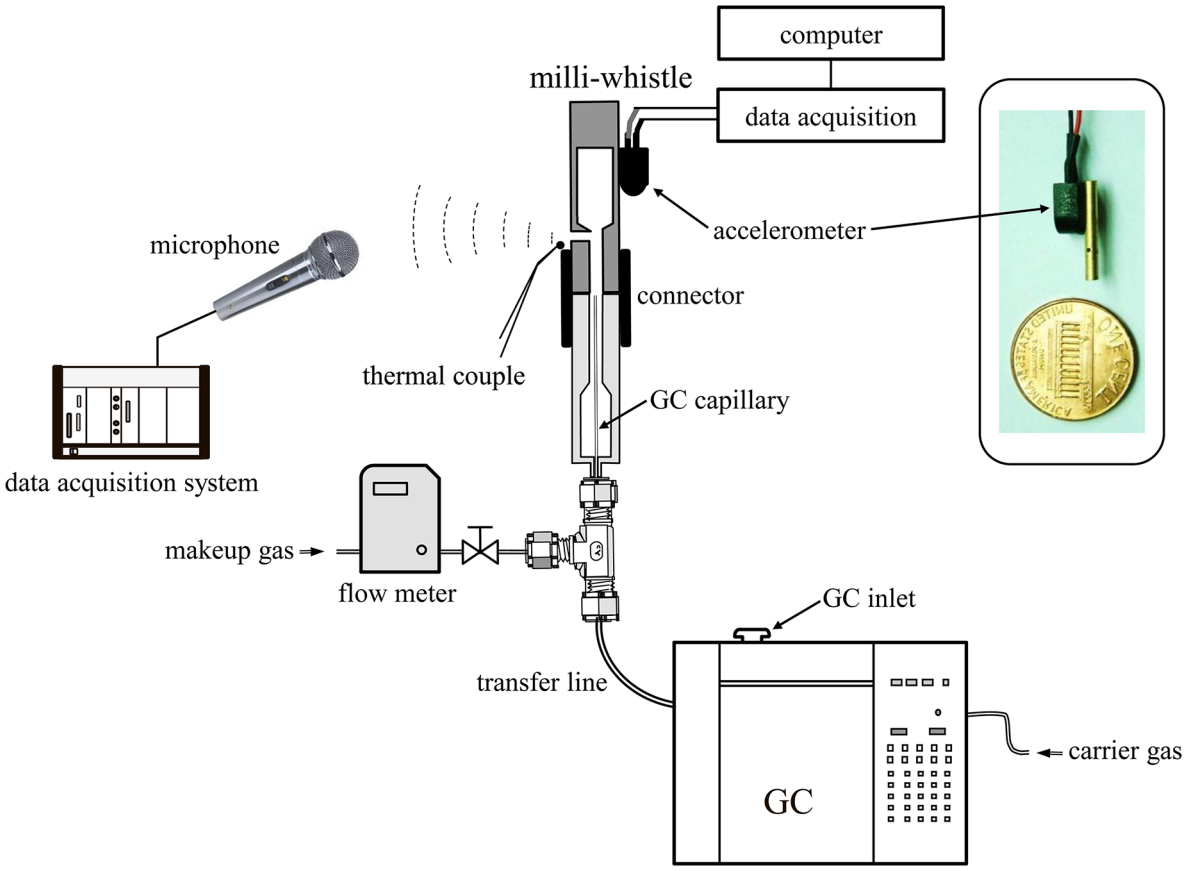

Figure 1. A schematic diagram of the GC/milli-whistle setup. The inset photo shows the actual scale of the brass milli-whistle and the accelerometer when they are compared to a one-cent coin.

materials,[17] the online quantitative monitoring, especially at the microliter level, continues to be a challenge.

In this study, the online quantitative determination of hydrogen gases from AB and composite membrane of AB/PC MTAM, respectively, using the milli-whistle/GC system, in which an accelerometer and a microphone were used for recording the frequencies, is described. An empirical formula was derived and used to compare the results obtained by a regular calibration curve. Details of the experimental conditions are reported and the real-time relationship between frequency shifts and hydrogen concentration are also discussed.

