# Analysis of explosives using corona discharge ionization combined with ion mobility spectrometry–mass spectrometry

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## ARTICLE INFO

## ABSTRACT

Corona discharge ionization combined with ion mobility spectrometry–mass spectrometry (IMS–MS) was utilized to investigate five common explosives: cyclonite (RDX), trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), cyclotetramethylenetetranitramine (HMX), and 2,4-dinitrotoluene (DNT). The MS scan and the selected ion IMS analyses confirmed the identities of the existing ion species and their drift times. The ions observed were $RDX \cdot NO_3^-$, $TNT^-$, $PETN \cdot NO_3^-$, $HMX \cdot NO_3^-$, and $DNT^-$, with average drift times of 6.93 ms, 10.20 ms, 9.15 ms, 12.24 ms, 11.30 ms, and 8.89 ms, respectively. The reduced ion mobility values, determined from a standard curve calculated by linear regression of (normalized drift times)$^{-1}$ versus literature $K_0$ values, were 2.09, 1.38, 1.55, 1.15, 1.25, and 1.60 $cm^2\,V^{-1}\,s^{-1}$, respectively. The detection limits were found to be 0.1 ng for RDX, 10 ng for TNT, 0.5 ng for PETN, 5.0 ng for HMX, and 10 ng for DNT. Simplified chromatograms were observed when nitrogen, as opposed to air, was used as the drift gas, but the detection limits were approximately 10 times worse (i.e., less sensitivity of detection).

## 1. Introduction

Ion mobility spectrometry (IMS) is frequently used for the detection of explosives, illegal drugs, and chemical warfare agents [1,2] because it uses equipment that is small and simple to operate. The most common ionization source for the analysis of explosives by IMS is radioactive $^{63}Ni$, used to ionize explosive vapors [1]. However, the health risks of $^{63}Ni$, as well as low ion signals, have led many researchers to investigate other ionization techniques for analyzing explosives. Two alternatives to $^{63}Ni$ as an ionization source are corona discharge and secondary electrospray ionization (for a review, see [3]). Corona discharge provides an approximately 100-fold greater electron current than $^{63}Ni$ [4]. Recently, corona discharge ionization was coupled with IMS to analyze explosives [4–6].

Mass spectrometry (MS) is popularly used to analyze explosives because of its accuracy in identifying explosives from the $m/z$ values [7]. Several groups have attempted to combine IMS with MS (IMS–MS) for the analysis of explosives [3,8–10]. IMS–MS is a powerful technique because it determines ion mobility and $m/z$ values simultaneously. In the current study, corona discharge ionization combined with IMS–MS was used to examine five explosives: cyclonite (RDX), trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), cyclotetramethylenetetranitramine (HMX), and 2,4-dinitrotoluene (DNT).

## 2. Experimental

### 2.1. Materials and chemicals

RDX, TNT, PETN, HMX, and DNT, shown in Fig. 1, were obtained from the Agency for Defense Development (Daejeon, Korea). Acetonitrile (ACN), used as the solvent, was purchased from Sigma-Aldrich (St. Louis, MO, USA).

### 2.2. Instrument

IMS–MS was performed using an RA4100 ion mobility spectrometer (Excellims, Acton, MA, USA) equipped with quadrupole MS and corona discharge ionization in negative ion mode. The operating conditions were as follows: source voltage, −10.9 kV; drift tube voltage, −8.9 kV; gate width, 70 µs; and temperature of the desorber and drift tube, 180 °C. The drift length, or the distance from the gate to the detector, was 10.5 cm. Details of the drift tube have been published by Excellims [11]. Purified dry air was used as the drift gas in most of the experiments, although some experiments used nitrogen gas for comparison.

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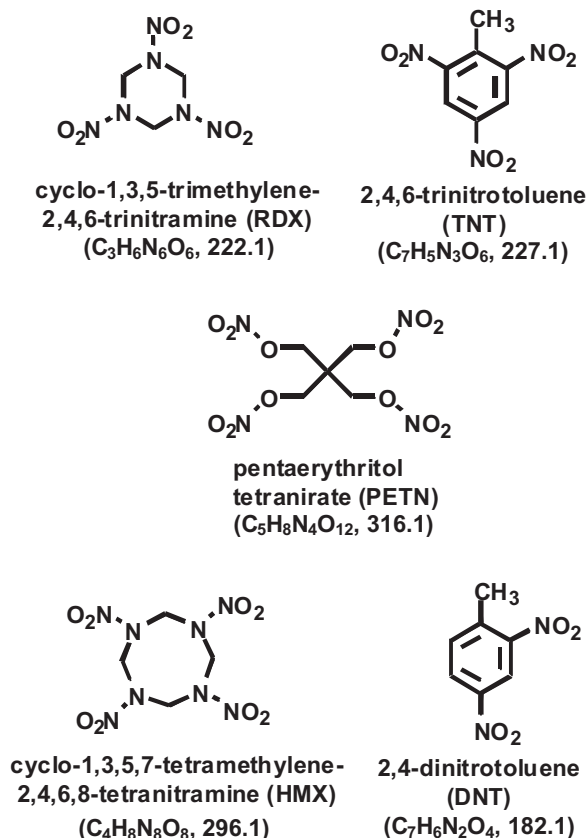Fig. 1. Structures of the five explosives investigated in this study.



**Fig. 2.** IMS–MS analysis of air. (A) Ion mobility spectrum and (B) mass-selected ion mobility spectra of $CO_3^-$ at $m/z$ 60, $NO_3^-$ at $m/z$ 62, and $HNO_3 \cdot NO_3^-$ at $m/z$ 125. The inset of (A) shows the mass spectrum from $m/z$ 50 to $m/z$ 140.



