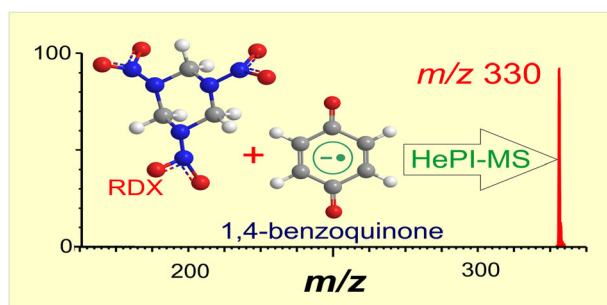


1,4-Benzoquinone as a Highly Efficient Dopant for Enhanced Ionization and Detection of Nitramine Explosives on a Single-Quadrupole Mass Spectrometer Fitted with a Helium-Plasma Ionization (HePI) Source

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Abstract. Previous investigations have evaluated the efficacy of anions such as NO_3^- , Cl^- , Br^- , CH_3COO^- , and CF_3COO^- as additives to generate or enhance mass spectrometric signals from explosives under plasma ionization conditions. The results of this study demonstrate that for detecting nitramine-class explosives, such as 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX), 1,4-benzoquinone (BQ) is a highly effective and efficient dopant.

When used in conjunction with ambient-pressure negative-ion helium-plasma ionization (HePI), 1,4-benzoquinone readily captures an electron, forming an abundant molecular anion (m/z 108), which upon exposure to vapors of RDX and HMX generates adduct ions of m/z 330 and 404, respectively. The signal level recorded for RDX upon adduction to the *radical anion* of 1,4-benzoquinone under our experimental conditions was significantly higher than that realized by chloride adduction using dichloromethane (DCM) as the dopant.

Keywords: 1,4-Benzoquinone, Nitramine explosives, Ambient mass spectrometry, Ionization methods, Gas-phase adducts, Electron-capture ionization

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Introduction

The marked rise in terrorist activities involving explosive devices has driven the interest in developing high-performing and portable analytical systems that enable the rapid, reliable, sensitive, and specific detection of energetic materials. Thus, the timely detection of explosives in the laboratory and, preferably, in the field has become a vital task to perform in order to protect society from terrorism [1, 2]. In

addition, explosives enter the atmosphere, water, and soil through military activities. Therefore, analytical chemists are challenged with the detection of post-explosion residues and the identification of traces of explosives on the bodies and clothing of suspects, and with monitoring effluents from munitions plants. A plethora of methods already exists for the detection of explosives [3, 4]. Among the available analytical methods, ion mobility spectrometry (IMS), which delivers low-nanogram-level detection, is one of the most widely used [5]. However, IMS is a low-resolution method that tends to yield false-positive results. Of course, there are a number of highly specific methods, such as liquid chromatography-mass spectrometry (LC-MS) [6–13], supercritical fluid extraction [14, 15], solid-phase micro-extraction [16, 17], capillary electrophoresis [18], ion chromatography [19], and gas chromatography-

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mass spectrometry [20, 21], but most of them are rather complicated and frequently require extensive sample preparation and relatively long analysis times. Consequently, they are not suitable for rapid sample analysis in a high-throughput manner, especially under field conditions.

Among the methods available for the detection of explosives, ambient mass spectrometry has evolved as a very promising technique because of its high specificity and sensitivity [22, 23]. For ambient ionization techniques, samples are introduced and ionized in their native environments with a minimal amount of preparatory handling [24–26]. Plasma-based mass spectrometric methods are known to be particularly efficient for ion generation from samples of explosives [27–31]. Many additive ions, such as NO_3^- [12, 32], NO_2^- , Cl^- , Br^- , HCO_3^- , CH_3COO^- , CF_3COO^- , and other chemical reagents [33–35] have been evaluated for their ability to enhance mass spectrometric signal intensities of explosives and other analytes [24] or sometimes to generate signals where none were initially observed [36]. For example, Chen et al. [37] developed a probe based on low-temperature plasma, which, assisted by a chloride-source dopant such as dichloromethane, provides for impressive sensitivity in the detection of nitramines and organic nitrate esters.

