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Reviews

The Use of a Milli-whistle as a Detector in Gas Analysis by Gas Chromatography

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This mini-review introduces a general understanding of the use of a milli-whistle as a gas chromatography (GC) detector in gas analysis, including our research on the methodology and theory associated with a number of different related applications. The milli-whistle is connected to the outlet of a GC capillary, and when the eluted gases and the GC carrier gas pass through it, a sound with a fundamental frequency is produced. The sound wave can be picked up by a microphone or an accelerometer, and after a fast Fourier transform, the online data obtained for frequency-change *vs*. retention time constitute a new method for detecting gases. The first part of this review discusses the fundamentals of the milli-whistle. Some modifications are also discussed, including various types of whistles and an attempt to maximize the sensitivity and stability of the method. The second part then focuses on several practical applications, including an analysis of hydrogen released from ammonia borane, inorganic gases produced from fireworks, the CO_2/O_2 ratio from expired human breath and a purity test for alcohols. These studies show that the GC-whistle method has great potential for use as a fast sampling ionization method, and for the direct analysis of biological and chemical samples at under ambient conditions.

Keywords Whistle, gas chromatography, microphone, accelerometer

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1 Introduction

The sound of a whistle from a steam locomotive gives a signal and a warning. Analogously, monitoring the frequency-changes[1,2] from sound from a whistle could be used as a method for gas detection in gas chromatography (GC). A number of commercially available gas detectors are currently available,

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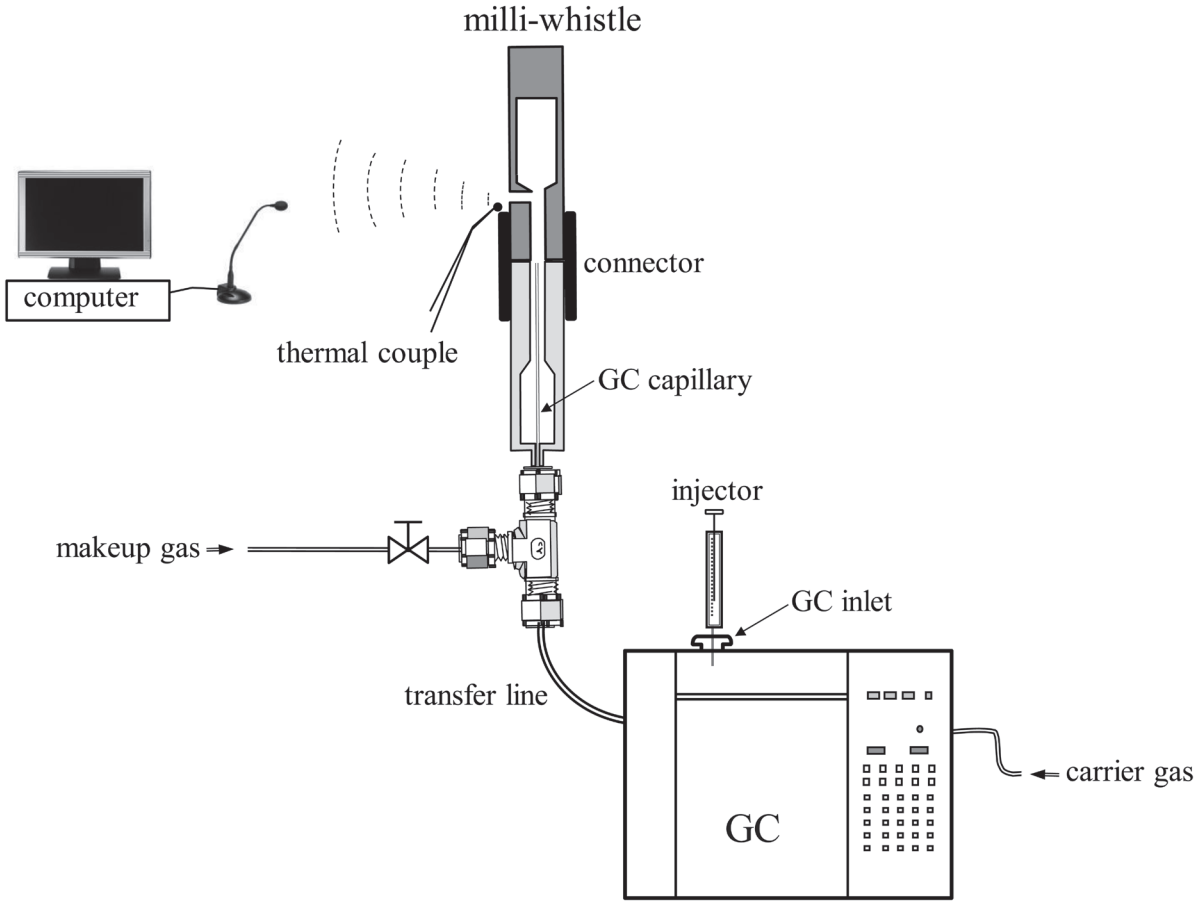

Fig. 1 Schematic diagram of the GC/milli-whistle setup.

and are in use as of this writing.[3-24] While they are based on different principles, each has unique advantages and disadvantages regarding sensitivity, precision, simplicity and cost. In our previous study, we reported on the development of a novel method for gas detection using a milli-whistle as a detector in gas chromatography.[25] The milli-whistle was connected to the outlet of a GC capillary, and when the GC-eluant and carrier gas passed through the whistle, a sound was produced. When the composition of the GC-eluant is altered, along with the retention time, the changes in the frequency of the sound produced can be detected using a microphone. After a Fourier transform,[26-31] a very sharp frequency peak can be observed. In terms of sensitivity, this method is superior to that for a typical thermal conductivity detector, and can be very useful in the analysis of gases, irrespective of whether they are organic, inorganic or rare gases. However, some issues remain to be solved: whistles are generally available in many types, but they all produce a sound when a stream of forced air passes through them, either by mouth or powered by air pressure, steam, or other means. In addition, whistles are available in a variety of sizes, from a small slide whistle to large multi-piped church organs. In the case of GC, typical carrier gases include helium, nitrogen, argon, hydrogen and air; the flow rate is usually maintained at a level of several mL per minute, depending on the situation and type of analysis being conducted. Whatever the type of carrier gases used, a small whistle, of mm size, is needed to produce a sound from the end of the GC capillary. Once the size of the whistle is reduced to the milli-meter scale, maintaining the repeatability and reproducibility of use, and the requirements of precision and accuracy become even more important. In this review, various types of milli-whistles were prepared and their performances compared. The optimized size of the milli-whistle, its physical characteristics and details of its construction are reported. Several applications, including our research on an analysis of hydrogen released from ammonia

