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Screening of inorganic gases released from firework-rockets by a gas chromatography/whistle-accelerometer method

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ABSTRACT

The use of an accelerometer for detecting inorganic gases in gas chromatography (GC) is described. A milli-whistle was connected to the outlet of the GC capillary and was used instead of a classical GC detector. When the GC carrier gases and the sample gases pass through the milli-whistle, a sound is produced, leading to vibrational changes, which can be recorded using an accelerometer. Inorganic gases, including SO_2, N_2 and CO_2, which are released from traditional Chinese firework-rockets at relatively high levels as the result of burning the propellant and explosive material inside could be rapidly determined using the GC/whistle-accelerometer system. The method described herein is safe, the instrumentation is compact and has potential to be modified so as to be portable for use in the field. It also can be used in conjunction with FID (flame ionization detector) or TCD (thermal conductivity detector), in which either no response for FID (CO_2, N_2, NO_2, SO_2, etc.) or helium gas is needed for TCD, respectively.

1. Introduction

As of this writing, a number of commercially available gas detectors are currently in use in GC (gas chromatography) separations. The mass spectrometer is undoubtedly the most popular and well-developed modern analytical instrument, although it is not very suitable for detecting inorganic and rare gases. In our previous study [1,2], we reported on the development of a novel universal detector for gas detection in which a milli-whistle is used as a detector. The milli-whistle was connected to the outlet of the GC capillary and the GC-eluants and carrier gas passing through the capillary together produce a sound as they pass through the milli-whistle. When the molecular weights of the GC-eluants are lower than the carrier gas, the observed frequencies are higher than that produced by the carrier gas alone, whereas GC-eluants with molecular weights higher than carrier gas produce lower frequencies. 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 using an accelerometer [3–6]. To date, we have used this GC/whistle system for the online quantitative determination of hydrogen from ammonia borane (NH_3BH_3), which has been proposed as a storage medium for hydrogen [2]. The optimized size of the milli-whistle, its physical characteristics and details of its construction are also investigated. Several applications, including the determination of the CO_2/O_2 ratio from a sample of human breath and a purity test for alcohols, were also investigated. Herein, we report on the expansion of this methodology to the detection of inorganic gases, released from gunpowder (as known as black powder), using the GC/whistle system as the detector. Gunpowder, which is different from smokeless powder, has been widely used as a propellant in firearms in the past and is currently used as a pyrotechnic composition in fireworks. The separation and identification of these two propellants by capillary electrochromatography and Fourier transform infrared/Raman spectroscopy have been reported [7–13]. Ion mobility spectrometry and time-of-flight secondary ion mass spectrometry are also reliable tools for their analysis [14,15]. However, due to legal issues, instead of modern gunpowder that is used in actual weapons of today, black powder that is used in traditional Chinese firework-rockets were used in this study. Details of the experimental conditions are reported and the real-time relationship between frequency-shifts and SO_2 concentration are also discussed.

2. Experimental

2.1. Reagents

All of the ultra-purified gases (>99.99%) were obtained from Fong-Ming Industrial (Taiwan), and included hydrogen, oxygen, nitrogen, sulfur dioxide and carbon dioxide. Firework-rockets were purchased from a local market. Sulfur powder was obtained from Shimakyu's Pure Chemicals (Osaka, Japan). All other chemicals

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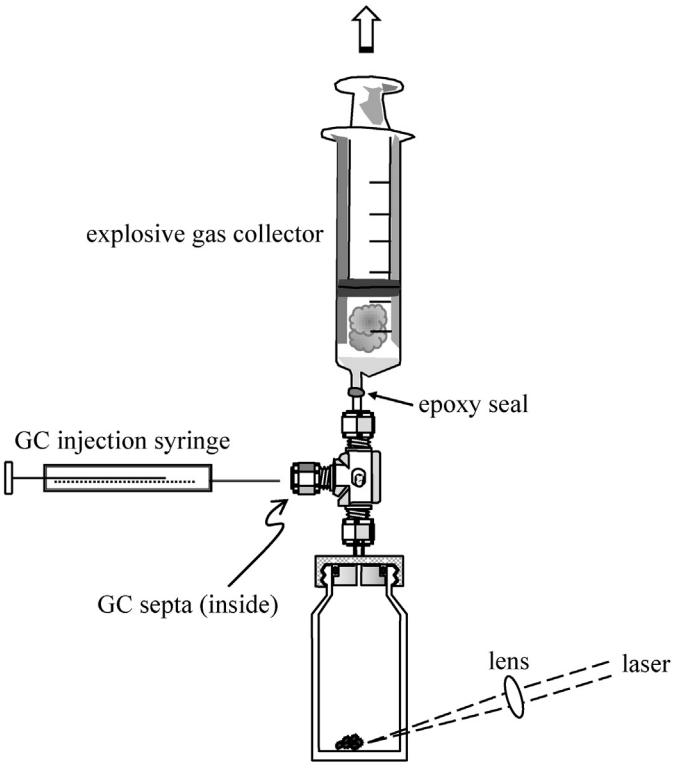