1,3,5-Trinitroperhydro-1,3,5-triazine (RDX; Figure 1, 1) (for security reasons, it was initially called “research department explosive,” hence the well-known abbreviation RDX) is the most important high-brisance explosive, a component of many formulations, including C-4 and Semtex. The detection of RDX and its homologue 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) (Figure 1, 2) by MS methods is particularly difficult because of their exceedingly low volatilities and inherent sluggishness to ionization (see Supplementary Table S1). For example, the vapor pressure of RDX at room temperature is reported as 0.006 ppb (about 5×10^{-10} mmHg, Supplementary Table S1), which is too low to be monitored even by electron-capture detection [38]. The vapor pressure of HMX is even lower (Supplementary Table S1). In addition, these nitramines are both poor bases and poor acids; therefore, attempts at analyzing them by electrospray ionization, either by protonation or deprotonation, does not generate high ion currents, unless a charged adduct is formed that can be monitored.

Herein, we report a trace analysis method for solid cyclic nitramines we devised and tested on a dedicated helium-plasma ionization (HePI) source installed on the *small-footprint* Waters QDa instrument. We demonstrate that the adduct-forming dopant 1,4-benzoquinone (BQ) causes a dramatic lowering of detection levels of nitramine energetic materials such as RDX and HMX when introduced to their trace vapors prior to MS detection.

Experimental Section

Chemicals and Reagents

1,4-Benzoquinone was purchased from Sigma-Aldrich (St. Louis, MO, USA), and methanol and acetonitrile (HPLC grade) were from Mallinckrodt Baker, Inc. (Phillipsburg, NJ, USA). HMX and RDX were available from our collection of research samples (Stevens Institute of Technology).

HePI Mass Spectrometry

A HePI source was fitted to a QDa single-quadrupole mass spectrometer (Waters Corp., Milford, MA, USA) (Figure 2, Supplementary Figure S1). An ionizing microplasma region (Figure 2, Supplementary Figure S1 B) was generated by passing a stream ($\sim 10 \text{ mL min}^{-1}$) of high-purity helium (99.999%; Airgas, Radnor, PA, USA), regulated by a needle valve, through a stainless steel capillary (130 μm internal diameter (i.d.)) held at high voltage (typically 1.3–1.5 kV). The voltage was supplied by an external power source. The capillary tip was set about 10 mm from the mass spectrometry–sampling cone orifice through which gaseous ions enter the instrument.

The source entrance was either kept open or covered with a glass window with orifices for the introduction of a sample holder (4 mm) and tubing for the flow of dopant vapors (2 mm) (Supplementary Figure S1 A). Samples were deposited by drying aliquots (2 μL) of methanol solutions on the outside surface of the sealed end of a disposable borosilicate-glass melting-point tube (Kimble, 1.5–1.8 mm \times 90 mm), and then the tube was positioned at about 15 mm

