Sensitive detection of black powder by stand-alone ion mobility spectrometer with chlorinated hydrocarbon modifiers in drift gas

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ABSTRACT

This paper introduces a simple method for selective and sensitive detection of black powder by adding chlorinated hydrocarbons in the drift gas instead of changing the structure of conventional ion mobility spectrometer (IMS). The function of chloride modifiers was to substitute $Cl^-(H_2O)_n$ for $O_2^-(H_2O)_n$ in the drift region so as to avoid the overlap between $O_2^-(H_2O)_n$ and sulfur ion peaks. Among CH_2Cl_2, $CHCl_3$ and CCl_4, CCl_4 was chosen as the modifier due to the best peak-to-peak resolution and stability towards the fluctuation of modifier concentration. With 1.4 ppm CCl_4 as the modifier, the minimum detectable quantity of 0.1 ng for sulfur was achieved. Moreover, this method showed the ability for detection of common explosives at sub-nanogram level, such as black powder (BP), ammonium nitrate fuel oil (ANFO), 2,4,6-trinitrotoluene (TNT), and pentaerythritol tetranitrate (PETN). In summary, this method requiring no configuration modification has high sensitivity and selectivity, and consumes trace amount of modifier. And these characteristics make it easy to be adopted in current deployed IMS to detect black powder explosives.

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1. Introduction

Black powder (BP) is a mixture of sulfur, charcoal, and potassium nitrate [1–3] and has been extensively used in the fireworks and pyrotechnic industries [4]. Today, black powder is hardly ever used as a firearm propellant; however, it may still be encountered, usually linked to persons involved in military re-enactments [5]. The unrestricted availability, low-cost, flammability and improvised explosive properties of BP are the common reasons for its frequent appearance in many bombing incidents, such as the Boston marathon terrorist attacks [6]. In total, black powder was responsible for 33.2% of injuries and 27.1% of deaths in bombings together with smokeless powder in the United State [7]. Therefore, it is significant to develop new method and instrument to sensitively detect trace amounts of black powder.

Ion mobility spectrometer (IMS) has been a popular apparatus in detection of trace levels of nitro-organic explosives due to the low detection limits, fast response and portability capabilities [8–10]. To our knowledge, the difficulty in the detection of BP with

commercial air-based negative IMS is due to the overlap of sulfur ion peak with reactant ion peak O_2^-, as the reduced mobility of negative product ions S_3^- of BP, $K_0 = 2.25 \pm 0.01$ cm^2 V^{-1} s^{-1} [11], is close to that of the negative reactant ion $O_2^-(H_2O)_n$ in ^{63}Ni-IMS, $K_0 = 2.30 \pm 0.01$ cm^2 V^{-1} s^{-1} [12]. To satisfy the requirement of the baseline separation for the ionic sulfur allotropes from oxygen-based reactant ions, the resolving power should be greater than 85, which was too high to be reached by commercial IMS apparatus with the resolving power of 20–60 [13].

Recently, we developed a stand-alone ion mobility spectrometer with an embedded titration region (TR-IMS) to detect trace black powder [11]. Based on the special design, the ionization reaction and the titration reaction took place in different regions. In the ionization region, the black powder was ionized by oxygen anions; in the titration region, the surplus oxygen anions were substituted with the chloride ions, which were provided by the dichloromethane. It is found that the chlorine ions and the black powder ions could coexist in the titration region, so the overlapping was avoided due to the differences in drift time for the chloride anions and the sulfur ions.

Meanwhile, the task to realize sensitive detection of BP in the conventional IMS without retrofitting the device is also worth to make great efforts. Neutral organic vapors could be added to the drift gases in the mobility system to improve the selectivity, and in

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such applications the term "modifier" is used [14]. The aim of this work is to introduce modifiers into the drift gas with the conventional IMS to selectively detect trace sulfur in BP. Modifier was supposed to substitute the chlorine ions for the remaining oxygen anions in the drift region rather than in the titration region in TR-IMS [11]. Three chlorinated hydrocarbons CH_2Cl_2, $CHCl_3$, and CCl_4 as the modifiers and their corresponding concentrations were investigated. Finally, this method was used to detect of trace amounts of BP explosives and other military explosives.

2. Experimental

2.1. Instrumentation

The ion mobility spectrometer constructed in our laboratory has been reported previously [15], as shown in Fig. 1. It includes 0.5-GBq radioactive ^{63}Ni foil ion source, a Bradbury–Nielsen (BN) gate, a drift region, a Faraday plate and an amplifier. The IMS was operated in the negative ion mode and the operating parameters are listed in Table 1. The ion was collected according to their drift velocities by a Faraday plate and amplified by a preamplifier (10^9 V/A), and the signal was sent to a computer via an A/D converter for averaging and storage.