Fig. 1. Schematic diagram of the system used to collect the explosive gas.

were of analytical grade and were obtained from commercial sources.

2.2. Apparatus

The GC/whistle-accelerometer system used was identical to our previous study and is abbreviated herein [2]. Briefly, a GC (Agilent 5890) equipped with a HP-Plot Q column (30 m × 0.53 mm × 40 μm) was used for the separations. The column pressure was set at 8 psi; the carrier gases used were nitrogen and hydrogen, respectively. Total flow was maintained at 63.72–65.68 mL/min, depending on the specific conditions. The GC column had an I.D of 2 mm and the splitless mode was used. The initial temperature was 115 °C and then increased to a final temperature of 180 °C, at a rate of 40 °C/min. A high power diode laser (532 nm/1 W; Sinhuang Technology Co., Ltd., Taiwan) was used to ignite the rocket powders. A Renishaw in Via Raman microscope (United Kingdom) was used to measure the powdered sulfur.

3. Results and discussion

Fig. 1 shows a schematic diagram of the explosive gas collection system developed in this study. It consists of a plastic medical syringe (25 mL), a stainless Union Tee (tube O.D.; 1/8″) and a tubular glass vial (7 mL), respectively. In fact, it was designed for the rapid collection of gases that are produced with smokeless powder or gunpowder are ignited, because we were interested in determining whether it would be possible to achieve an online quantitative of inorganic gases generated from these materials based on this novel system. Typical black powder is a granular mixture of a nitrate, typically potassium nitrate (KNO_3; supplies oxygen for the reaction), charcoal (C; provides carbon and other fuel for the reaction) and sulfur (S; also serving as a fuel), respectively. The firework rocket (made in China) also contains potassium perchlorate, aluminium magnesium alloy, aluminium powder, carbon powder,