EXPERIMENTAL SECTION

Reagents. All of the ultrapurified gases (>99.99%) were obtained from Fong-Ming Industrial (Taiwan), including hydrogen, helium, methane, nitrogen, and argon. The borane-ammonia complex (technical grade, 90%), tetrahydrofuran (THF), and polyethylene glycol (PEG; M_w, 35 and 900 kDa) were purchased from Sigma-Aldrich Inc. (St. Louis, MO). Polycarbonate (PC; M_w, 2.25 kDa) and dichloromethane (DCM) were obtained from Nytex and Mallinckrodt, respectively. All other chemicals were of analytical grade and were obtained from commercial sources.

Apparatus. A gas chromatograph (GC 5890; Hewlett-Packard, Avondale, PA) equipped with an HP-PLOT Q column (30 m × 0.53 mm ×40 μm) was used in this study. The milli-whistle was made of brass and was 1.0 mm in diameter and 5 mm in depth. An accelerometer (Endevco; model 2250AM1-10/lightweight, 0.4 g; amplitude response ± 1 dB, 2−15000 Hz) and a microphone (PCB Piezotronics, Inc.; model 426E01; detectable range: 6.3−125000 Hz) were used to acquire the vibrational frequency of the whistle body and the sound frequency, respectively. Both devices were located inside an insulated sound chamber. The sampling rate of the microphone and the accelerometer were set at 51200 Hz and 40000 Hz, respectively, and all of the collected data were used for Fourier transformation. The sampling rate for the chromatogram was 5 points/sec. An electromagnetic pulse injector, triggered by a PCI-6221 device, was used for pressurized gas injection, as described in a previous study.[18] A mica electric heater (350 W/max 350 °C; preciseness, 0.25%), equipped with a controller (NEWLAB, HT-720) and a K-Type thermal couple, was used for temperature control. The NI cDAQ-9171 device, connected to the accelerometer, was used to record the vibrational frequency. A data acquisition system (NI PXI-1042Q), equipped with a PXI-4461 device, was used to acquire real-time sound data from the microphone. A LabVIEW program (National Instruments) and a FleXense STD program (Chief SI Company, Ltd., Taiwan) were used for real-time frequency monitoring, both with a built-in Fourier transform function.

RESULTS AND DISCUSSION

The GC/Milli-Whistle System. Figure 1 shows a schematic diagram of the GC/milli-whistle setup, which was similar to that used in our previous study,[1] except for the accelerometer and data acquisition devices. In addition, the milli-whistle has been modified to make it more compact and to have a higher sensitivity and stability. The inset photo shows the actual scale of the brass milli-whistle and the accelerometer, compared to a one-cent coin. A detailed scale of the cross section of the milli-

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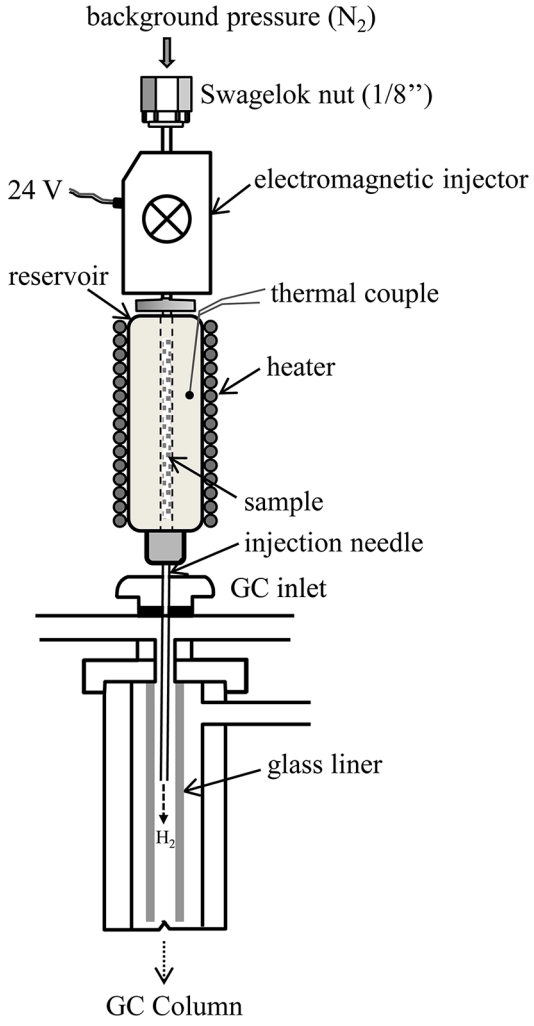

Figure 2. A schematic diagram of the magnetic injection setup.