Laboratory air, which was purified by silica gel, activated carbon and $13 \times$ molecular sieves, was used as the instrument gas. One stream was sent into the thermal desorption (TD) as the IMS carrier gas, while the other stream was purged into the modifier unit as the IMS drift gas. Various concentrations of chlorinated hydrocarbons were obtained from an in-house vapor generation and dilution system, which were provided according to our previous work [16]. The chlorinated hydrocarbon was located in the carrier gas flow or in the drift gas flow as a dopant or a modifier.

2.2. Sample preparation and methods

All the solvents and reagents used in experiments were of analytical grade unless otherwise specified. Dichloromethane (CH_2Cl_2), trichloromethane ($CHCl_3$), tetrachloromethane (CCl_4) and sulfur (S) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Standard stock solution of S (50 ng/μL) was prepared by dissolving solid sulfur standards in acetone. The standard solutions were stored in amber glass vials equipped with Teflon caps and stored at room temperature (23 ± 2 °C) until used. Black powders (BP), firecracker, tri-nitro-toluene (TNT), ammonium nitrate fuel oil (ANFO), and pentaerythritol tetranitrate (PETN) were all commercial grade and used as received unless otherwise specified. Explosives with different concentrations in acetone were prepared by successive dilution of their stock solutions (50 ng/μL). As shown in Fig. 1, A few microlitres sample solution was first placed onto a Teflon-coated fiber glass swab, after the solvent was vaporized, the swab was inserted into the TD.

3. Results and discussions

3.1. Optimizing the Doping mode

As shown in Fig. 2a, in the conventional air-based IMS, drift times for the reactant ion peak (RIP) and product ion peak (PIP) were 6.96 ms and 7.16 ms, respectively, and the peak time difference was only 0.20 ms. Thus, it is very difficult to identify a weak product signal from the tail of the strong reactant ion peak, especially for detection of trace BP samples. As 40 ppm CH_2Cl_2 was added into the carrier gas, the signal intensity dramatically declined, and only less than 10 mV ion signal was observed for sulfur, while a predominant chlorine reactant ion peak appeared at 5.80 ms, as shown in Fig. 2b; in this case, although the drift time difference between RIP and PIP was 1.36 ms, large enough for the base line separation, the produced chlorine ions would inhibit the ionization of black powder due to higher electron affinity of chlorine than that of sulfur, resulting in an unsatisfied sensitivity. When CH_2Cl_2 was added into the drift gas as shown in Fig. 2c, the drift time of RIP and PIP appeared at 6.20 ms and 7.16 ms, respectively. The PIP signal intensity was higher than 100 mV, about ten-folds stronger than that of PIP in Fig. 2b. This may be attributed to the ionization of sulfur and the depletion of hydrated oxygen ions taking place in different regions of spectrometer. The drift time difference between RIP and PIP was about 0.94 ms, which was four-folds larger than that in Fig. 2a. It should be noted that although the detection sensitivity for sulfur was depended on the doping modes, the peak position of sulfur ion remained at constant drift time of 7.16 ms.

IMS apparatus run in purified air without a dopant gave the best sensitivity but the worst peak separation; doping CH_2Cl_2 in

Table 1
The IMS parameters used in this work.

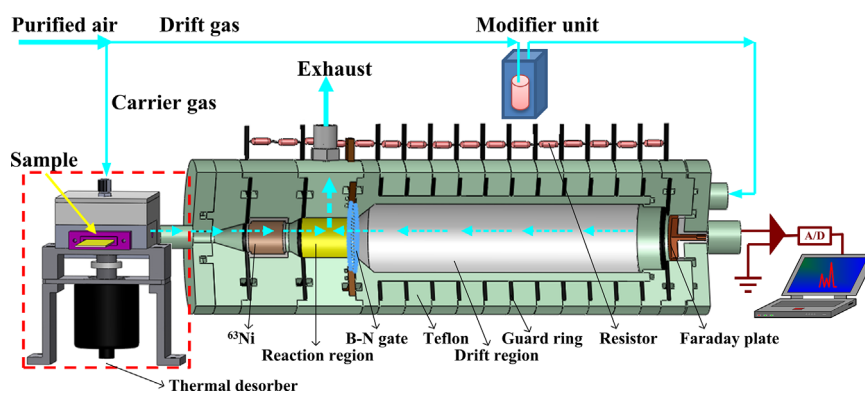| Parameters	Setting
Ionization source	^{63}Ni in negative mode
Desorption temperature	180 °C
Drift tube temperature	90 °C
Drift tube length	62 mm
BN gate opening time	200 μs
Carrier gas	Purified Air
Drift gas	Purified Air
Carrier gas flow rate	400 mL min^{-1}
Drift gas flow rate	400 mL min^{-1}