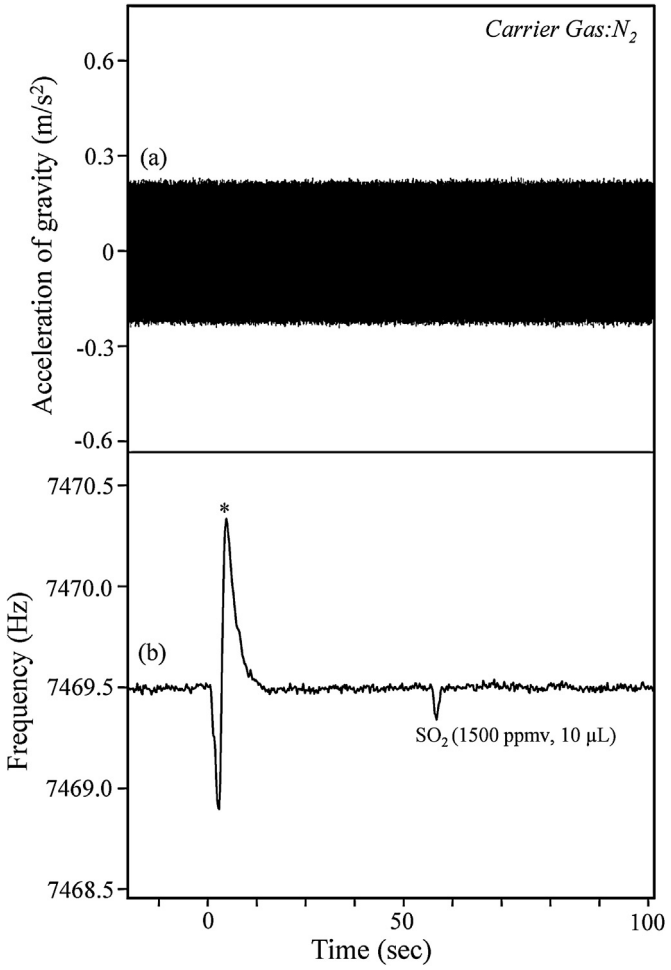

Fig. 2. Typical GC chromatogram for standard SO_2 gas (1500 ppmv) based on the milli-whistle/accelerometer GC system; the carrier gas and make-up gas used was nitrogen. Chromatogram (a) shows the spectrum of real-time vibrational frequency of whistle when a 10 μL sample of SO_2 gas was injected into the GC column *X*-axis and *Y*-axis show the retention time (min) of the GC chromatogram and the values for the acceleration of gravity (m/s^2), respectively. Chromatogram (b) shows the result after a Fast Fourier transformation.

strontium carbonate, copper oxide, barium nitrate and a phenolic-formaldehyde resin, etc. Before applying the GC/whistle system to the determination of explosive gases, it was necessary to collect information on the limit of detection for SO_2 gas. In order to construct a calibration curve, SO_2 standard gases were prepared using a Tedlar bag. Fig. 2 (a) shows the raw data for the real-time vibrational frequency of the whistle when a 10 μL sample of standard SO_2 gas (concentration level, 1500 ppmv; 1.5 mL SO_2 diluted in 1.0 L N_2) was injected into the GC capillary; both the carrier and make-up gas was nitrogen. The *X*-axis 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 Fig. 2(b). When the carrier/make-up gases continuously pass through the whistle, the fundamental frequency was determined to be ~7469.5 Hz. When the additional component, SO_2 in this case, passes through the whistle a sharp frequency change is produced. The molecular weight of SO_2 is larger than that of nitrogen, so that the frequency change is lower than the fundamental frequency. The "*" mark shows the system peak. This is because, when the gas sample was suddenly injected into the GC inlet, the background pressure (1.8 kg/cm^2) dramatically decreased and then increased, resulting in frequency changes (down and up, respectively). Based

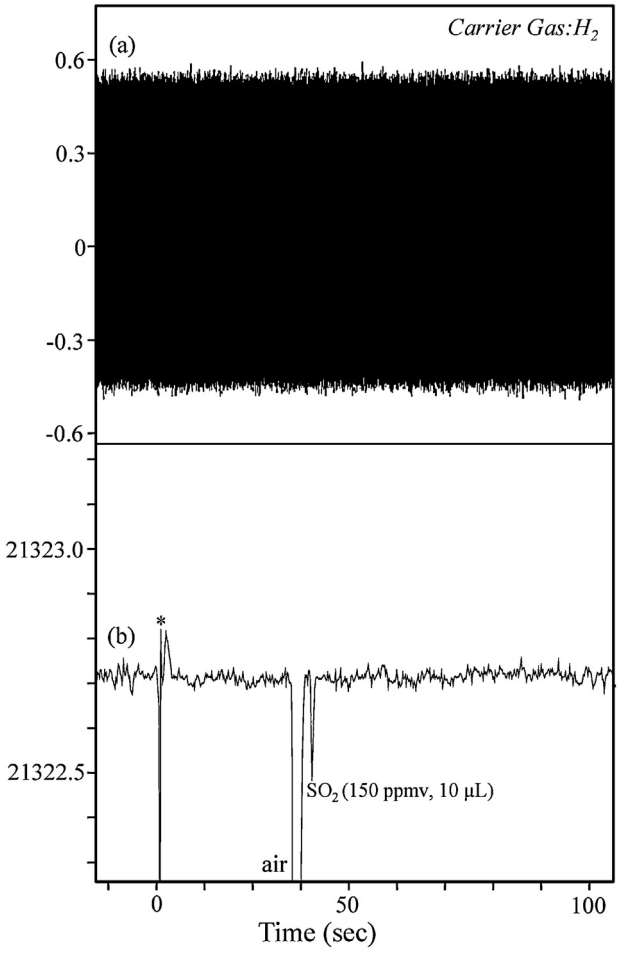

Fig. 3. Typical GC chromatogram for standard SO_2 gas (150 ppmv) based on the milli-whistle/accelerometer GC system; both the carrier gas and make-up gas was hydrogen. Chromatogram (a) shows the spectrum of real-time vibrational frequency of whistle when a 10 μL of SO_2 gas was injected into the GC column *X*-axis and *Y*-axis show the retention time (min) of GC chromatogram and the values for the acceleration of gravity (m/s^2), respectively. Chromatogram (b) shows the result after Fast Fourier transformation.

