# SCIENTIFIC REPORTS

### **OPEN**

SUBJECT AREAS: ANALYTICAL CHEMISTRY CHEMISTRY

> Received 25 June 2014

Accepted 29 September 2014

Published 16 October 2014

Correspondence and requests for materials should be addressed to H.L. (hli@dicp.ac.cn)

## On-site Rapid Detection of Trace Non-volatile Inorganic Explosives by Stand-alone Ion Mobility Spectrometry via Acid-enhanced Evaporization

Liying Peng<sup>1,2</sup>, Lei Hua<sup>1</sup>, Weiguo Wang<sup>1</sup>, Qinghua Zhou<sup>1,2</sup> & Haiyang Li<sup>1</sup>

<sup>1</sup>Key Laboratory of Separation Science for Analytical Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, People's Republic of China, <sup>2</sup>University of Chinese Academy of Sciences, Beijing, 100049, People's Republic of China.

New techniques for the field detection of inorganic improvised explosive devices (IEDs) are urgently developed. Although ion mobility spectrometry (IMS) has been proved to be the most effective method for screening organic explosives, it still faces a major challenge to detect inorganic explosives owing to their low volatilities. Herein, we proposed a strategy for detecting trace inorganic explosives by thermal desorption ion mobility spectrometry (TD-IMS) with sample-to-sample analysis time less than 5 s based on in-situ acidification on the sampling swabs. The responses for typical oxidizers in inorganic explosives, such as  $KNO_3$ ,  $KCIO_3$  and  $KCIO_4$  were at least enhanced by a factor of 3000 and their limits of detection were found to be subnanogram. The common organic explosives and their mixtures with inorganic oxidizers were detected, indicating that the acidification process did not affect the detection of organic explosives. Moreover, the typical inorganic explosives such as black powders, firecrackers and match head could be sensitively detected as well. These results demonstrated that this method could be easily employed in the current deployed IMS for on-site sensitive detection of either inorganic explosives or organic ones.

n recent years, rapid and sensitive detection of improvised explosive devices (IEDs) has become the most pressing issues with the increase of the globalization of terrorist acts during the last 2 decades, such as those in Oklahoma, U.S.A. (1995), Bali, Indonesia (2002, 2005), Pune, India (2010), Oslo, Norway (2011), Boston, U.S.A. (2013) and Abuja, Nigeria (2014)<sup>1-3</sup>. On-site screening is an effective way to reduce the risk of explosion, which demands the analytical methods with high requirements in terms of speed, sensitivity, and robustness<sup>4-10</sup>.

The instrumental methods such as X-rays, neutron analysis, nuclear quadrupole resonance, and colorimetric detection are always adopted for the bulk detection of organic and inorganic explosives, while the thermal desorption ion mobility spectrometry (TD-IMS) is proven to be a practical technique for trace detection (from ng to pg) of organic explosives such as 2,4,6-trinitrotoluene (TNT) and cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) *et al*<sup>11-15</sup>. IMS is a gas-phase ion separation and detection technique in a uniform electric field based on the mobility difference of gaseous ions<sup>16-19</sup>. More than 20,000 stand-alone IMS have been deployed at airports and subway stations worldwide for security applications, due to the advantages of fast speed, low cost, analytical flexibility, portability and commercial availability<sup>20-23</sup>. However, it still remains a great challenge for TD-IMS to detect trace inorganic explosives except for ammonium nitrate-fuel oil (ANFO) and sulphur (S) in black powder, owing to their ultra-low vapour pressure even at the typical maximum desorber temperature ( $\leq 280^{\circ}$ C)<sup>13,20,24,25</sup>.