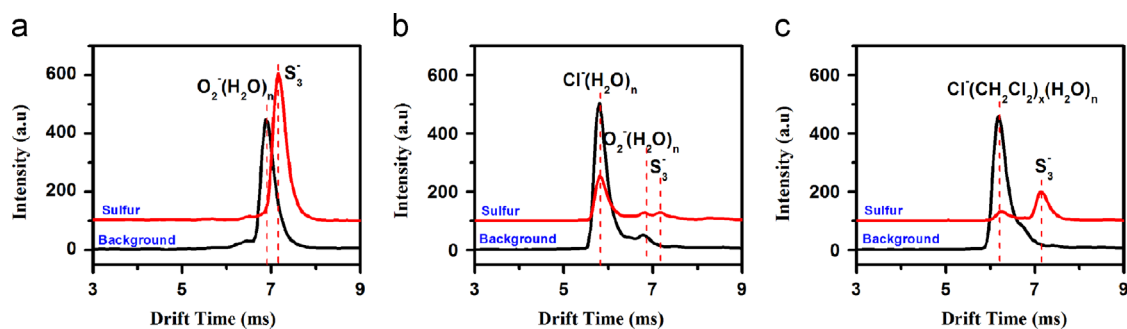**Fig. 1.** Schematic experimental setup for ion mobility spectrometer.

Fig. 2. Ion mobility spectra for detection of 10 ng S (a) without dopant, (b) with 40 ppm CH_2Cl_2 added into the carrier gas and (c) with 40 ppm CH_2Cl_2 added into the drift gas.
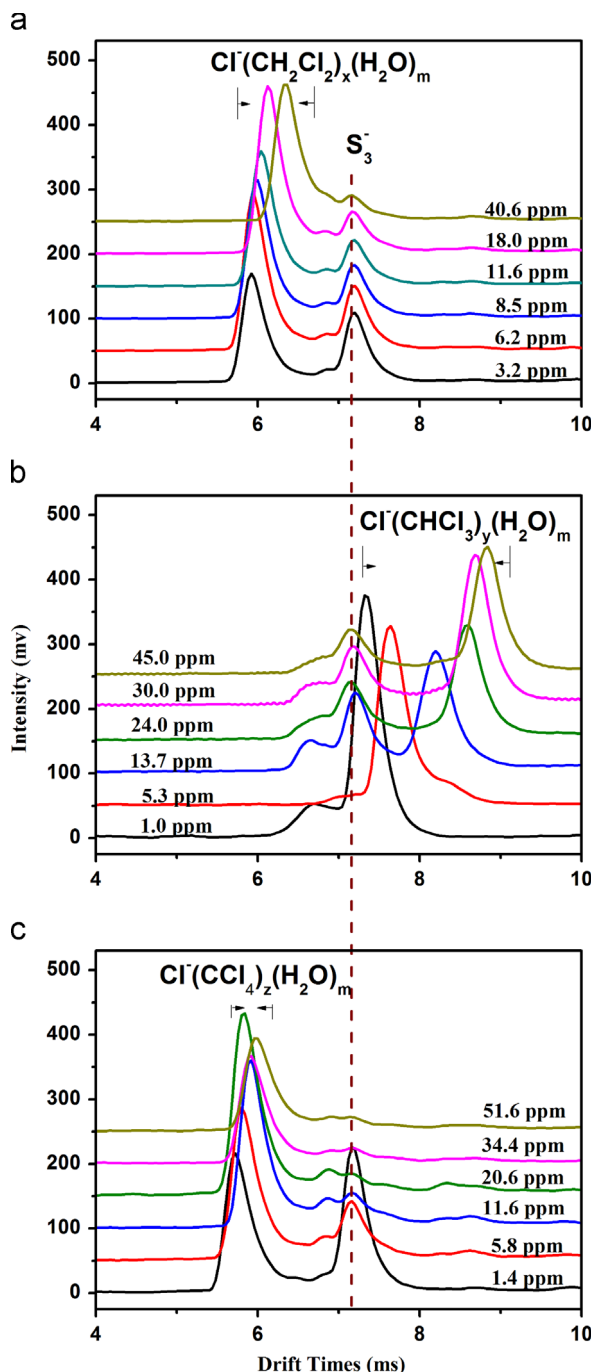