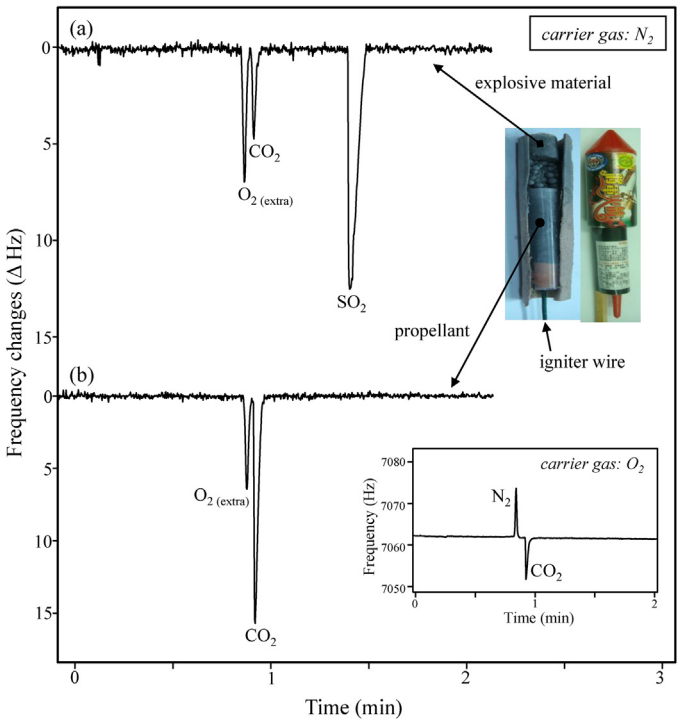

Fig. 4. Typical GC chromatograms of explosive material (a) and propellant (b). The inset photo shows the actual scale of one of the firework-rocket (top view of firework-rocket, right; a cross-section photo, left). The inset below chromatogram (b), typical GC chromatogram when the carrier/make-up gases changed to O_2, the peak for N_2 was clearly observed. 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 weight of the GC-eluant (in this case, CO_2) is higher, lower frequencies are produced.

on this method, the detection of limit for SO_2 was determined to be ~500 ppmv. Instead of nitrogen, when the carrier/make-up gas was changed to hydrogen, the intensity was dramatically improved. As shown in Fig. 3 (a, raw data; b, FFT spectrum), when a 10 μL sample of standard SO_2 gas (concentration level, 150 ppmv in hydrogen) was injected into the GC capillary, a response of 0.2 Hz is obtained and the fundamental frequency changes to ~21322.7 Hz. Based on the calibration, curve a concentration level of SO_2 as low as 50 ppmv can be detected. It should be noted that the background noise is less than 0.05 Hz, indicating that the milli-whistle/GC system also provides a high degree of stability. In order to compare the results obtained here with the GC–MS method, the milli-whistle was replaced with a mass spectrometer (HP 5972 MSD). As a result, the limit of detection for the GC/milli-whistle system is comparable to the results obtained by the GC–MS method. Furthermore, the milli-whistle system is much more economical and the instrument can also be configured so as to be very compact. As real samples, we used pyrotechnic firework-rockets composed of a paper tube packed with gunpowder that propels itself into the air in order to fly. The firework-rockets are basically separated into two parts: explosive materials (top) and propellants (bottom), in which an ignition wire is inserted. As shown in the inset picture in Fig. 4 (top view of a firework-rocket at right; a cross-section photo, at left), 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 propellants can be ignited easily by a laser beam. After focusing a laser on a 25 mg sample of propellant using a quartz lens, the resulting combustion gases were collected. Chromatogram (b) in Fig 4 shows the spectrum for the real-time vibrational frequency of the whistle vs. retention time when a 10 μL volume of the combustion gases were examined using nitrogen 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