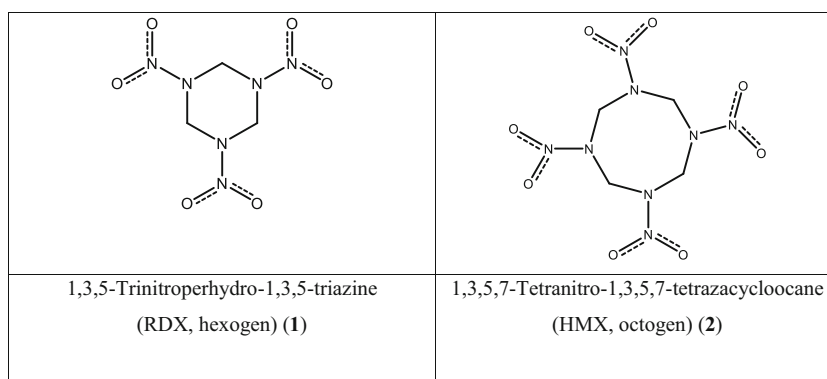


Figure 1. Structures of RDX and HMX

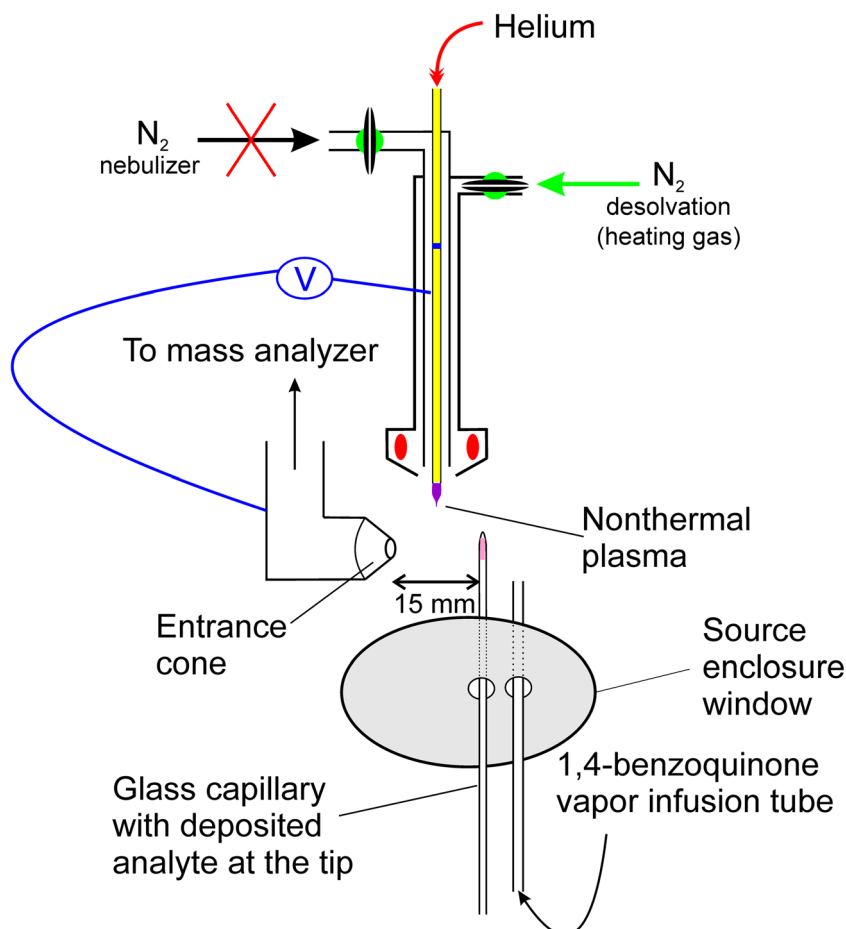


Figure 2. A schematic diagram depicting the introduction of samples and 1,4-benzoquinone vapor to the HePI source

away from the cone orifice in the same horizontal plane as the cone orifice. The solid sample deposits obtained by drying were introduced to a precise point in the vicinity of the microplasma region with the aid of a movable mechanical stage (Supplementary Figure S1 C).

Headspace vapors emanating from a few milligrams of BQ enclosed in an externally placed glass vial (Supplementary Figure S1, 4) were introduced passively to the source through a short piece of 1/16-in.-i.d. Teflon™ tubing (Supplementary Figure S1 A, 3) and controlled by a gas-sampling valve. The vapor pressure of BQ was carefully increased by slightly warming the BQ container (Supplementary Figure S1) with a heat gun, typically to about 40–45 °C. The tubing transferring the dopant vapor was inserted into the HePI source through the 2-mm opening in the front window or through a dedicated orifice on the side of the source enclosure. Benzoquinone vapor was introduced to the source first, and after 3–5 s (or when a dip in the selected-ion current signal was observed), the sample probe with deposited solid nitramine was inserted. A stream of heated nitrogen *desolvation* gas was used to desorb analyte samples from the glass rod. The flow of nitrogen was controlled manually at 50 L h⁻¹ by means of an external flow meter. The temperature of the desorption gas heater was optimized for each analyte as needed (typical setting for RDX and HMX was 220–250 °C). The ion source temperature was held

at 100 °C. The sampling cone voltage was kept low (2 V) to reduce in-source dissociation of charged species.

For comparison, an experiment was conducted with dichloromethane (DCM) as the dopant. DCM was kept in a gas-tight vial with a septum valve. The dopant vapors were continuously introduced using a length of Teflon™ tubing (1/16 in. i.d.) through the 2-mm opening in the front window of the ion source, and the formation of the chloride adduct RDX was monitored. The sample capillary with deposited solid nitramine was inserted 5 s after the DCM infusion started.