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Hsin-Kai Chen received her bachelor's degree in 2011 at National Kaohsiung Normal University. His current research is focused on micro-extraction. By means of electrospinning, polycarbonate and polylactic acid were prepared as hollow fibers, which are used for off-line and on-line extraction, respectively.

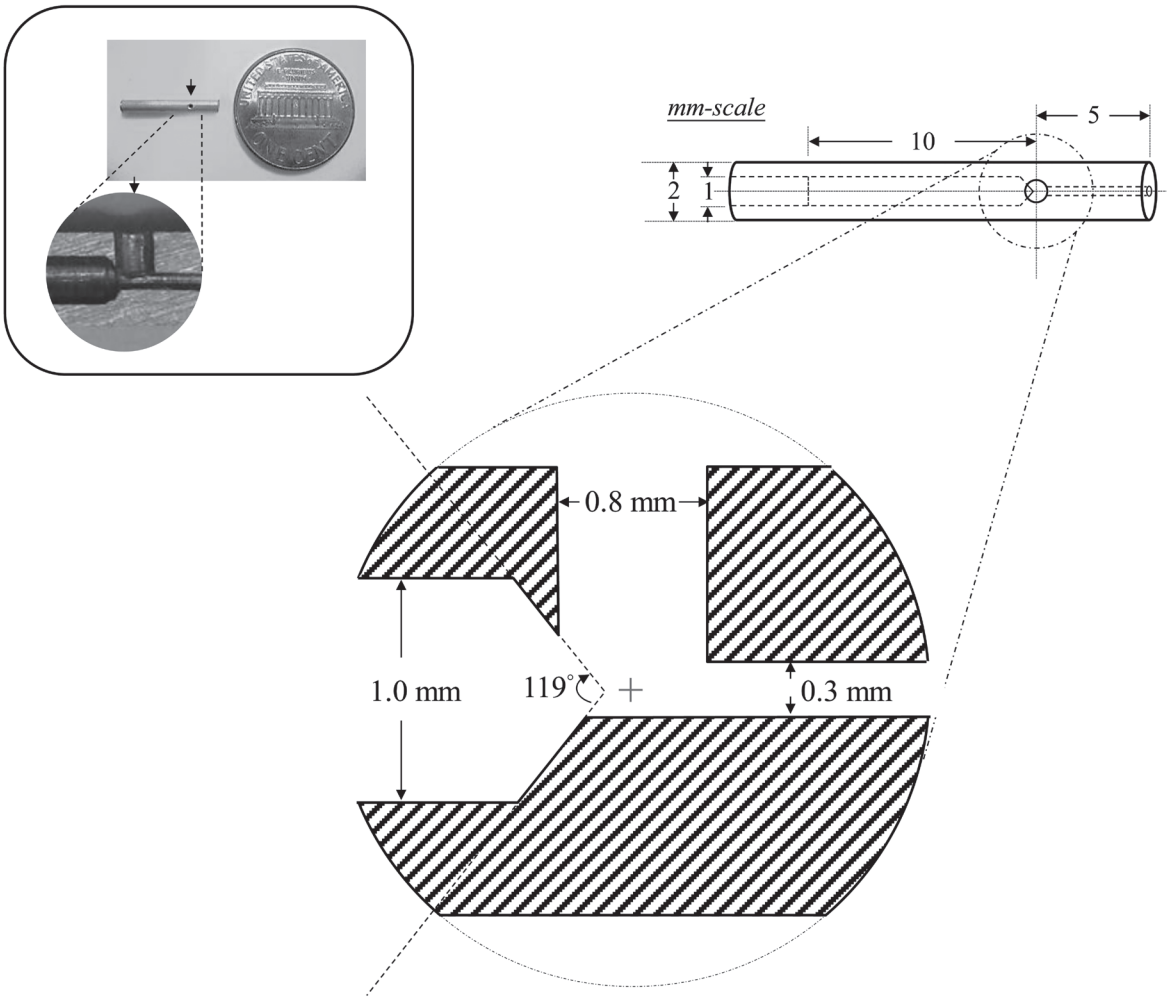

Fig. 2 Schematic drawing of the milli-whistle used in this study. The inset photo shows the actual scale of the brass milli-whistle, compared to a one-cent coin. The arrow marker points the hole of the sound exit.

borane,[32] inorganic gases produced from fireworks,[33] expired CO_2/O_2 ratio from a sample of human breath and a purity test for alcohols, are also demonstrated herein.