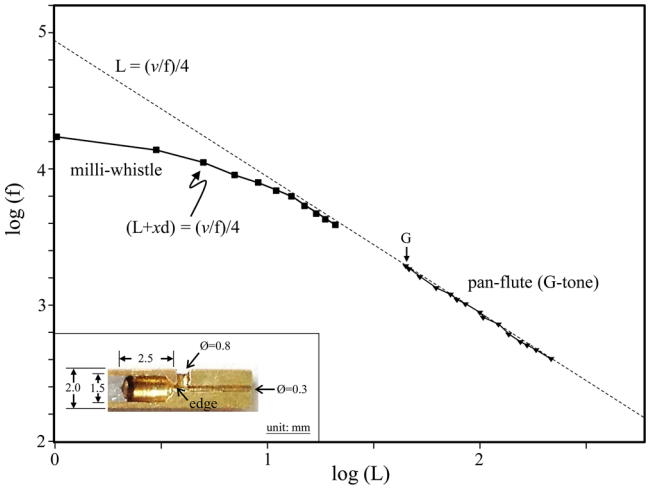

Figure 3. The relationship between frequencies and the actual length of a G-tone pan-flute (15 pipes; pipe length, 218−45 mm/pipe width, 17.5−9.8 mm) and the optimized milli-whistle [5 mm in length (L), 1 mm in width (d), tunnel diameters were 0.3 (for gas blown in) and 0.8 mm (for gas going out), respectively]. An empirical formula for this, $(L + xd) = (v/f)/4$, was derived, where x is equal to 2.8.

whistle is shown in Figure 3. When nitrogen was used as the carrier gas associated with makeup gas, the milli-whistle

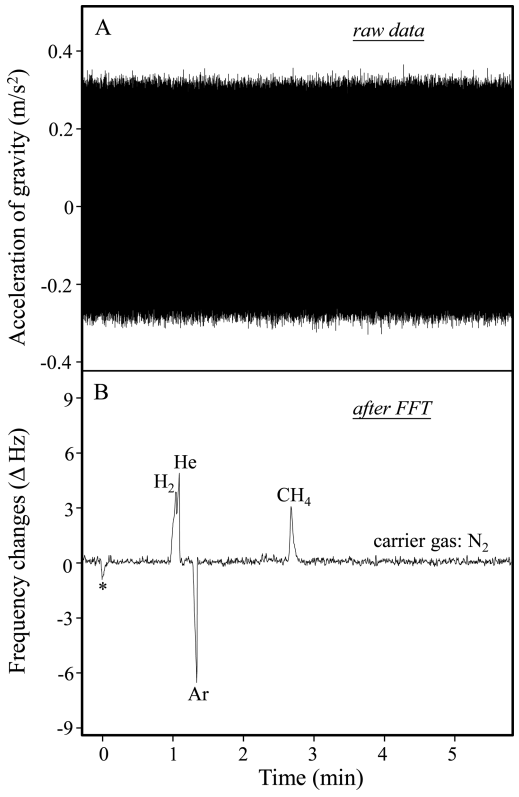

Figure 4. Typical GC chromatograms for four test gases based on the milli-whistle/accelerometer GC system. Figure 3A (raw data) shows the spectrum of real-time vibrational frequency of the whistle when a mixture of the four gases (with same volume ratio), including H_2, He, CH_4, and Ar, was used as the test samples; the carrier gas used was nitrogen. The x and y axis show the retention time (min) of the GC chromatogram and the values of acceleration of gravity (m/s^2), respectively. Figure 3B shows the GC chromatogram after fast Fourier transformation.