Fig. 3. Ion mobility spectra of 5 ng sulfur with various concentrations of (a) CH_2Cl_2, (b) $CHCl_3$, and (c) CCl_4 doped in drift gas, respectively.
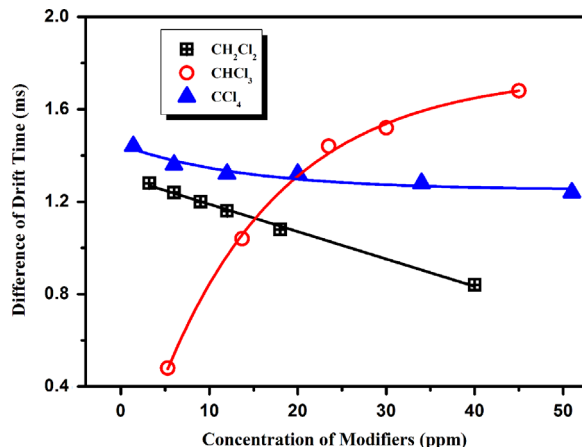

Fig. 4. Drift time difference between Cl^- ions and S_3^- ions versus the concentrations of modifiers (CH_2Cl_2, $CHCl_3$, and CCl_4) doped in the drift gas.

the carrier gas gave the best separation between RIP and PIP but the worst sensitivity; while the drift gas doped CH_2Cl_2 mode showed good peak separation and sensitivity. Thus, the mode of doping modifier in the drift gas was chosen for selective detection of trace black powder. In this mode, the dopant worked as a modifier to adjust the drift time of reactant ion in the drift region to avoid overlap with the product ions of sulfur. This differs from the reported modifiers used to vary the arrival times of analyte ions [17].
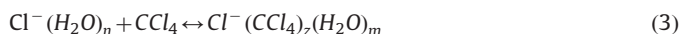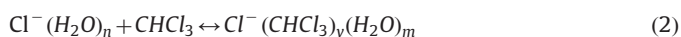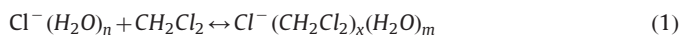
3.2. Selection of chlorinated hydrocarbons

In order to achieve efficient separation between Cl^- reactant ion and sulfur product S_3^-, three chlorinated hydrocarbons including CH_2Cl_2, $CHCl_3$, and CCl_4 were tested to be doped in the drift gas for the measurement of 5 ng sulfur, and the results are shown in Fig. 3. The peak position of S_3^- showed up at 7.16 ± 0.02 ms, and maintained this value over all the concentration varying from 1.0 to 51.6 ppm. Whereas, the behavior of the chloride ion peak in Fig. 3 was quite different from that of sulfur ion peak, suggesting that its drift time varied with the species of modifiers and their concentrations. For example, the RIP was shifted from 7.32 to 8.80 ms when increasing $CHCl_3$ concentration from 1.0 to 45 ppm, while RIP position was only shifted by 0.24 ms when CCl_4 concentration was increased from 1.4 to 51.6 ppm.

Fig. 4 shows the drift time difference between RIP and product PIP versus the concentrations of modifiers (CH_2Cl_2, $CHCl_3$, and CCl_4) doped in the drift gas, which was extracted from Fig. 3. The drift time gap was maintained around 1.35 ms when the concentration of CCl_4 was lower than 51.6 ppm, while the gap was linearly decreased from 1.24 ms to 0.84 ms with the concentration

of CH_2Cl_2 increasing from 3.2 to 40.6 ppm. With the increasing concentration of $CHCl_3$, the drift time gap was dramatically varied, and the drift time of RIP even moved toward right of S_3^- ion peak, which would overlap with the other explosive product ions, such as TNT, PETN, etc.