2 Fundamentals

Figure 1 shows a schematic diagram of the GC/milli-whistle setup, in which a typical GC syringe injector was used for the injection of either gas or liquid samples. The temperature of the GC oven and the flow rate of the carrier gas could be controlled very precisely; after supplying makeup gas, a stable sound wave could be generated from the milli-whistle. Herein, the flows rate of the carrier gas and makeup gas were usually maintained at 8 – 10 and 50 – 60 mL/min, respectively. The flow meter and a K-type thermal couple were used to continuously monitor the flow rate and the temperature, respectively. A regular microphone could be used to pick up any frequency changes when nitrogen was used as the carrier gas and makeup gas, but a supersonic microphone was needed when hydrogen gas was used (frequency greater than 20 K Hz). The modified whistle developed in this study (schematic drawing shown in Fig. 2) is more compact and provides higher sensitivity and stability. The inset photo shows the actual scale of the brass milli-whistle compared to a one-cent coin and a photo of the cross section shown below. The arrow indicates the opening where the sound exits. The milli-whistle was fabricated from a piece of brass wire (16 mm in length; o.d., 2 mm) using a bench-type engine lathe. A 1.0-mm drill bit (cutting angle, 119°), operating at a speed of 1500 rpm, was initially used to open a 10.8 mm barrel from the left side (as shown in Fig. 2). This drill bit was then replaced with a 0.3 mm drill bit, which was used to open a mouthpiece through the brass piece. The most important issue was how to determine the position where the sound exits. We found that it should be located exactly 5.0 mm from the right side; the center position is indicted by a "+" symbol in this diagram. The sound exit opening was initially made using a 0.8-mm drill bit, and the end was then sealed using a piece of brass wire. It should be noted that the procedure used to open the sound exit is very important, since this step involves creating a sharp edge for producing a sound. This is because, when a fast-moving air jet is forced through the edge and is split into two vortices, the vortices interact and oscillate to produce a continuously periodic groove of air, *i.e.* a specific sound, which is called the edge tone.[34-36] The edge tone frequency increases with increasing carrier gas velocity. The actual frequency is well-coupled by edge tone phenomenon and air column resonance. This process is analogous to the sound made by

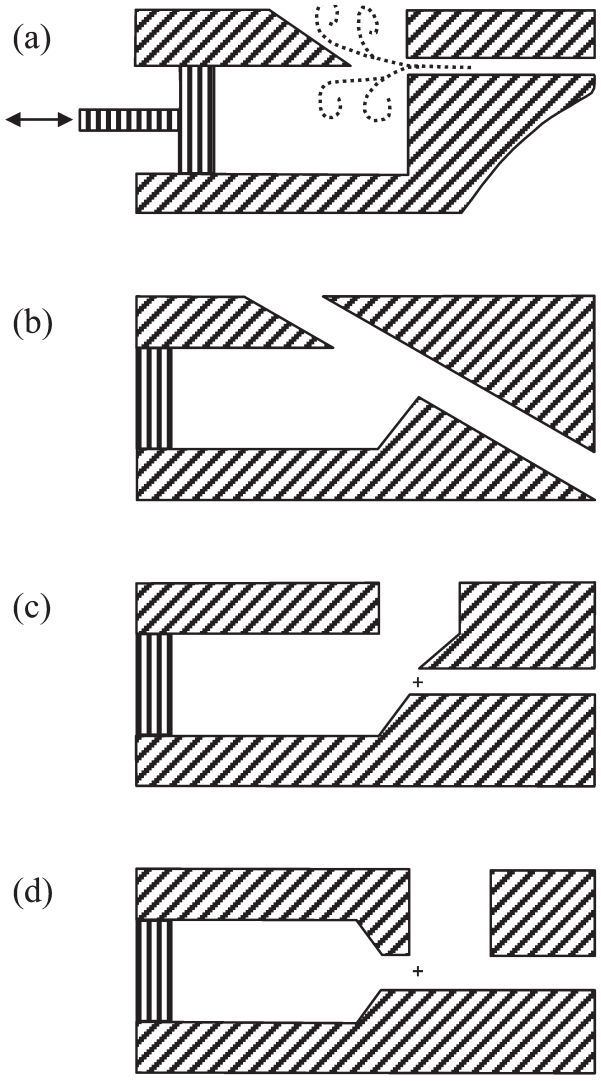

Fig. 3 Four types of whistles compared in this study. Type (a), schematic drawing of a typical slide whistle; (b) a new designed whistle which is available for use; (c) and (d) demonstration of a poorly designed whistle.

a slide whistle; a schematic diagram of which is shown in Figs. 3a. Based on this model, several types of whistles were prepared and tested, and one is shown in Fig. 3b. This type of whistle also produced an acceptable sound, and could be used in GC, but it was quite difficult to open an incline mouthpiece, especially when a 0.3-mm drill bit was used. Furthermore, when the position of the exit for the sound is shifted slightly from the center, the slit edge cannot be shaped, and a huge edge can be formed, leading to the air jet not being split into two vortices, as shown in Figs. 3c and 3d, respectively. It is well known that if the humidity and temperature are neglected, the formula for calculating the length of a closed pipe is L = (*v*/f)/4 (the "theoretical length" [L] equals the speed of sound [*v*], divided by the frequency of the sound in hertz [f], with the resulting quantity being divided by 4,[15] as shown in Fig. 4 (dashed line)). The *x*-axis and *y*-axis show the logarithmic relationship between the length of a closed pipe (mm) and the frequency (Hz), respectively. It was found that when the length (L) becomes shorter, or if the width (d) of the barrel becomes larger, the phenomenon of edge tone would be stronger than the air column resonance, leading to a deviation from the equation L = (*v*/f)/4. Thus, a modified equation is needed, especially in the case of a whistle constructed on a milli-scale. As shown by solid lines in Fig. 4, a series of five different (i.d., d; 1.0, 1.7, 2.0, 2.3 and 3.0 mm) milli-whistles were prepared and examined (length, from 1 mm to 25 mm; L). It is clear that when the barrel width (d) is increased, the deviation becomes larger. We found that the optimal diameter of the barrel should be 3-fold larger than that of mouthpiece and the optimized diameter of the mouthpiece should be 2-fold larger than that of the sound exit. The inset in Fig. 4 shows the relationship between the i.d. of the mouthpiece (mm) and flow rate (mL/min), respectively. When the mouthpiece was expanded to 0.5 mm i.d., the flow rate of the carrier/makeup gas had to be maintained at a level greater than 94 mL/min to produce a sound. In contrast to this, if the mouthpiece was opened to 0.3 mm and 0.4 mm i.d., respectively, the flow rate had to be decreased to 21 and 41 mL/min. Since a minor interference can be easily detected as a signal or a warning, a lower flow rate provides better sensitivity. Hence, if it were possible to have a micro-channel separation kit and a micro-whistle could be constructed and used for GC, the limit of detection could be further improved. Thus far, the construction on a micro-scale remains a difficult issue, and for these reasons, in this study we used one type of whistle, which was 10 mm in length (L), 1 mm in barrel width (d) and the diameters of the mouthpiece and sound exit were 0.3 and 0.8 mm, respectively, in subsequent experiments.