simultaneously produces sound and body vibrations. We found that, interestingly, the frequency of the whistle vibration (detected by the accelerometer) and the sound frequency (detected by the microphone) were identical. When the components of GC elutes change, a minor frequency difference can be sensitively detected either by the accelerometer or by the microphone. In fact, we concluded that a solid transmits sound faster than a gas, and for this reason, the limit of detection would be improved if an accelerometer were to be used. However, in the meantime, similar results were obtained by the two methods. In order to measure the amplitude of the whistle vibration, a displacement sensor (SICK Sensor Intelligence) was used, but it was not possible to obtain clear data. Figure 2 shows a schematic diagram of the magnetic injection setup developed in this study. It consists of an electromagnetic pulse injector and a reservoir that can be heated. The pulse injector was an in-house fabricated microcontrol injector, which was prepared by modifying a standard pulse nozzle. It was controlled by a personal computer through a PCI-6221 device. The injection volume of the pressurized sample was adjusted by changing the background pressure, the inner diameter/length of the injection needle (0.028/0.06 in. o.d./i.d.; length, 2.0 in.) and the injection time. During regular operation at a background pressure of 1.6 kg/cm^2 and at 50 ms of open time, the volume of hydrogen gas injected can be readily controlled in the range of 129 ± 0.9 μL

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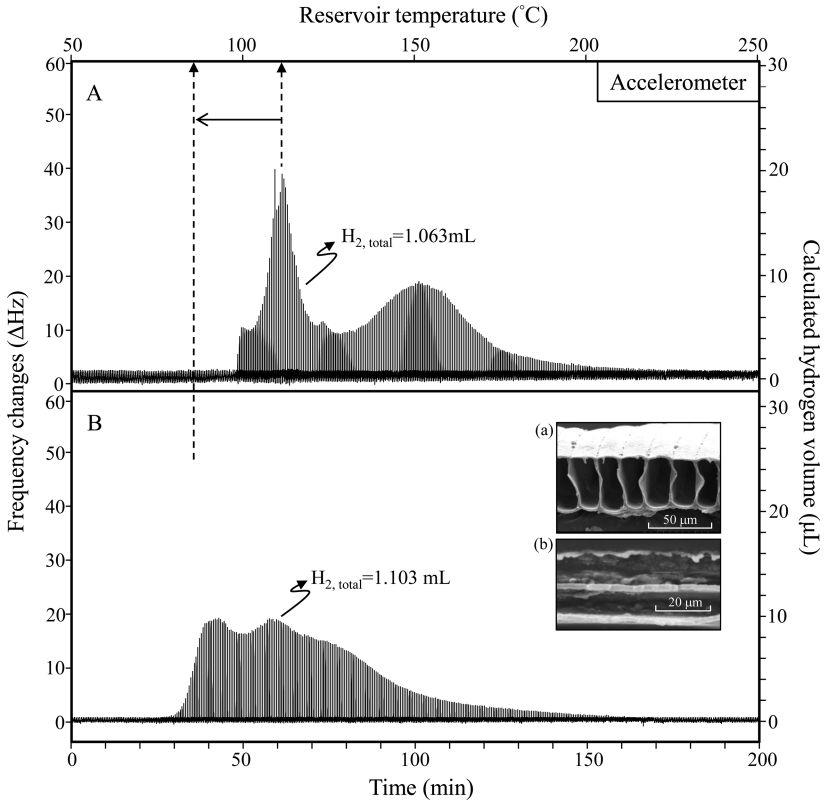

Figure 5. The relationship between the frequency of changes by released hydrogen and the time scale of the process by heating ammonia borane. The accelerometer was used as the gas detector. (A) Bulk ammonia borane and (B) a 40 wt % ammonia borane/microtube array composite membrane was examined. The inset is the scanning electron microscope (SEM) images that show the microtube array membrane (image a) of polycarbonate and doped ammonia borane, inside the membrane (image b), respectively.

(n = 50). For loading the sample, the inside volume of the brass reservoir was estimated to 237 mm^3. The reservoir can be simultaneously heated by a built-in program and monitored by a K-type thermal couple.