The concentration effect of modifiers on the signal intensity of sulfur was also observed in Fig. 3. The signal intensity of sulfur ions declined from 226 to 36 mV when the concentration of CCl_4 was increased from 1.4 to 52 ppm, and similar sensitivity trends were observed for CH_2Cl_2 and $CHCl_3$. This may be attributed to the diffusion of modifier into the reaction region at higher concentrations, which would inhibit the ionization of sulfur. Obviously, with 1.4 ppm CCl_4 as the modifier, the highest signal intensity for sulfur was observed. It worth to point out that when the concentration of CH_2Cl_2 was below 3.0 ppm, O_2^- ions could not be completely replaced by Cl^- ions, which may hamper the identification of a weak S_3^- signal.

$$Cl^-(H_2O)_n + CH_2Cl_2 \leftrightarrow Cl^-(CH_2Cl_2)_x(H_2O)_m \qquad (1)$$

$$Cl^-(H_2O)_n + CHCl_3 \leftrightarrow Cl^-(CHCl_3)_y(H_2O)_m \qquad (2)$$

$$Cl^-(H_2O)_n + CCl_4 \leftrightarrow Cl^-(CCl_4)_z(H_2O)_m \qquad (3)$$

The shifted RIP (chloride ions) with modifier added in the drift tube could be attributed to attachment/detachment of chlorinated hydrocarbon modifiers to the Cl^- ions and formation of short-lived ion-neutral intermediates [18]. These reactions (Eqs. (1)–(3)) were expected to occur throughout the length of the drift region. And the degree of shifting is thought to depend on the collisional stability and the attachment rate of ion-neutral intermediates as well as the modifier concentration [19]. Among the three modifiers CH_2Cl_2, $CHCl_3$, and CCl_4, the Gibbs free energy $\Delta_r G$ of -8.7 kcal/mole [20] for formation of $Cl^-(CHCl_3)$ was the largest, indicating the corresponding intermediates for $CHCl_3$ was the highest stable, which leaded to obvious shifting towards longer drift time with the rising of concentration of $CHCl_3$, as shown in Fig. 3b. It is clear that CCl_4, with the least $\Delta_r G$ of -2.4 kcal/mole [20] for formation of $Cl^-(CCl_4)$, had the smallest effect on the shift of the reactant ion peak, as seen in Fig. 3c. Similar conclusion was reported by Daum et al. [21]. And CCl_4 was chosen as the optimized modifier considering the good peak-to-peak resolution of chloride ions and sulfur ions, the high sensitivity as well as its high stability to the fluctuations of modifier concentration.

3.3. Quantitative response curve for sulfur detection

With 1.40 ppm CCl_4 as the modifier, we investigated the ion mobility spectra of 0–5.0 ng sulfur, as shown in Fig. 5a. In Fig. 5b,
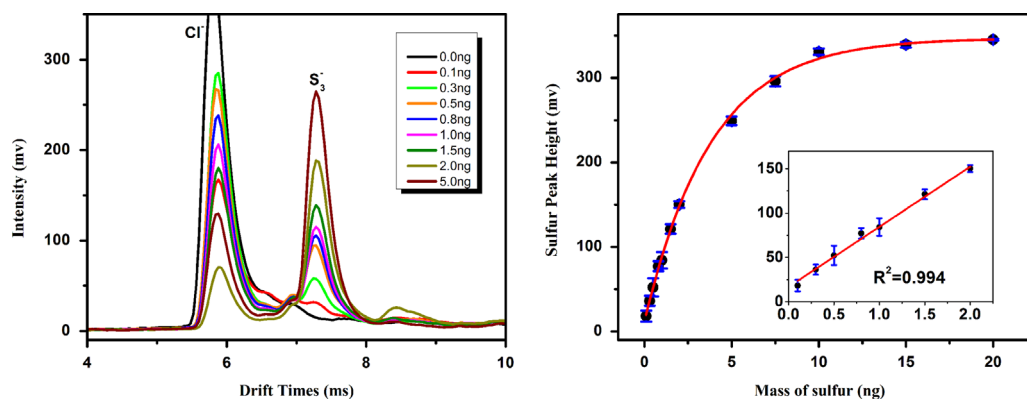
the evolution of peak heights of S_3^- as a function of sulfur amounts was displayed. It is clear that the PIP intensity is increased with the increasing amount of sulfur from 0.1 to 10 ng, and the PIP intensity is saturated at amount of sulfur higher than 10 ng, which might due to complete consumption of limited $O_2^-(H_2O)_n$ reactant ions. As can be seen, the signal intensity for 0.1 ng sulfur was reached about 18 mV, while the maximal fluctuation of signal intensity around S_3^- ion peak was less than 3 mV, so the signal-to-noise ratio (SNR) for 0.1 ng sulfur was about 6. The linear calibration curve was obtained in the range of 0.1–2 ng with a correlation coefficient R^2 of 0.994, as shown in the inset of Fig. 5b. So, we regard 0.1 ng as the minimum detected quantity (MDQ) for sulfur. It is indicated that this method exhibited a good performance on the detection of sulfur at sub-nanogram level.