3 Applications

3·1 Hydrogen released from ammonia borane

Ammonia borane (NH_3BH_3, AB) has attracted attention as a source of hydrogen fuel cells.[37–40] It is more dense than liquid hydrogen, and has been proposed for use as a hydrogen storage medium. It can be stored at room temperature and pressure relatively safely, and hydrogen is released upon heating.[41] Since the particles of AB can be minimized, leading to high-efficiency hydrogen release at lower temperature, we recently developed a novel hydrogen storage and delivery device for AB. Micro-composite of AB/polycarbonate hollow fibers were prepared by encapsulating AB within a polycarbonate fiber. Figure 5A shows how a photo of a co-axial electrospinning device was used in our laboratory; Fig. 5B shows scanning electron microscope (SEM) images of the hollow fibers, where micro-AB particles appear on the surface (up) and inside the hollow fibers (bottom), respectively. In general, differential scanning calorimetry (DSC) is used to measure the amount of released hydrogen. However, online quantitative monitoring, especially at the micro-liter level, continues to be a challenge. In Fig. 6, the *x*-axis shows the time scale of the process during the heating of ammonia borane; the *y*-axis shows the frequency in Hz after a Fast Fourier transformation. As shown by the black curve, when 1.0 mg of AB (100 wt%) was placed in the reservoir, which was then heated at a rate of 1°C/min, the pulse injector was opened every 0.5 min for a period of 50 ms, for a total of 400 injections. Nitrogen gas at a pressure of 1.6 kg/cm^2 was used as the background pressure for the sample injection. In the beginning, the regular noise arose from either the sound or vibration from the electromagnetic pulse injector, and could be considered as system peaks. Compared to the carrier gas, the frequency changes started from 50 min (black curve); meanwhile, the reservoir temperature was ~100°C (as shown in the upper *x*-axis). The maximum amount of hydrogen generated occured at 60 min/115°C. The amount of hydrogen

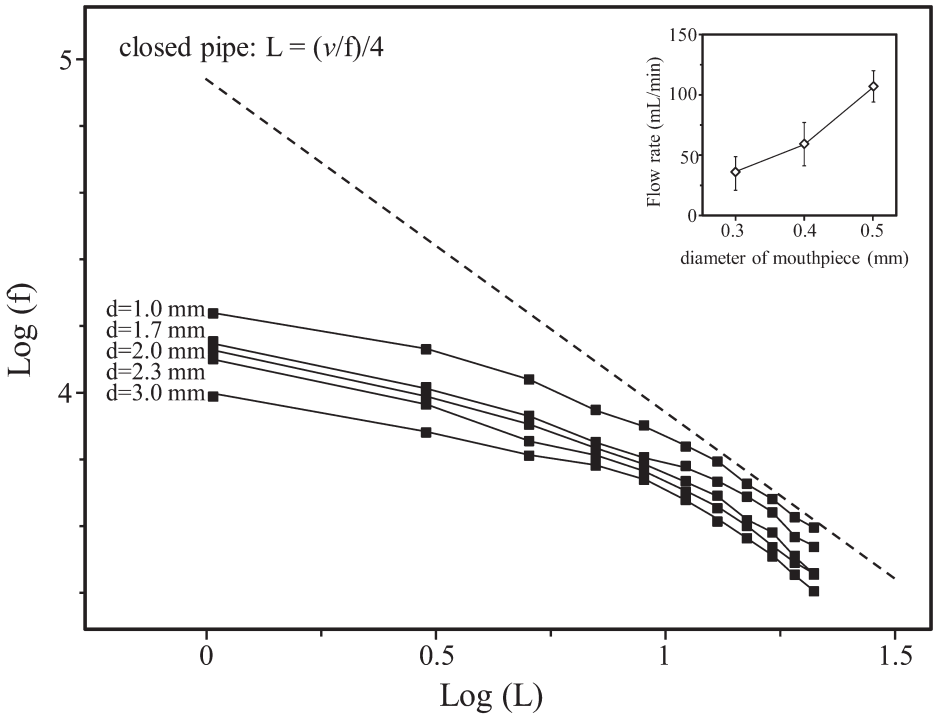

Fig. 4 Relationship between the frequencies and the various milli-whistles. Dashed line shows the basic formula between "theoretical length" [L] of closed pipe, speed of sound [*v*] and sound frequency in hertz [f]. Solid lines show the data obtained from a series of five different (i.d., d; 1, 1.7, 2, 2.3 and 3 mm) milli-whistles by different length (1 – 25 mm). When the barrel width (d) is increased, the deviations become larger.