Quantitative Analysis Based on Frequency Shifts. As shown in Figure 3 (dashed line), it is well-known that if humidity and temperature are neglected, the formula for calculating the length of a pan-flute pipe is $L = (v/f)/4$ [the "theoretical length" (L) equals the speed of sound (v), divided by the desired frequency (f) in hertz, with the resulting quantity divided by 4]. As can be seen, the relationship between the frequencies and the actual length of a G-tone pan-flute (15 pipes; pipe length, 218−45 mm/pipe width, 17.5−9.8 mm), which was purchased from a local musical instrument store, basically follows this equation (line, -▼-). Herein, the x axis and y axis show the logarithm of the pipe length (L) and frequency (Hz), respectively. The relationship is clearly linear, although the factors of pipe width, air density, and temperature are ignored. However, when the pipe length was shorter than 10 mm, as in the case of a milli-whistle, a deviation was observed (line, -■-). This is because when a fast-moving air jet is forced through an edge and split into two vortices, the vortices interact and oscillate to produce a specific sound called the edge tone. The edge tone frequency increases with increasing streamflow velocity. An actual frequency of a pipe is well-coupled by edge tone phenomenon and air column resonance. When the pipe length becomes shorter, or if the pipe width becomes larger, the phenomenon of edge tone would be stronger than the air column resonance, leading to a deviation from the equation of $L = (v/f)/4$. The inset in Figure 3 shows the smallest whistle that we have been able to use to date. A modified equation is absolutely needed in the case of such a small milliscale whistle. A series of five different milli-whistles (i.d. of d = 1, 1.7, 2, 2.3, and 3 mm) were examined (all L = 5 mm). The optimized sizes are shown as follows: 5 mm in length (L), 1 mm in width (d), and the tunnel diameters were 0.3 (mouthpiece, for gas blown in) and 0.8 mm (for gas goes out), respectively.

Applications. In the case of detection using an accelerometer, Figure 4A (raw data) shows the spectrum of the real-time vibrational frequency of the whistle when a mixture of four gases, including H_2, He, CH_4, and Ar (with same volume ratio), was used as test samples; the carrier gas was nitrogen. The x and y axis show the retention time (min) of the GC chromatogram and the values for the acceleration of gravity (m/s^2), respectively. This complex spectrum became clear after carrying out a Fourier transformation, as shown in Figure 4B. The findings show that H_2, He, and CH_4 (molecular weight smaller than carrier gas) produces a higher frequency, whereas Ar (molecular weight greater than carrier gas) produces a lower frequency. The "*" mark shows the starting point, since the gas sample was suddenly injected into the GC inlet. This milli-whistle/accelerometer system was also successfully applied to practical analyses. Figure 5A, x axis (bottom) shows the time scale of the process during the heating of ammonia borane; the y axis (left) shows the frequency changes in Hz after Fast Fourier transformation (fundamental frequency, 11100 Hz which was produced by the nitrogen carrier gas). Herein, the experimental conditions are as follows. High pressure nitrogen (1.6 kg/cm^2) was used as the background pressure for gas

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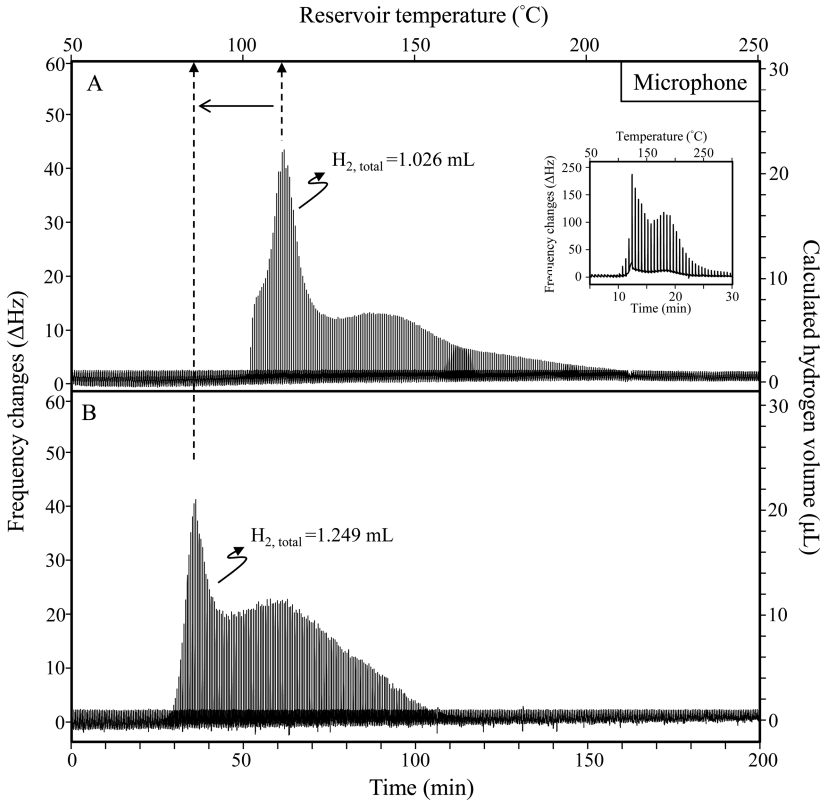