Inorganic explosives generally consist of an inorganic oxidizer such as potassium nitrate (KNO<sub>3</sub>), potassium chlorate (KClO<sub>3</sub>), or potassium perchlorate (KClO<sub>4</sub>) and a fuel such as carbon source, sulphur (S), sugar or powdered metals<sup>26,27</sup>. Inorganic explosives are extensively used in terrorist attacks owing to the readily available, low cost and legally purchased components. Ion chromatography (IC)<sup>28,29</sup>, capillary electrophoresis (CE)<sup>30,31</sup>, electrospray ionization mass spectrometry (ESI-MS)<sup>32–34</sup> and electrospray ionization ion mobility spectrometry (ESI-IMS)<sup>35</sup> have been performed to identify their characteristic ions, such as nitrate (NO<sub>3</sub><sup>-</sup>), chlorate (ClO<sub>3</sub><sup>-</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>) and perchlorate (ClO<sub>4</sub><sup>-</sup>) etc. contained within inorganic explosives<sup>36,37</sup>. However, the field-deployment of these techniques is hampered by the tedious and time-consuming procedures for handling the



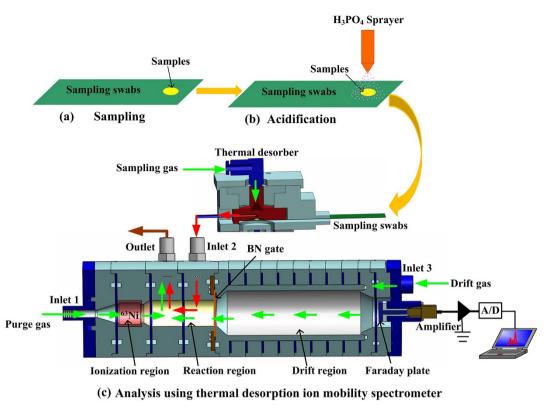


Figure 1 | Schematic of thermal desorption ion mobility spectrometer and the analysis process of inorganic explosives. (a) Sampling: sampling swabs were swiped with samples; (b) Acidification: samples on the swab were sprayed with minimal regime 3% H<sub>3</sub>PO<sub>4</sub>; (c) Analysis: the swab was inserted into the thermal desorber and analysed by IMS.

aqueous samples. Additionally, the relatively long analysis time (>5 minutes) of IC and CE, and the relatively large bulk, high expensive cost of mass spectrometer make them not suitable for on-site screening as well.

Obviously, an analytical method which could rapidly and sensitively detect both inorganic and organic explosives is highly demanded. Herein, we firstly reported a simple method to detect inorganic explosives involving KNO<sub>3</sub>, KClO<sub>3</sub> and KClO<sub>4</sub> using TD-IMS via acid-enhanced evaporization for on-site detection. Samples on the swab were acidized by spraying  $H_3PO_4$ , and enhancements of signal for KNO<sub>3</sub>, KClO<sub>3</sub> and KClO<sub>4</sub> by a factor of over 3000 were achieved, realizing the detection of inorganic explosives at ng even pg level. Moreover, the common nitro-explosives and its mixture with the inorganic oxidizers and the frequently-used inorganic explosives such as black powder, firecracker and match head were sensitively detected. The influence of acidification process on the detection of organic explosives was also investigated.

#### **Results and Discussion**

**Design of TD-IMS for analysis.** A swiped-based TD-IMS apparatus operated in negative mode is schematically shown in Fig. 1. The key structure of IMS is similar to those reported in detail previously<sup>25,38</sup> expect that an extra inlet named inlet 2 used for the sample inlet was punched in the reaction region at the vicinity of BN ion gate. Thus, only the purge gas flowed through the <sup>63</sup>Ni source, so the pollution and acid corrosion of <sup>63</sup>Ni source could be effectively avoided. In the test, samples were deposited on the swabs firstly (Fig. 1(a)) and then sprayed with minimal regime 3% H<sub>3</sub>PO<sub>4</sub> (Fig. 1(b)). Afterwards, the swab was inserted into the thermal desorber with temperature of 180°C for IMS analysis (Fig. 1 (c)).