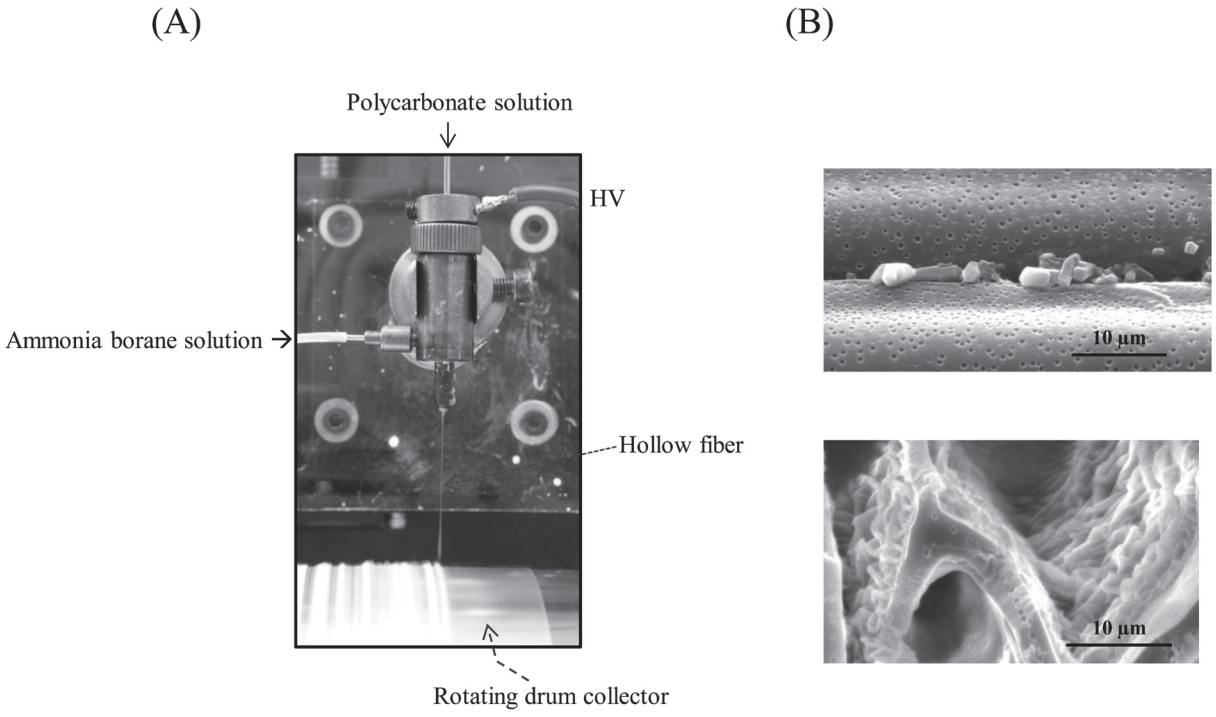

Fig. 5 A, a photo of the co-axial electrospinning device that was used in our laboratory. B, scanning electron microscope (SEM) images of the hollow fibers, where micro-AB particles appeared on the surface (up) and inside the hollow fibers (bottom), respectively.

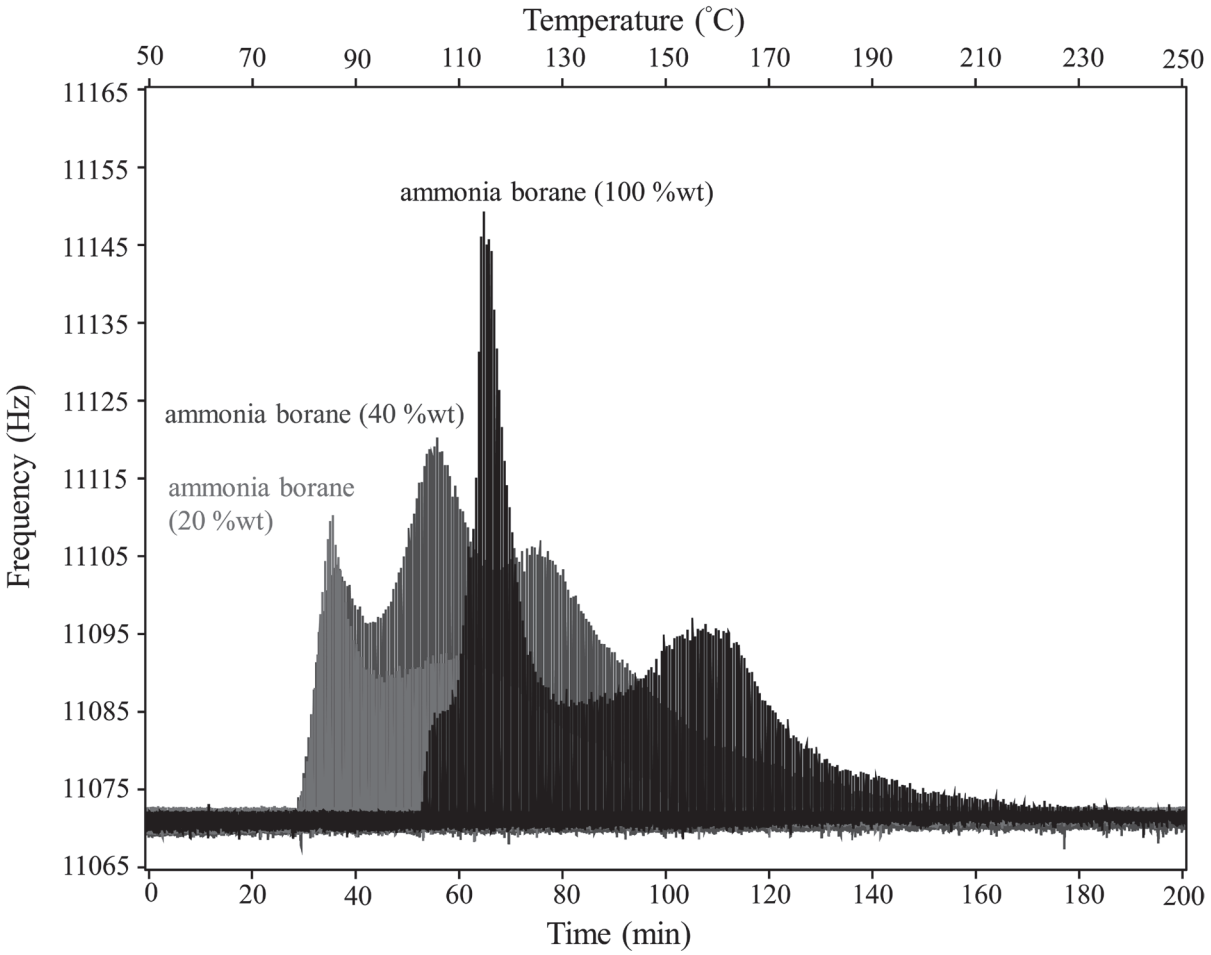

Fig. 6 Relationship between frequency changes by released hydrogen and the time scale of the process by heating ammonia borane. Black, blue and red curves show the assay of AB (100, 40 and 20 wt%), respectively. *x*-axis shows the time scale of the process during the heating of ammonia borane; the *y*-axis shows the frequency in Hz after Fast Fourier transformation.