Collision-induced dissociation (CID) experiments were performed on a Waters Micromass Quattro Ultima triple-quadrupole mass spectrometer. Its ion source was modified to function as a HePI source [31, 38]. High-purity helium (10 mL min⁻¹) was passed through the metal capillary (130 μm i.d.) whose tip was positioned approximately 10 mm from the entrance cone orifice. The capillary was held at 3 kV. The source temperature was kept at 100 °C. The cone voltage was set at 10 V. The pressure of the argon collision gas was held at 3 × 10⁻³ mbar. The collision energy was 10 eV. The heater for the desolvation gas (N₂) was set at 250 °C, and a low flow stream of the gas was used to desorb solid samples introduced to the source as fine powders deposited on glass slides. Benzoquinone vapor was co-introduced to the source by opening the vial with the solid in the proximity of the samples.

Results and Discussion

Nitramines are typically ionized and detected by various negative-mode MS methods as adducts with small, mostly inorganic anions (including acetate and trifluoroacetate), which are generated by a dissociation of a neutral precursor dopant. For example, RDX and HMX from acetonitrile solutions are known to generate adduct species such as $[M+NO_2]^-$, $[M+NO_3]^-$, $[M+HCO_3]^-$, and $[M+HCO_4]^-$ under thermal desorption ambient mass spectrometric conditions [39]. Under these conditions, Saha et al. [39] achieved detection limits as low as 20 pg and 100 pg for RDX and HMX, respectively, at a S/N ratio > 3. We envisaged that a high-electron-affinity volatile organic compound that would undergo electron capture and generate abundant ions would potentially act as a better dopant and provide even lower detection levels for nitramine explosives. Thus, we selected 1,4-benzoquinone, a well-known electron-capturing compound, as the test dopant [40].

Both RDX and HMX are known to decompose at elevated temperatures and release nitrite and nitrate ions, which add onto volatilized intact analyte molecules and form charged adducts that can be detected [39]. For example, a negative-ion mass spectrum we recorded under HePI conditions from RDX showed peaks at m/z 268 and 284 (Figure 3a), and another from HMX at m/z 342 and 358 (Figure 3c), for the respective nitrite and nitrate adducts. Although it is possible that some NO_2^- and NO_3^- ions required for the adduct formation originate from air that leaks into the ion source, primarily they are generated by thermal decomposition of RDX and HMX because ion generation was noticed only after the source temperatures reached at least 200 °C. On the other hand, the overall appearance of the acquired spectrum changed dramatically when BQ vapor was introduced to the ion source. The

original two peaks at m/z 268 and 284 in the native RDX spectrum virtually disappeared; instead, a new peak appeared at m/z 330. A product-ion spectrum recorded from the mass-selected m/z 330 ion on a tandem quadrupole mass spectrometer confirmed that this ion represents the BQ adduct of RDX (Supplementary Figure S2). The behavior of HMX upon interaction with BQ was similar: the m/z 342 and 358 peaks in the native spectrum (Figure 3c) were substituted by a peak at m/z 404 for the BQ adduct of HMX (Figure 3d, Supplementary Figure S2). Moreover, the co-introduction of benzoquinone vapors to the ion source increased the overall signal intensity of RDX 30-fold (Figure 3a, b) and that of HMX 15-fold (Figure 3c, d). Moreover, both BQ and RDX/HMX-BQ signals clear rapidly from the source, with negligible tailing in the chromatogram peaks, indicating minimal carryover and cross-contamination between samples (Figures 4, 5, and 6).

Furthermore, a comparison showed that under HePI conditions, the efficacy of BQ is far superior to dichloromethane, which is widely used as a signal-enhancing dopant for nitramine explosive detection under APCI conditions. In one experiment, using a continuous stream of dichloromethane vapor as the dopant, the signal intensity of m/z 257 for the $^{35}Cl^-$ adduct obtained from a 5-ng sample of RDX could be matched approximately at the same level of signal-to-noise ratio with a 50-fg sample when BQ was used as the additive in HePI conditions (Figure 4).