**Enhancement of acidification on the sensitivity.** Ion mobility spectra for typical inorganic oxidizers of KNO<sub>3</sub>, KClO<sub>3</sub> and KClO<sub>4</sub>

obtained without and with 3% H<sub>3</sub>PO<sub>4</sub> acidfication were depicted in Fig. 2, respectively. Clearly, in lack of H<sub>3</sub>PO<sub>4</sub> acidfication on the swab, only two weak product ion peaks with  $K_0$  of 2.18 and  $2.05~\text{cm}^2 V^{-1} \text{s}^{-1}$  were observed for  $20~\mu g~\text{KNO}_3$  and the signal intensity of characteristic peak (2.05 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) was only about 83 mV. Whereas, its response for  $0.02 \ \mu g$  KNO<sub>3</sub> instantly increased to 280 mV in the existence of H<sub>3</sub>PO<sub>4</sub>. It was over 3 times higher than that of 20 µg KNO3 obtained without acidification and the sensitivity were at least enhanced by a factor of 3000. Similarly, no responses for KClO3 and KClO4 even with quantity of 50 µg and 600 µg, respectively were obtained in the absence of H<sub>3</sub>PO<sub>4</sub>, while two strong ion peaks of 0.05 µg KClO<sub>3</sub> were appeared at 2.16 and 1.88 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and peaks with  $K_0$  of 2.15 and 1.77  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  were observed for 0.60 µg KClO<sub>4</sub> in the assistance of H<sub>3</sub>PO<sub>4</sub>. And the signal intensities for ion peaks of KClO<sub>3</sub> (1.88 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>), KClO<sub>4</sub> (1.77 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) were 184 and 179 mV, respectively. Furthermore, we also adopted other weak acids such as acetic acid (CH<sub>3</sub>COOH) and boric acid (H<sub>3</sub>BO<sub>3</sub>) to perform the acidification process. The results demonstrated that H<sub>3</sub>PO<sub>4</sub> was the most suitable for the analysis due to the perfect sensitivity and its simple background (see Supplementary Fig. S1-2). It is noteworthy that the time taken for sample-to-sample analysis is less than 5 s, and the analysis speed is fast enough for rapid on-site screening.

Mechanism for the acid-enhancement. The product ions of inorganic oxidizers in <sup>63</sup>Ni source were assigned by an atmospheric pressure negative ionization time-of-flight mass spectrometer (TOF-MS) (see Supplementary Fig. S3). The typical mass spectra were demonstrated in Fig. 3; the reduced ion mobilities ( $K_0$ ), mass-to-charge ratios (m/z) and corresponding product ions were summarized in Table 1. Accordingly, two product ions of KNO<sub>3</sub> at m/z 62 and m/z 125 were assigned to NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub>·NO<sub>3</sub><sup>-</sup>, and

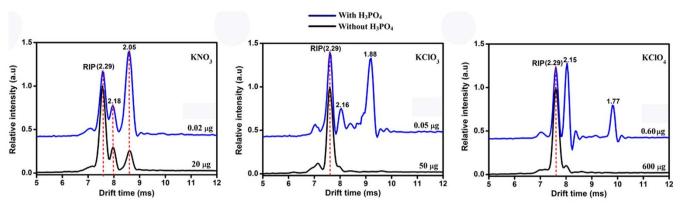


Figure 2 | Ion mobility spectra of 20  $\mu$ g KNO<sub>3</sub>, 50  $\mu$ g KClO<sub>3</sub>, and 600  $\mu$ g KClO<sub>4</sub> obtained without 3% H<sub>3</sub>PO<sub>4</sub> and ion mobility spectra of 0.02  $\mu$ g KNO<sub>3</sub>, 0.05  $\mu$ g KClO<sub>3</sub>, and 0.6  $\mu$ g KClO<sub>4</sub> obtained with 3% H<sub>3</sub>PO<sub>4</sub>.

