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



Xixi Liang<sup>a,b</sup>, Xin Wang<sup>a</sup>, Weiguo Wang<sup>a</sup>, Qinghua Zhou<sup>a,b</sup>, Chuang Chen<sup>a</sup>, Liying Peng<sup>a,b</sup>, Meng Wen<sup>a,b</sup>, Tuanshuai Qu<sup>a</sup>, Zhenxin Wang<sup>a</sup>, Kun Zhao<sup>a</sup>, Jinghua Li<sup>a</sup>, Haiyang Li<sup>a,\*</sup>

<sup>a</sup> Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China

<sup>b</sup> Graduate University of Chinese Academy of Sciences, Beijing 100039, People's Republic of China

### ARTICLE INFO

#### Article history:

Received 23 October 2013

Received in revised form

31 December 2013

Accepted 3 January 2014

Available online 18 January 2014

#### Keywords:

Black powder

Ion mobility spectrometer

Chlorinated hydrocarbons

Modifier

### 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  $\text{Cl}^-(\text{H}_2\text{O})_n$  for  $\text{O}_2^-(\text{H}_2\text{O})_n$  in the drift region so as to avoid the overlap between  $\text{O}_2^-(\text{H}_2\text{O})_n$  and sulfur ion peaks. Among  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$ ,  $\text{CCl}_4$  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  $\text{CCl}_4$  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  $\text{O}_2^-$ , as the reduced mobility of negative product ions  $\text{S}_3^-$  of BP,  $K_0 = 2.25 \pm 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [11], is close to that of the negative reactant ion  $\text{O}_2^-(\text{H}_2\text{O})_n$  in  $^{63}\text{Ni}$ -IMS,  $K_0 = 2.30 \pm 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [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

\* Correspondence to: Group 102, 457 Zhongshan Road, Dalian, Liaoning 116023, China. Tel.: +86 411 84379509; fax: +86 411 84379517.

E-mail address: [hli@dicp.ac.cn](mailto:hli@dicp.ac.cn) (H. Li).

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  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  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  $^{63}\text{Ni}$  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 ( $\text{CH}_2\text{Cl}_2$ ), trichloromethane ( $\text{CHCl}_3$ ), tetrachloromethane ( $\text{CCl}_4$ ) and sulfur (S) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Standard stock solution of S ( $50 \text{ ng}/\mu\text{L}$ ) 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 ( $23 \pm 2$  °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 ( $50 \text{ ng}/\mu\text{L}$ ). 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

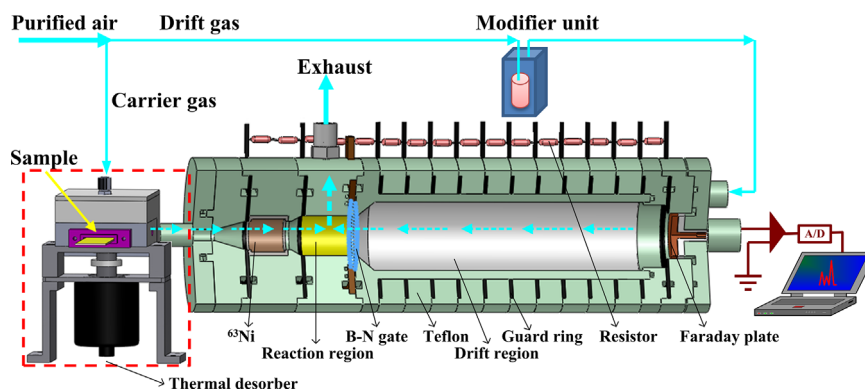
### 3.1. Optimizing the Doping mode

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  $\text{CH}_2\text{Cl}_2$  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  $\text{CH}_2\text{Cl}_2$  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  $\text{CH}_2\text{Cl}_2$  in

**Table 1**  
The IMS parameters used in this work.

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



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

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