3.4. Performances on detection of explosives

We also measured the ion mobility spectra of trace BP, firecracker, ANFO, TNT, and PETN with adding 1.4 ppm CCl_4 into the drift gas. In Fig. 6a and b, only one dominant product ion peak at the drift time of 7.16 ms can be observed for black powder and firecracker, which is corresponding to the sulfur ions with reduced mobility constants of 2.25 $cm^2 V^{-1} s^{-1}$. It is worth to point out that the other components (for an example, KNO_3) in black powder were not detected. This might be attributed to the higher vaporization temperature needed for nitrates [22]. There are two product ion peaks appearing for 5 ng ANFO, as shown in Fig. 6c, their reduced mobility constants are 2.36 and 2.04 $cm^2 V^{-1} s^{-1}$, and are assigned to NO_3^- and $NO_3^-(HNO_3)$ ions, respectively. As shown in Fig. 6e, three product ion peaks are observed for PETN, with reduced mobility constants of 2.36, 1.22 and 1.18 $cm^2 V^{-1} s^{-1}$, respectively. These assignments were based on comparison with the literatures [23–25]. The SNR for 10 ng BP, 10 ng Firecracker, 5 ng ANFO, 0.5 ng TNT, and 0.5 ng PETN were about 23, 32, 32, 31, and 21, respectively.

4. Conclusion

A simple method was developed for the sensitive detection of black powder by the conventional ion mobility spectrometer with adding chlorinated hydrocarbons in the drift gas. Among the three reagents CH_2Cl_2, $CHCl_3$, and CCl_4, CCl_4 was chosen as the best modifier in the drift gas considering that it had the smallest effect on the shift of the chloride ion peak to the concentration fluctuations as well as the highest peak-to-peak resolution for the chloride and sulfur peaks. With 1.4 ppm CCl_4 as the modifier, the
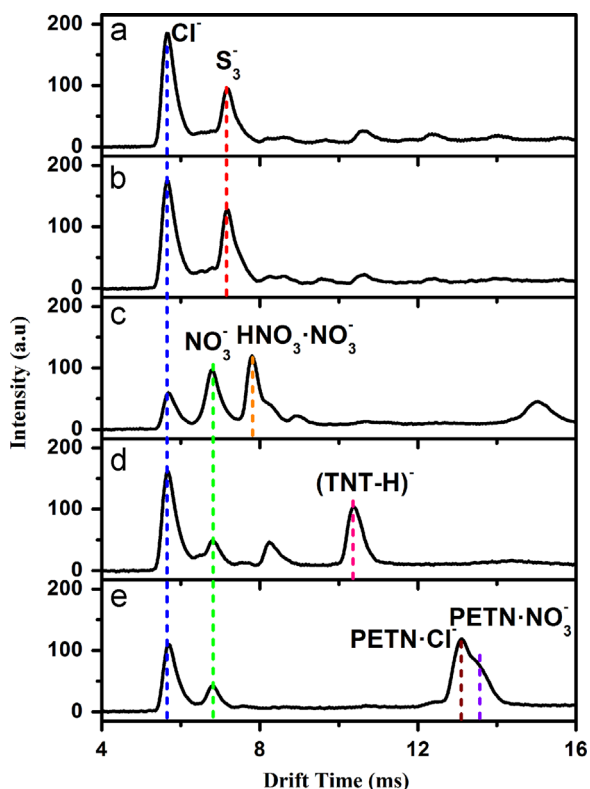

Fig. 5. (a) Ion mobility spectra of 0–5.0 ng sulfur with 1.4 ppm CCl_4 added into the drift gas. (b) Response curve and linear calibration curve (insert plot) for sulfur.

Fig. 6. Ion mobility spectra for trace explosives via doping 1.4 ppm of CCl$_4$ into drift gas: (a) 10 ng black powder; (b) 10 ng firecracker; (c) 5 ng of ANFO; (d) 0.5 ng of TNT; and (e) 0.5 ng of PETN.

minimum detectable amount of 0.1 ng for sulfur with SNR of 6 was achieved. Moreover, it also showed the ability for sensitive detection of explosives such as BP, ANFO and other common military explosives. Although the sensitivity for BP in this work is not as good as that in TR-IMS [11], the current method does not need any modification of the configuration of the drift tube, which makes it easier to be adopted in the commercial ion mobility spectrometer for explosives detection.

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