two ions of  $\mathrm{KClO}_3$  at m/z 83, 85 and m/z 167, 169, 171 were attributed to  $ClO_3^-$  and  $HClO_3 \cdot ClO_3^-$ , while the ions assigned to  $ClO_4^-$  (m/z = 99, 101) and  $HClO_4 \cdot ClO_4^-$  (m/z = 199, 201, 203) were observed for KClO<sub>4</sub>. The product ions observed for KNO<sub>3</sub> were same as those in previous experiments of ammonium nitrate (AN, the main component of ANFO) where NO3- and complex  $HNO_3 \cdot NO_3^-$  were the dominant ions, likely formed by  $HNO_3$  (the decomposition product of AN)3. According to the observed product ions, gaseous inorganic acids, such as HNO<sub>3</sub>, HClO<sub>3</sub> and HClO<sub>4</sub> were believed to be released in the thermal desorber after acidification through the metathesis reaction beween the solid oxidizers and H<sub>3</sub>PO<sub>4</sub> at high temperature of 180°C, and then ionized by the reactant ions  $O_2^-$  in the ion source. Hence, inorganic oxidizers could be indirectly detected by identifying their gaseous inorganic acids in the existence of H<sub>3</sub>PO<sub>4</sub>. It was further verified by ion mobility spectra of trace HNO<sub>3</sub> and HClO<sub>4</sub> (see Supplementary Fig. S4) where the ion peak positions of HNO<sub>3</sub> and HCIO<sub>4</sub> were same as those of KNO<sub>3</sub> and KClO<sub>4</sub> with acidification in

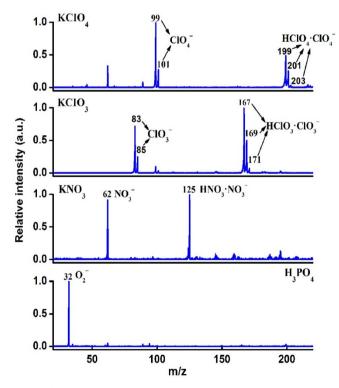


Figure 3 | TOF-mass spectra of 20 ng KNO<sub>3</sub>, 50 ng KClO<sub>3</sub> and 600 ng KClO<sub>4</sub> obtained with 3% H<sub>3</sub>PO<sub>4</sub>.

Fig. 2. The mechanism of acid-enhanced detection of inorganic salt oxidizers are summarized as equation (1) to (3) and X presents N or Cl atom.

$$3KXO_n + H_3PO_4 \rightarrow 3HXO_n \uparrow + K_3PO_4 \tag{1}$$

$$HXO_n + O_2^- \rightarrow XO_n^- + HO_2$$
 (2)

$$XO_n^- + HXO_n \rightarrow HXO_n \cdot XO_n^-$$
 (3)

**Quantitative analysis.** To further investigate the sensitivities of inorganic explosives, we used ion peaks at  $K_0$  of 2.05, 1.88 and 1.77 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for quantitative analysis of KNO<sub>3</sub>, KClO<sub>3</sub> and KClO<sub>4</sub>. The results were summarized in Table 1; their detectable linear range were 2–60 ng, 10–120 ng and 50–600 ng, respectively and the RSD (n = 9) were 17.10%, 16.27%, and 9.99%, respectively. The limits of detection (LOD, S/N = 3) for KNO<sub>3</sub>, KClO<sub>3</sub> and KClO<sub>4</sub> were 0.10 ng, 0.84 ng and 6.30 ng, respectively. These results exhibit the good quantitative capability of the current method for detection of inorganic explosive.

**Detection performances of actual samples.** The acidification process did not affect the detection of organic explosives and typical nitro-explosives such as TNT and RDX could be sensitively detected by current method, and their ion mobility spectra were displayed in Fig. S5 in the Supplementary Information. Clearly, product ion with  $K_0$  of  $1.54 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  was observed for TNT, and the product ion peaks at  $K_0$  of 1.65, 1.53 and  $1.44 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  were observed for RDX. Additionally, the mixtures of TNT and inorganic oxidizers could also be sensitively measured as well, and Fig. 4 shows the ion mobility spectra of 5 ng TNT mixed with 20 ng KNO<sub>3</sub> and 50 ng KClO<sub>3</sub>, respectively. From the spectra, the characteristic ion peaks of TNT, KNO<sub>3</sub> and KClO<sub>3</sub> are clearly observed simultaneously for the mixtures.