corresponding to the peak at ΔHz = 38.2 Hz was calculated to be 19.4 mL. A total volume of hydrogen generated from 1.0 mg of ammonia borane during the heating process was estimated to be 1.063 mL. However, as a hydrogen storage medium, it would be convenient if the temperature for the release of hydrogen could be decreased. For this purpose, ammonia borane was minimized by doping 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 blue (40 wt%) and red (20 wt%) curves, ammonia borane can be encapsulated by the polycarbonate in the fibers and release hydrogen. In the case of 40 wt% of AB, the total volume of hydrogen generated was estimated to be 1.103 mL, and the operation temperature was decreased to 85°C. It was found that the hydrogen generation temperature could be 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. It is obvious that the GC-whistle system permitted the successful online quantitative detection of hydrogen released from ammonia borane.

3·2 Inorganic gases from fireworks

Firework-rockets are basically separated into two parts: explosive materials (top) and propellants (bottom), in which an ignition wire is inserted. Pyrotechnic firework-rockets are composed of a paper tube packed with gunpowder that propels itself into the air in order to fly. Released from traditional Chinese firework-rockets, SO_2, N_2 and CO_2 were used as the model gases in this study. The inset picture in Fig. 7A shows a top view of a firework-rocket and a cross-section photo, respectively. The explosive materials made up ~1/4 of the length (2.9 g) of the rocket body and the remainder contained the propellant (4.81 g). The resulting combustion gases were collected after focusing a laser on a 25-mg sample of propellant using a quartz lens. Figure 7A shows a GC chromatogram for the real-time vibrational frequency of the whistle *vs*. retention time when 10 μL volumes of the combustion gases were examined; nitrogen was used as the carrier/make-up gas. The major component of the sample was CO_2 gas. The presence of O_2 is because the bottle was initially purged with oxygen so as to exclude N_2. Based on a comparison with the calibration curve, the propellant contained 25% carbon. It is well known that a simple, commonly cited chemical equation for the combustion of black powder is

$$2\ KNO_3 + S + 3\ C \longrightarrow K_2S + N_2 + 3\ CO_2.$$

Basically, N_2 and O_2 are difficult to separate, unless a molecular sieve column is used. In this case, the carrier/make-up gas used

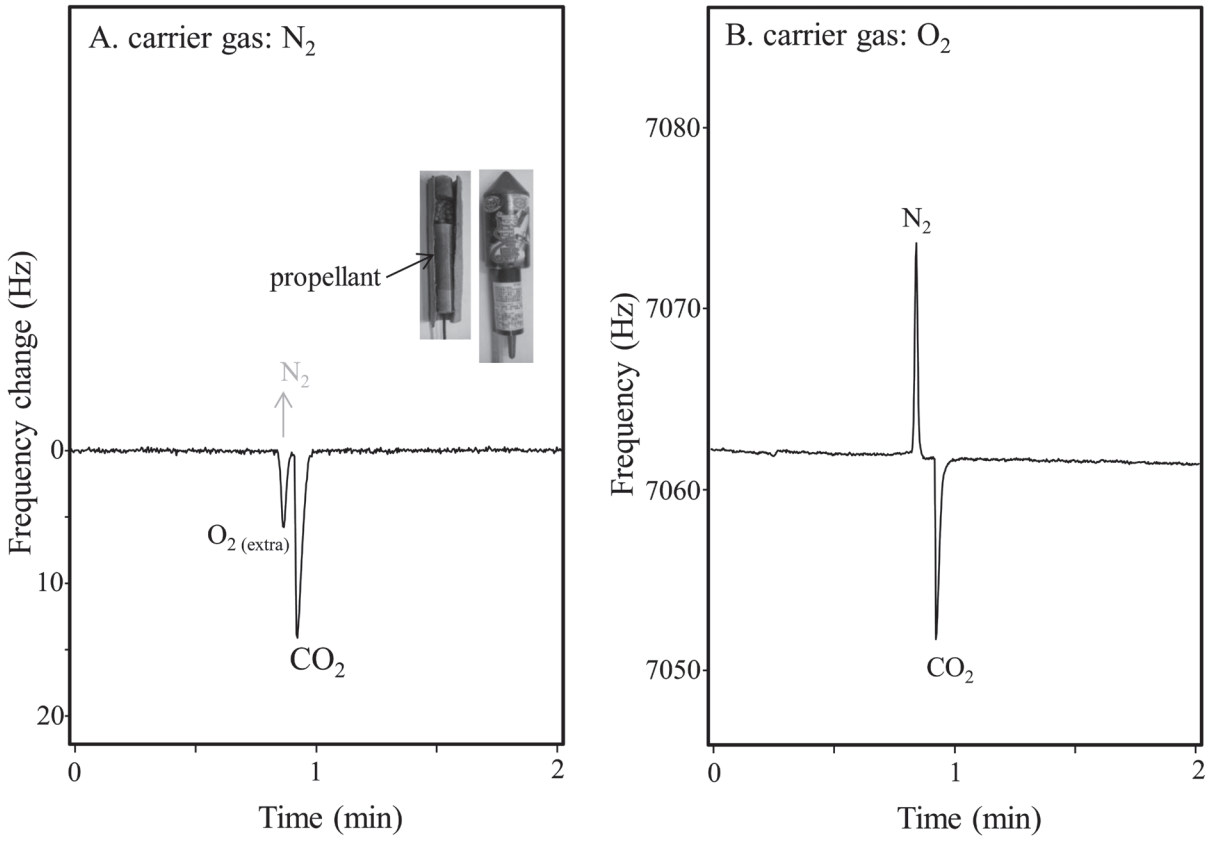

Fig. 7 A, GC chromatogram for the real-time vibrational frequency of the whistle *vs*. retention time. Sample injection volume, 10 μL of the combustion gases (obtained from explosive materials); carrier/make-up gas, nitrogen. B, GC chromatogram for the real-time vibrational frequency of the whistle *vs*. retention time. Sample injection volume, 10 μL of the combustion gases (obtained from explosive materials); carrier/make-up gas, oxygen. The inset picture (in frame A) shows a top view of a firework-rocket and a cross-section photo, respectively.