Figure 6. The relationship between frequency changes by released hydrogen and time scale of the process by heating ammonia borane. The microphone was used as the gas detector. (A) Bulk ammonia borane and (B) a 20 wt % ammonia borane/microtube array composite membrane was examined. The inset shows that the maximum amount of hydrogen generated is observed at 13 min at 129 °C, where 1.066 mL of hydrogen was generated when the reservoir was heated at a rate of 10 °C/min.

injection. The reservoir was heated at a rate of 1 °C/min, where the pulse injector was opened every 0.5 min for a period of 50 ms; a total of 400 injections were made. The GC capillary and the whistle were kept at room temperature. In the beginning, the regular noise arises from either the sound or the vibration from the electromagnetic pulse injector and can be considered as system peaks. Compared to the carrier gas, the frequency changes start from 50 min, meanwhile the reservoir temperature was 100 °C (as shown in the upper *x* axis). The maximum amount of hydrogen generated is observed at 60 min/115 °C. On the basis of the modified equation described, the amount of hydrogen corresponding to the peak at ΔHz = 38.2 Hz was calculated to be 19.4 μL (as shown in the right *y* axis). In order to confirm this, a calibration curve was also constructed for comparison, and the results show that no differences are apparent, irrespective of whether the modified equation or the calibration curve was used. A total volume of hydrogen generated from 1.0 mg of ammonia borane during the heating process was estimated to be 1.063 mL. As a hydrogen storage medium, it would be convenient if the hydrogen release temperature could be decreased. For this purpose, ammonia borane was doped into a polymeric microtube array membrane by means of an electrospinning technique, since this permits the total surface area to be increased. As shown in the inset in Figure 5B, scanning electron microscope (SEM) images show the microtube array membrane (image a) of polycarbonate and doped ammonia borane, inside the membrane (image b), respectively. It was found that, up to 40 wt % of ammonia borane can encapsulated by the polycarbonate in the microtube array composite membrane. The total volume of hydrogen generated was estimated to be 1.103 mL from 1.0 mg of ammonia borane, and it was possible to decrease the operation temperature to 85 °C. As shown in Figure 5B (dashed line), it is found that the hydrogen generation temperature was decreased from ∼110 °C to ∼85 °C. The amount of released hydrogen increased with the ammonia borane content and, interestingly, was slightly higher than that released by bulk ammonia borane. In order to evaluate the performance of the milli-whistle/accelerometer setup, the results were compared to data obtained using a microphone. As shown in Figure 6, using a microphone, a 20 wt % of ammonia borane/microtube array composite membrane was examined. In Figure 6 (panels A and B), 1.0 mg ammonia borane was used in the experiment, and the findings show that 1.026 and 1.249 mL hydrogen, respectively, were generated. When the reservoir was heated at a rate of 10 °C/min, where the pulse injector was opened every 0.5 min for a period of 50 ms, a total of 50 injections were made. As shown in the inset in Figure 6A, the maximum amount of hydrogen generated is observed at 13 min/129 °C, where 1.066 mL hydrogen was generated. In each case, it is obvious that the online quantitative detection of hydrogen released from ammonia borane is successful.

■ CONCLUSION

The development and testing of a novel GC detector based on frequency changes using a milli-whistle based on an accelerometer is described. The optimized sizes of the whistle, as well as the empirical formula used in the determinations, were reported. The frequency of the whistle vibration and the sound frequency are identical; the components of GC elutes

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can be sensitively detected using either the accelerometer or the microphone, respectively. The limit of detection was the same for both detectors. This milli-whistle/accelerometer system was successfully applied to the online quantitative detection of hydrogen released from ammonia borane. The present method is simple, quick, and online quantitative data can be obtained. Further practical analyses can be expected.

AUTHOR INFORMATION

Corresponding Author

*C.-H.L.: e-mail, chenglin@ntnu.edu.tw; C.-C.C: e-mail, polyjack@tmu.edu.tw.

Notes

The authors declare no competing financial interest.

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