Moreover, the oxidizers in typical inorganic explosives were also detected. Figure 5 shows the ion mobility spectra of black powder, firecracker and match head obtained in the existence of  $H_3PO_4$ . From the spectra, the characteristic ion peaks of KNO<sub>3</sub>, KClO<sub>4</sub> and KClO<sub>3</sub> were distinctly observed for black powder, firecracker and match head, respectively. It indicates that inorganic oxidizers in black powder, firecracker and match head are KNO<sub>3</sub>, KClO<sub>4</sub> and KClO<sub>3</sub>, respectively and other substances in the explosives such as powdered metals and charcoals had little impact on the identification. In particular, only S was detected in the firecracker and black powder without  $H_3PO_4$  acidification (see Supplementary Fig. S6), so the detection of both S and inorganic oxidizers all could help identification the materials used in IEDs. Finally, as shown in Supplementary Fig. S7, KNO<sub>3</sub>, KClO<sub>3</sub>, KClO<sub>4</sub> in sugar (20 ng KNO<sub>3</sub>/sugar (4:1),

	KNO3		KClO <sub>3</sub>		KClO <sub>4</sub>	
	Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2
$K_0 (cm^2 V^{-1} s^{-1})$	2.18	2.05	2.16	1.88	2.15	1.77
n/z	62	125	83,85	167, 169, 171	99, 101	199, 201, 203
Product ions	$NO_3^-$	HNO3·NO3-	ClO <sub>3</sub> -	HClO <sub>3</sub> ·ClO <sub>3</sub> -	$ClO_4^-$	HClO <sub>4</sub> ·ClO <sub>4</sub> -
inear equation	_	y = 9.83x + 22.90	_	y = 5.01x + 2.18	_	y = 0.61x + 1.48
inear range (ng)	_	2–60	_	10–120	_	, 50–600
$OD^{[\alpha]}$ (ng, $S/N = 3$ )	_	0.10	_	0.84	_	6.30
RSD <sup>[b]</sup> (%, n = 9)	_	17.10	_	16.27	_	9.99
[ <sup>i</sup> ]LOD = limit of detection. [ <sup>i</sup> ]RSD = relative standard deviation		17.10	_	10.27	_	7.77

Table 1 | Reduced ion mobilities ( $K_0$ ), mass-to-charge ratios (m/z), product ions and quantitative analysis results obtained with 3% H<sub>3</sub>PO<sub>4</sub>

50 ng KClO<sub>3</sub>/sugar (4:1) and 600 ng KClO<sub>4</sub>/sugar (3:2)) could also be sensitively measured, which means that the common fuel in inorganic explosives did not affect the detection.

#### Conclusions

We demonstrated a new rapid and sensitive method based on IMS via acid-enhanced detection of oxidizers including  $KNO_3$ ,  $KClO_3$  and  $KClO_4$  to detect inorganic explosives. It owns the advantages of fast speed (about 5 s), low cost, analytical flexibility, portability, commercial availability, and suitable for detecting inorganic explosives and organic ones at the level of ng even pg. Moreover, it is envisioned to be easily deployed to the rapid and sensitive on-site screening of both inorganic explosives and organic ones at airports, subway stations, sports venues and even blast site, being an effective way to screen the substances in the detonation scene and reduce the risk of explosion.

#### Methods

**Experiment.** A 500 ng  $\mu$ L<sup>-1</sup> KNO<sub>3</sub>, KClO<sub>3</sub> and 600 ng  $\mu$ L<sup>-1</sup> KClO<sub>4</sub> standard stock solutions and 3% H<sub>3</sub>PO<sub>4</sub> solution were prepared by weighing sample and dissolving in distilled water. The standard solutions and test samples were obtained by gradually diluting the relevant stock solutions with distilled water or other volatile solvents. 20 ng KNO<sub>3</sub>/sugar (4:1), 50 ng KClO<sub>3</sub>/sugar (4:1), 600 ng KClO<sub>4</sub>/sugar (3:2) were made up by mixing KNO<sub>3</sub>, KClO<sub>4</sub> and sugar in corresponding proportion while match head, firecrackers, black powders, 2,4,6-trinitrotoluene (TNT) and cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) were commercial grade.