was N_2, which explains why a peak corresponding to N_2 is not seen. However, when the carrier/make-up gas was changed to O_2, a peak corresponding to N_2 can clearly be seen, as shown in chromatogram in Fig. 7B. It is interesting to note that, when the molecular weights of the GC-eluent (in this case, N_2) are lower than the carrier/make-up gas (O_2), the observed frequencies are higher than that of the carrier gas, whereas when the molecular weights of the GC-eluant (in this case, CO_2) are higher, lower frequencies are produced. In fact, when we used a so-called universal detector, a thermal conductivity detector (using in a GC instrument; Agilent 3000 Micro GC), to separate these gases for comparison, the findings showed that these gases (N_2 and O_2; O_2 and SO_2) were very difficult to separate. However, when the GC/whistle system is used, even GC-eluants having exactly the same retention times can be easily distinguished simply by changing the carrier gas. Although we were unable to identify SO_2 in this experiment, sulfur is a well-known component of black powder. In the case of explosive material, it was very difficult to ignite the sample using a laser beam, unless it was mixed with propellants (at least 25% by weight), thereby increasing the rate of combustion. Instead of a laser, we simply used a spirit lamp to ignite the explosive material (25 mg.) The results are shown in Fig. 8; the carrier/make-up gas was nitrogen. We found that the major component was SO_2. Based on a comparison with the calibration curve, the explosive material was composed to 24.8% sulfur and 3.4% carbon. In order to confirm that both the propellant and explosive material contained sulfur, we examined them by Raman spectrometry; the findings showed that the Raman shifts for a standard sample of sulfur matched with the explosive material and the propellant, respectively. Although both the propellant and the explosive components contained sulfur, these materials are not homogeneous, making it difficult to carry out a quantitative analysis. Finally, neither CO nor NOx was detected in this study, because either the burning-temperature was too low to generate them or the column used was not suitable for their separation.

3·3 The CO_2/O_2 ratio from expired human breath

It has been reported that the exhaled end-tidal CO_2/O_2 ratio and D-dimer concentration are diagnostic markers of a pulmonary embolism.[42,43] We were curious as to whether the milli-whistle/GC system could be used in diagnostic applications such as this. The exhaled CO_2/O_2 samples were acquired from a healthy volunteer, and were used without any pretreatment. Figure 9 show typical GC chromatograms for two types of breath samples (a, normal breath; b, after holding the breath for 30 s). The injection volume was 10 μL in both cases. Nitrogen was used as the makeup and carrier gases and the fundamental frequency observed was 7305 Hz. In Fig. 9a, the frequency changes for CO_2 and O_2 are shown to be –1.22 and –1.46 Hz. The negative values show that the observed frequency was lower than the fundamental frequency. This is because, when the molecular weights of the GC-eluants are lower than the

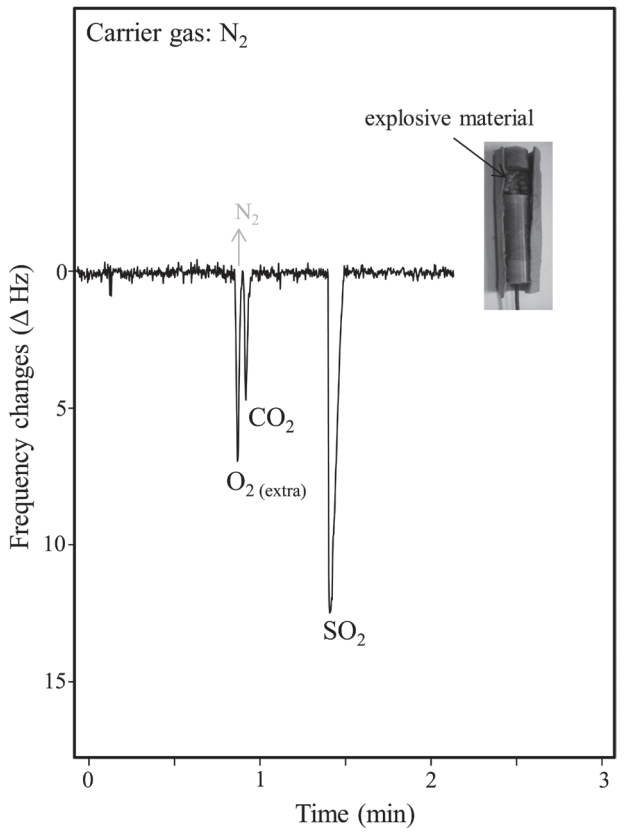

Fig. 8 Typical GC chromatogram for the real-time vibrational frequency of the whistle *vs*. retention time. Sample injection volume, 10 µL of the combustion gases (obtained from explosive materials); carrier/make-up gas, nitrogen.