**Fig. 3.** IMS–MS analysis of 100 ng RDX. (A) Ion mobility spectrum and (B) mass-selected ion mobility spectrum of $[RDX \cdot NO_3]^-$ at $m/z$ 284. The inset of (A) shows the mass spectrum from $m/z$ 50 to $m/z$ 300.

## 2.3. Sample preparation

Stock solutions were prepared by dissolving each explosive in ACN to a concentration of 10 mg/mL. Aliquots of the stock solutions were then serially diluted with ACN to provide sample solutions at concentrations of 0.1, 0.5, 1.0, 5.0, 10.0, 50.0, 100, 500, and 1000 μg/mL. Finally, 1.0 μL of each sample solution was deposited onto a Nomex swab (Excellims, part number 1002252.03), which was then introduced into the desorption port of the spectrometer after the solvent had evaporated. For qualitative analysis, the sample concentration of 100 μg/mL was used unless otherwise specified.

## 2.4. Description of procedure

The drift time for each explosive was acquired for 20 ms. The acquisition time for the chromatogram was set to 40 s. A Faraday detector was used to determine the drift time. To determine the $m/z$ value for each explosive, the MS scan mode was used with a scan range of $m/z$ 50–$m/z$ 500. To identify the drift time of a specific ion with a certain $m/z$ value, the selected ion IMS was used, whereby the quadrupole was set to pass the specific $m/z$ ion while the drift time was acquired by the Faraday detector.

## 3. Results and discussion

### 3.1. Identification of the peaks

#### 3.1.1. Analysis of air

To investigate whether air without any sample would provide any signals, an empty swab was introduced to the IMS–MS. Fig. 2A shows the ion mobility spectrum of the empty swab. The mass spectrum showed three distinctive peaks at $m/z$ 60, $m/z$ 62, and
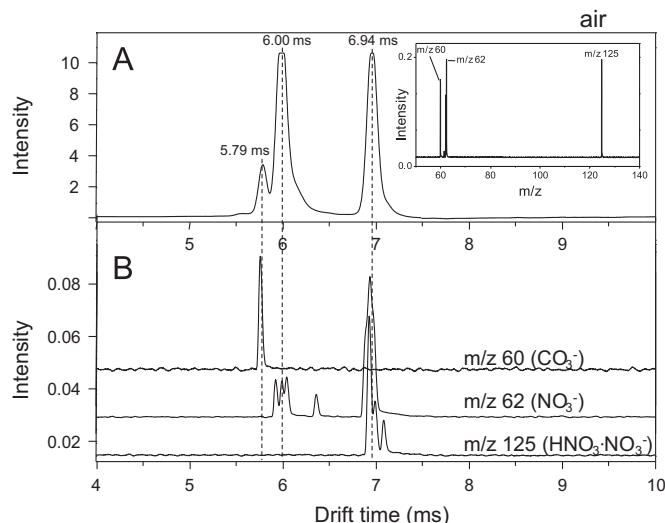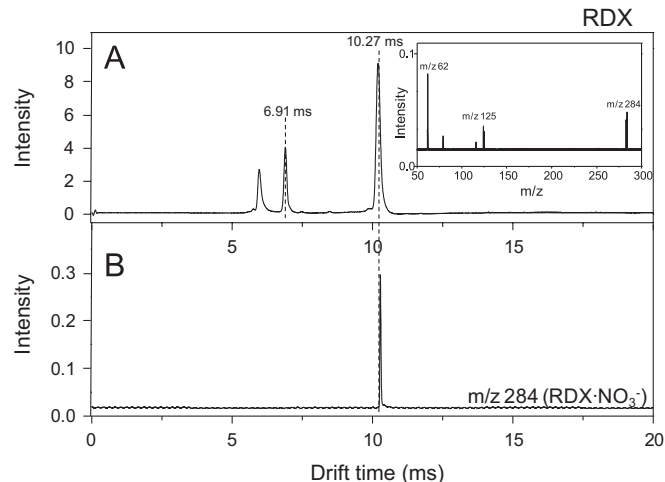
$m/z$ 125, as shown in the inset of Fig. 2A. Negative corona discharge of air at ambient pressure generates the $CO_3^-$ ion at $m/z$ 60 [12], $NO_3^-$ ion at $m/z$ 62 [13], and $HNO_3 \cdot NO_3^-$ at $m/z$ 125 [14]. The mass-selected IMS spectrum obtained for the three candidate ions confirmed the drift times of the three ions at 5.79 ms for $CO_3^-$, 6.00 ms for $NO_3^-$, and 6.94 ms for $HNO_3 \cdot NO_3^-$ (Fig. 2B). In the mass-selected IMS spectrum for $m/z$ 62 of $NO_3^-$, two major peaks were observed at 6.00 ms and 6.94 ms; the peak at 6.94 ms is believed to be from the fragmentation of $HNO_3 \cdot NO_3^-$.

#### 3.1.2. Analysis of RDX

Fig. 3 shows the ion mobility spectrum of 100 ng RDX. The drift time was 10.27 ms (Fig. 3A). The MS scan (inset) and the selected ion IMS analysis (Fig. 3B) showed that RDX was observed as a nitrate adduct ($RDX \cdot NO_3^-$) at $m/z$ 284. RDX has been previously observed as $RDX \cdot NO_3^-$ using corona discharge ionization [3].

#### 3.1.3. Analysis of TNT

Fig. 4 shows the ion mobility spectrum of 100 ng TNT. The drift time was 9.25 ms (Fig. 4A). The MS scan (inset) and the mass-selected