A known quantity sample solutions were added on or solid samples were rubbed on the swabs firstly and the solvent was evaporated to dryness on a hot plate of  $50^{\circ}$ C, and

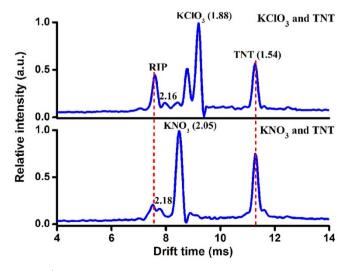


Figure 4 | Ion mobility spectra of the mixture of 5 ng TNT and 20 ng KNO<sub>3</sub> and mixture of 5 ng TNT and 50 ng KClO<sub>3</sub> obtained with 3% H<sub>3</sub>PO<sub>4</sub>.

then the swabs with samples were sprayed minimal regime 3% H<sub>3</sub>PO<sub>4</sub> (several microlitres). After that the swab was inserted into the thermal desorber for analysis by IMS operated in negative mode. It is noted that enough acid content is essential for the sensitivity.

**Operating process and conditions.** The sample on the swab ( $2 \text{ cm} \times 8 \text{ cm}$ ) made of Teflon was heated to  $180^{\circ}$ C in the thermal desorber and vaporized into a gas flow that passed into the drift tube for analysis. In the <sup>63</sup>Ni ionization source, the sample molecules were ionized, and then the product ions were injected into the drift region, ions were separated according to their mobility with an electric field of 391 V/cm and then detected by the Faraday plate and the ion current was amplified with a gain of  $10^{\circ}$  V/A. The drift tube temperature was kept at a constant of  $90^{\circ}$ C. Air dried by silica gel, activated carbon and  $13 \times$  molecular sieve traps was divided into drift, carrier and purge gases via flow controllers which were optimized at 800, 400 and 400 mL/min, respectively. The operating parameters were summarized in Table 2.

**Calculation**. The reduced ion mobility,  $K_0$  for unknown peaks were calculated with a standard via the following equation,

$$K_{0a} = K_{0s} \times \frac{t_{d_s}}{t_{da}} \tag{4}$$

where  $K_{0a}$  is the reduced mobility of the analyte,  $t_{ds}$  and  $t_{da}$  is the drift time of the standard and the analyte, respectively. (TNT-H)<sup>-</sup> was used as the standard substance,

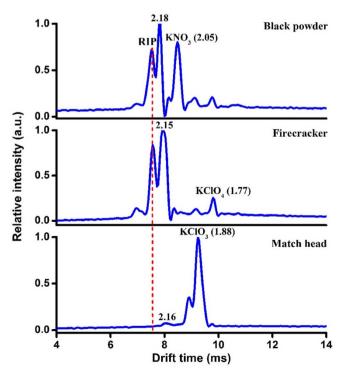
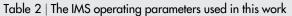


Figure 5 | Ion mobility spectra of 200 ng match head, 600 ng firecracker and 20 ng black powder obtained with 3% H<sub>3</sub>PO<sub>4</sub>.



Operating conditions	Setting	
Desorber temperature	180°C	
Drift tube temperature	90°C	
Electric field	391 V cm <sup>-1</sup>	
BN gate opening time	300 μs	
Carrier gas	Purified Air	
Drift gas	Purified Air	
Carrier gas flow rate	400 mL min <sup>-1</sup>	
Drift gas flow rate	800 mL min <sup>-1</sup>	
Purge gas flow rate	400 mL min <sup>-1</sup>	

whose  $K_0$  was 1.54 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and its drift time was 11.28 ms under the same experimental conditions.