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

Basically, N_2 and O_2 are difficult to separate, unless a molecular sieve column is used. In this study, a HP-MOLESIEVE column (30 m × 0.53 mm × 50 μm) was used and the findings show that N_2 was indeed present in the sample (data not shown). In this case, the carrier/make-up gas used was N_2 and this 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 the inset below chromatogram (b). 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 show that these gases (N_2

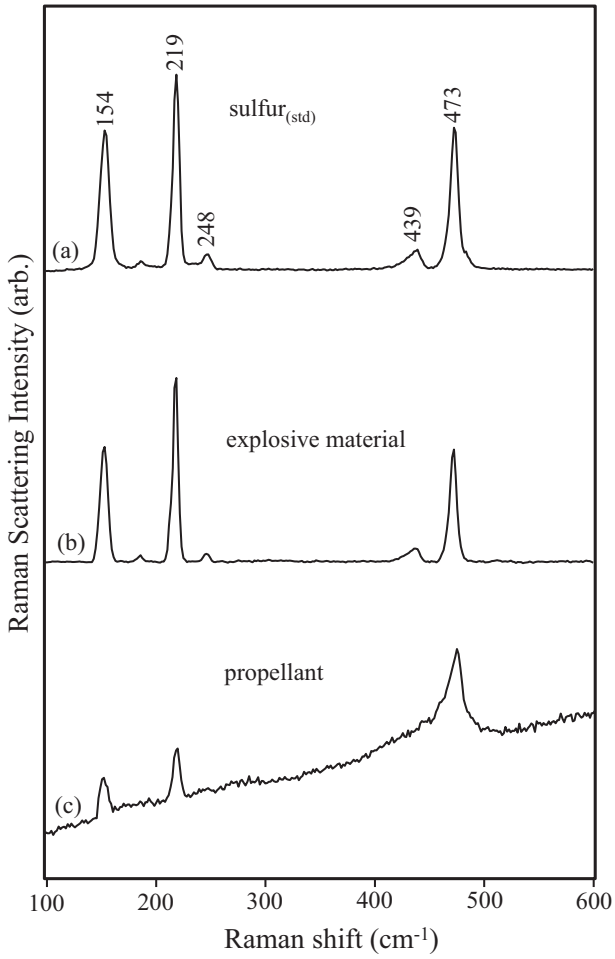

Fig. 5. Raman spectra of sulfur standard (a), explosive material (b) and propellant (c), respectively.

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 gas in this propellant experiment, it is well known that sulfur is a component of black powder. We used a Raman spectrometer to examine the powder and this is described below. In contrast to the propellant, it was very difficult to ignite the explosive material 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) and the results are shown in chromatogram (a) in Fig. 4. The carrier/make-up gas used was nitrogen in this case. 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. It is clear that, when the GC/milli-whistle system is used, these inorganic gases can be detected very easily. Neither CO nor NO*x* were detected in this study. This is could be because either the burning-temperature was too low to generate them or the column used was not suitable for their separation. Finally, in order to confirm that both the propellant and explosive material contain sulfur, we examined them by Raman spectrometry, and the findings are shown in Fig. 5. Spectra (a)–(c) shows the Raman shifts for a standard sample of sulfur, the explosive material and the propellant, respectively. Herein, a green laser (532 nm; 50 mW/exposure time, 20 s; objective lens, 20×) was used to ignite the samples. It is clear that both the propellant and the explosive components contained sulfur. However, these materials are not homogeneous, making it difficult to carry out a quantitative analysis.

4. Conclusion

Novel detection techniques and detection devices are needed for use in the analysis of inorganic gases. In this study, we were successfully demonstrated the rapid detection of inorganic gases released from both the propellant and explosive material inside traditional Chinese firework-rockets. In the former, CO_2 and N_2 were the major gases and sulfur appears to form K_2S, which cannot be detected as SO_2 gas. In the explosive material, SO_2 was found to be the major gas. CO and NO*x* were not detected in this study. Based on this method, the LODs for SO_2 were determined to be ~500 and 50 ppmv when nitrogen and hydrogen used as the carrier gases, respectively. Some additional efforts remain in terms of improving the limit of detection, including the use of a micro-channel associated with the micro-whistle in the future. The method described herein is simple, is consistent with sustainable science and has the potential for use in practical analyses.

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