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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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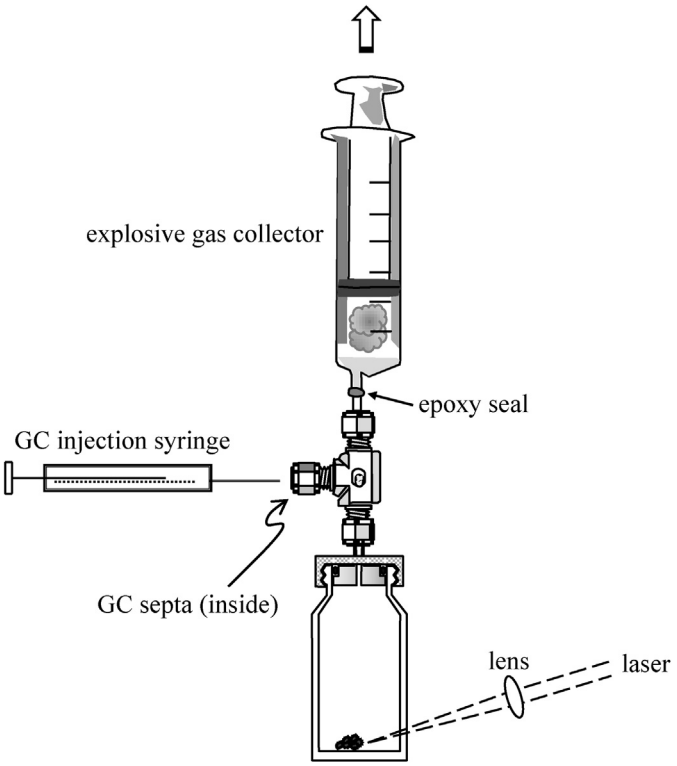

Fig. 1. Schematic diagram of the system used to collect the explosive gas.

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,

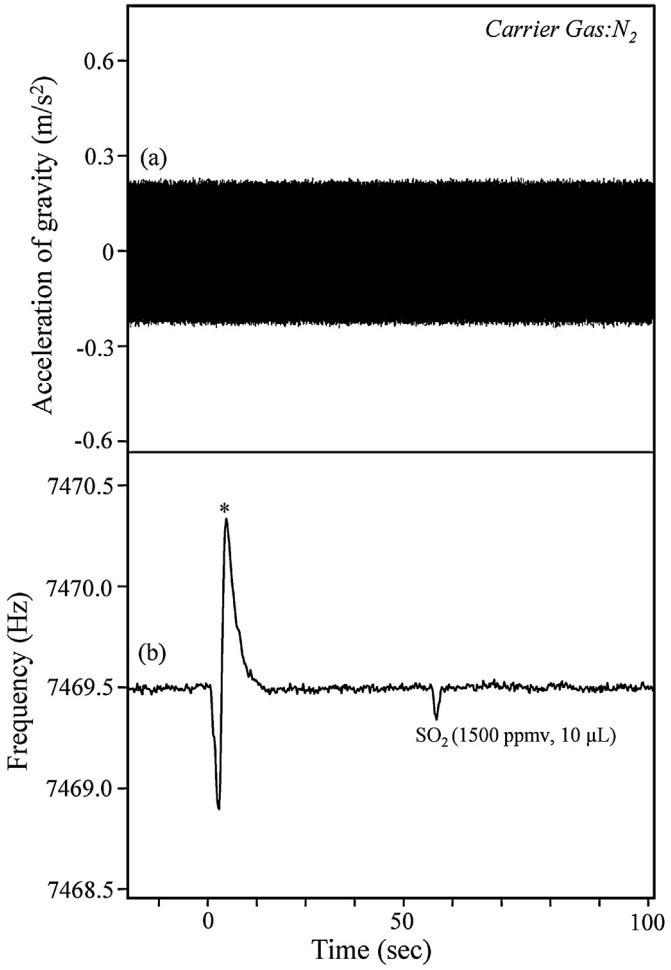

Fig. 2. Typical GC chromatogram for standard SO_2 gas (1500 ppmv) based on the milli-whistle/accelerometer GC system; the carrier gas and make-up gas used was nitrogen. Chromatogram (a) shows the spectrum of real-time vibrational frequency of whistle when a 10 μL sample of SO_2 gas was injected into 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