- Stierstorfer, J. & Klapötke, T. M. High energy materials. propellants, explosives and pyrotechnics. Angew Chem Int Ed 49, 6253–6253 (2010).
- Blanco, G. A. *et al.* Identification of inorganic improvised explosive devices using sequential injection capillary electrophoresis and contactless conductivity detection. *Anal Chem* 83, 9068–9075 (2011).
- Cheng, S. *et al.* Fast switching of CO<sub>3</sub><sup>-</sup>(H<sub>2</sub>O)<sub>n</sub> and O<sub>2</sub><sup>-</sup>(H<sub>2</sub>O)<sub>n</sub> reactant ions in dopant-assisted negative photoionization ion mobility spectrometry for explosives detection. *Anal Chem* 86, 2687–2693 (2014).
- Nagarkar, S. S., Joarder, B., Chaudhari, A. K., Mukherjee, S. & Ghosh, S. K. Highly selective detection of nitro explosives by a luminescent metal-organic framework. *Angew Chem Int Ed* 52, 2881–2885 (2013).
- Bhattacharjee, Y. New efforts to detect explosives require advances on many fronts. *Science* 13, 1416–1417 (2008).
- Hutchinson, J. P. *et al.* Identification of inorganic improvised explosive devices by analysis of postblast residues using portable capillary electrophoresis instrumentation and indirect photometric detection with a light-emitting diode. *Anal Chem* 79, 7005–7013 (2007).
- Dicinoski, G. W., Shellie, R. A. & Haddad, P. R. Forensic identification of inorganic explosives by ion chromatography. *Anal Lett* 39, 639–657 (2006).
- Hazarika, P. & Russell, D. A. Advances in fingerprint analysis. Angew Chem Int Ed 51, 3524–3531 (2012).
- Ewing, R. G., Clowers, B. H. & Atkinson, D. A. Direct real-time detection of vapors from explosive compounds. *Anal Chem* 85, 10977–10983 (2013).
- Arndt, J. et al. Preliminary evaluation of the persistence of organic gunshot residue. Forensic Sci Int 222, 137–145 (2012).
- 11. Marshall, M. & Oxley, J. C. Aspects of explosives detection. Elsevier (2009).
- Caygill, J. S., Davis, F. & Higson, S. P. J. Current trends in explosive detection techniques. *Talanta* 88, 14–29 (2012).
- Najarro, M., Dávila Morris, M. E., Staymates, M. E., Fletcher, R. & Gillen, G. Optimized thermal desorption for improved sensitivity in trace explosives detection by ion mobility spectrometry. *Analyst* 137, 2614–2622 (2012).
- Staymates, M. E., Smith, W. J. & Windsor, E. Thermal desorption and vapor transport characteristics in an explosive trace detector. *Analyst* 136, 3967–3972 (2011).
- Yinon, J. Field detection and monitoring of explosives. *Trac-trend Anal Chem* 21, 292–301 (2002).
- Davis, E. J., Grows, K. F., Siems, W. F. & Hill, H. H. Improved ion mobility resolving power with increased buffer gas pressure. *Anal Chem* 84, 4858–4865 (2012).
- Du, Y., Wang, W. & Li, H. Bradbury–nielsen–gate–grid structure for further enhancing the resolution of ion mobility spectrometry. *Anal Chem* 84, 5700–5707 (2012).
- Dietiker, R., Lena, F. D. & Chen, P. Fourier transform ion mobility measurement of chain branching in mass-selected, chemically trapped oligomers from methylalumoxane-activated, metallocene-catalyzed polymerization of ethylene. *J Am Chem Soc* **129** (10), 2796–2802 (2007).
- Ewing, R. G. Ion mobility spectrometry, 2nd Edition. J Am Chem Soc 128 (16), 5585–5586 (2006).
- Mäkinen, M., Nousiainen, M. & Sillanpää, M. Ion spectrometric detection technologies for ultra-traces of explosives: A review. *Mass Spectrom Rev* 30, 940–973 (2011).
- 21. Song, J., Grün, C. H., Heeren, R. M. A., Janssen, H. G. & van den Brink, O. F. Highresolution ion mobility spectrometry-mass spectrometry on poly (methyl methacrylate). *Angew Chem Int Ed* **49**, 10168–10171 (2010).
- Eiceman, G. A. & Stone, J. A. Ion mobility spectrometers in national defense. *Anal Chem* 76, 390A–397A (2004).
- Buryakov, I. A. Detection of explosives by ion mobility spectrometry. *Anal Chem* 66, 674–694 (2011).