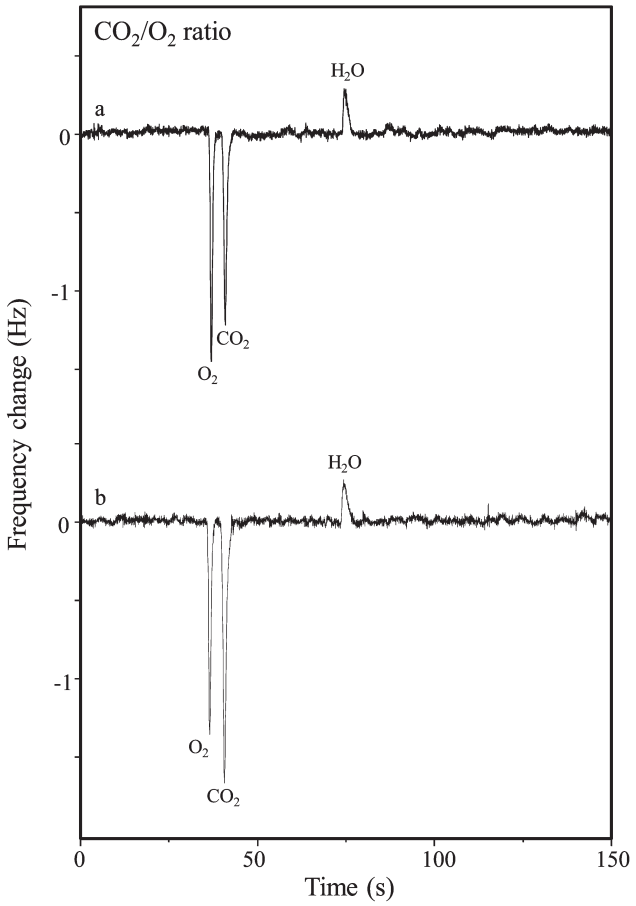

Fig. 9 Typical GC chromatograms of exhaled CO_2/O_2 analysis; chromatogram (a), sample acquired from a normal breathing; chromatogram (b) sample acquired after holding the breath for 30 s, respectively.

carrier/makeup gas, the observed frequencies are higher than that of the carrier gas, whereas GC-eluants with molecular weights higher than that would produce lower frequencies. The peak corresponding to H_2O (moisture in the exhaled breath) was found to be +0.18 Hz. Based on the modified equation developed herein, the amounts of CO_2 and O_2 were calculated to be 3.83 and 15.10%, respectively. It is well-known that the percentage of CO_2 in conventional human breath is around 4%, and that value increases slightly when the breath is held for a few seconds. After holding the breath for 30 s, as shown in Fig. 9b, the frequency changes for CO_2 and O_2 were found to be –1.65 and –1.35 Hz, respectively, and the amount of CO_2 and O_2 were calculated to be 5.54 and 14.35%. In order to confirm this, a calibration curve was also constructed for a comparison; the results showed that no differences were apparent, irrespective of whether the modified equation or the calibration curve was used. In addition, H_2O in both exhaled breath samples can be detected by the frequency change, and were calculated to be 1.97%. The signal to noise appears to poor because nitrogen was used as the carrier gas/makeup gas in this case. This can be dramatically improved if hydrogen or helium is used.

3·4 Solvent purity grades

Figure 10a shows the results obtained for a sample of spectrometric-grade ethanol where hydrogen was used as the carrier/makeup gas (fundamental frequency was 27215 Hz); sample injection volume was 0.8 µL. As one of the contaminants, the frequency change of water was found to be 3 Hz, which was calculated to be 0.3% in this assay. Components corresponding to 2-propanol and MeOH were also found, and the data were consistent with claims made by the manufacturer. Under the same conditions, a sample of an anhydrous grade of ethanol was analyzed, although it had been in use for a period of time, as shown in Fig. 10b. The results show a water content of 1.3% in the solvent ethanol. Basically, alcohols can contain water, and it is very difficult to completely remove it. However, by using the milli-whistle/GC system, low levels of contaminating water can be determined very rapidly and easily, indicating the merits and potential of this system.

4 Conclusion

In this review, we describe the details of constructing a milli-whistle that can be used for GC separation based on detecting frequency changes. The characteristics and optimized sizes of the milli-whistle are reported. It is clear that, when the GC/milli-whistle system is used, gases can be detected very easily. Some additional efforts remain in terms of improving the limit of detection, including the use of a micro-channel associated with a micro-whistle in the future. Even though the present method is simple and safe, the instrumentation is compact and has potential to be modified so as to be portable for use.

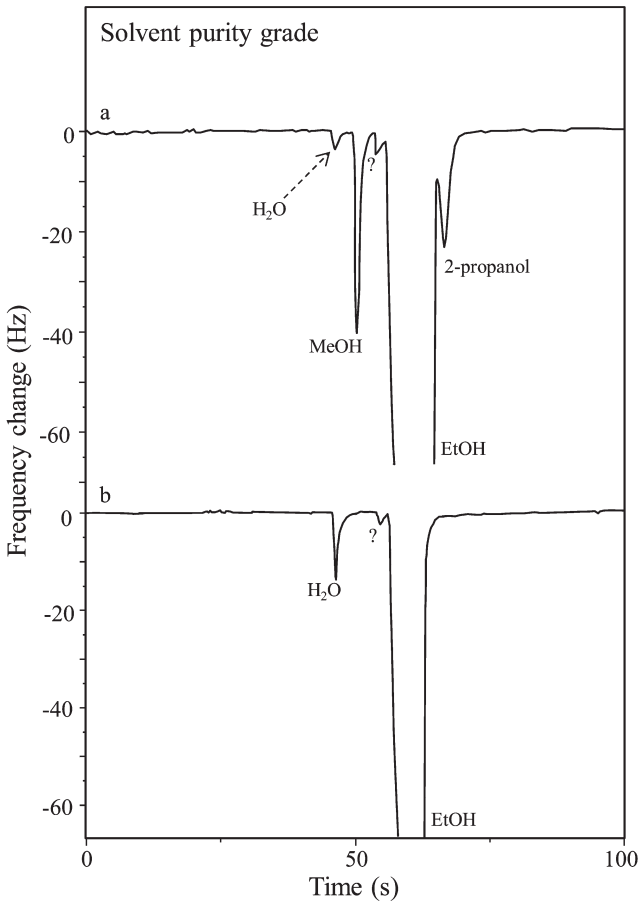

Fig. 10 Typical GC chromatograms of purity tests; chromatogram (a), a spectrometric grade ethanol; chromatogram (b), a deliquesced anhydrous grade of ethanol.

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