- Steinfeld, J. I. Explosives detection: a challenge for physical chemistry. Annu Rev Phys Chem 49, 203–232 (1998).
- Liang, X. *et al.* Sensitive detection of black powder by a stand-alone ion mobility spectrometer with an embedded titration region. *Anal Chem* 85, 4849–4852 (2013).
- 26. Marshall, A. The nature of explosives. Nature 96, 637-639 (1916).
- 27. Moretti, J. D., Sabatini, J. J. & Chen, G. Periodate salts as pyrotechnic oxidizers: development of barium- and perchlorate-free incendiary formulations. *Angew Chem Int Ed* **51**, 6981–6983 (2012).
- Johns, C. *et al.* Identification of homemade inorganic explosives by ion chromatographic analysis of post-blast residues. *J Chromatogr A* 1182, 205–214 (2008).
- Meng, H., Wang, T., Guo, B., Hashi, Y., Guo, C. & Lin, J. Simultaneous determination of inorganic anions and cations in explosive residues by ion chromatography. *Talanta* 76, 241–245 (2008).
- 30. Hutchinson, J. P. *et al.* Identification of inorganic improvised explosive devices by analysis of postblast residues using portable capillary electrophoresis instrumentation and indirect photometric detection with a light-emitting diode. *Anal Chem* **79**, 7005–7013 (2007).
- Doyle, J. M. & Mccord, B. R. Novel electrolyte for the analysis of cations in low explosive residue by capillary electrophoresis. *J Chromatogr B* 714, 105–111 (1998).
- 32. Tamiri, T. Characterization of the improvised explosive urea nitrate using electrospray ionization and atmospheric pressure chemical ionization. *Rapid Commun Mass Spectrom* **19**, 2094–2098 (2005).
- Sigman, M. E. & Armstrong, P. Analysis of oxidizer salt mixtures by electrospray ionization mass spectrometry. *Rapid Commun Mass Spectrom* 20, 427–432 (2006).
- Flanigan, P. M., Brady, J. J., Judge, E. J. & Levis, R. J. Determination of inorganic improvised explosive device signatures using laser electrospray mass spectrometry detection with offline classification. *Anal Chem* 83, 7115–7122 (2011).
- Dwivedi, P., Matz, L. M., Atkinson, D. A. & Hill, J. H. H. Electrospray ionizationion mobility spectrometry: a rapid analytical method for aqueous nitrate and nitrite analysis. *Analyst* 129, 139–144 (2004).
- Detata, D. A., Collins, P. A. & McKinley, A. J. A comparison of common swabbing materials for the recovery of organic and inorganic explosive residues. *J Forensic Sci* 58, 757–763 (2013).
- Pavlov, J. & Attygalle, A. B. Direct Detection of inorganic nitrate salts by ambient pressure helium-plasma ionization mass spectrometry. *Anal Chem* 85, 278–282 (2013).
- Du, Y., Wang, W. & Li, H. Resolution enhancement of ion mobility spectrometry by improving the three-zone properties of the bradbury-nielsen gate. *Anal Chem* 84, 1725–1731 (2012).

#### Acknowledgments

This research is partially supported by NSF of China (21177124, 21077101) and the National Key Scientific Instrument and Equipment Development Project (2013YO09070302).

#### Author contributions

L.P. designed the study and wrote the manuscript. L.H. contributed significantly to the measurements on TOF-MS identification. W.W. contributed significantly to the discussion of results and manuscript refinement. Q.Z. contributed to the construction of IMS. H.L. contributed to propose of the project and the refinement of this paper. All the authors contributed to the writing of the manuscript.

#### **Additional information**

Supplementary information accompanies this paper at http://www.nature.com/ scientificreports

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Peng, L., Hua, L., Wang, W., Zhou, Q. & Li, H. On-site Rapid Detection of Trace Non-volatile Inorganic Explosives by Stand-alone Ion Mobility Spectrometry via Acid-enhanced Evaporization. *Sci. Rep.* **4**, 6631; DOI:10.1038/srep06631 (2014).