Initially, a slight suppression of the background m/z 330 signal level was noted when the benzoquinone vapor was first introduced to the source, and then the intensity of the m/z 330 signal increased in a repetitive manner depending on the amount of sample applied to the probe (Figure 5). In fact, if an excessive amount of benzoquinone is introduced to the source, only an m/z 108 peak is observed, with all others signals

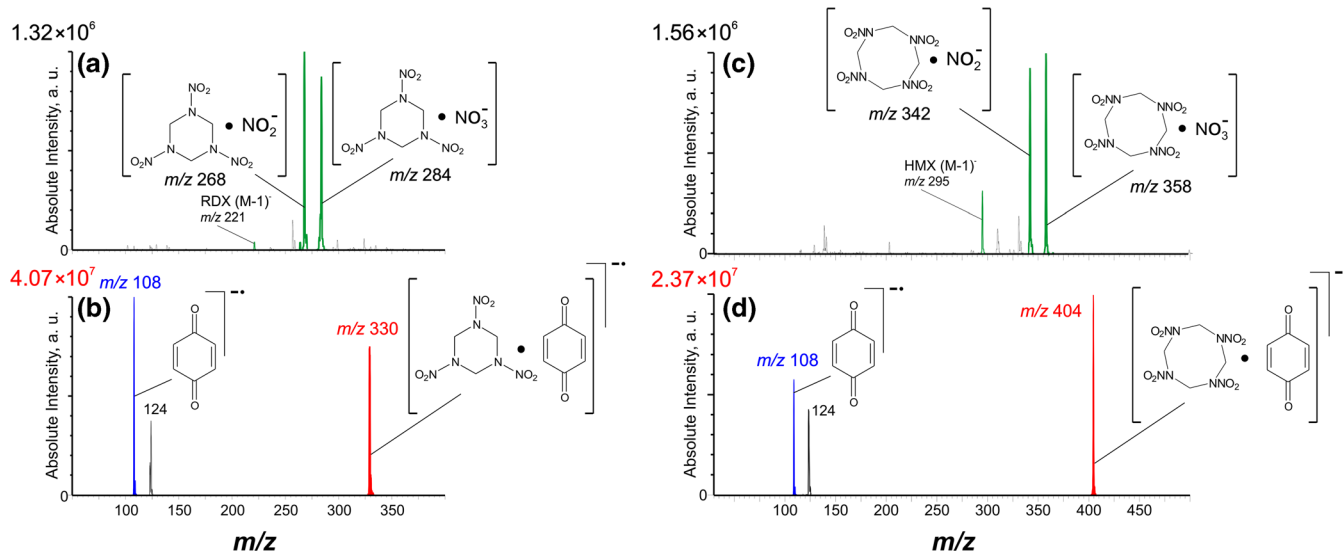


Figure 3. Negative-ion HePI mass spectra recorded from RDX and HMX samples desorbed using a nitrogen flow of 50 L h^{-1} at 250 °C (a and c), and those acquired from samples co-introduced with benzoquinone vapor under identical experimental conditions (b and d)

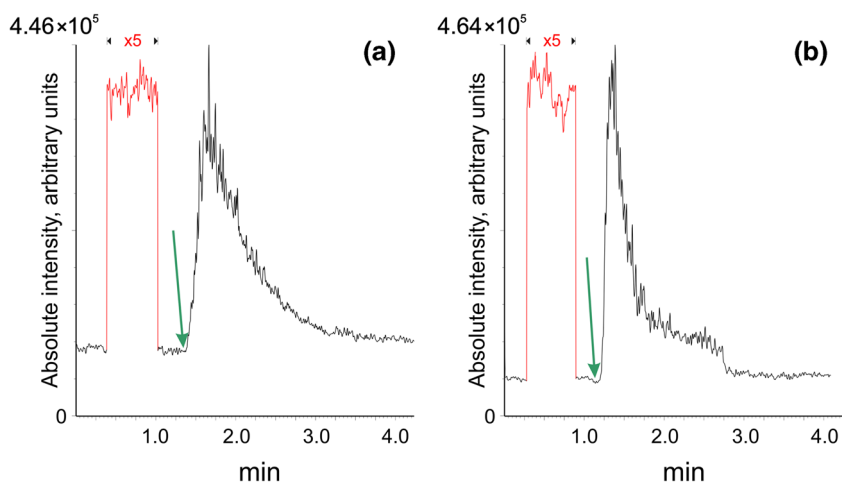


Figure 4. Selected-ion chromatograms recorded for m/z 257, the $^{35}\text{Cl}^-$ adduct (a), and m/z 330, the benzoquinone adduct (b), from samples of RDX: 5 ng, using dichloromethane (a), and 50 fg, using benzoquinone (b), as the dopant. The RDX samples were introduced at the points indicated by green arrows. The sections shown in red have been expanded vertically to show the signal-to-noise ratio

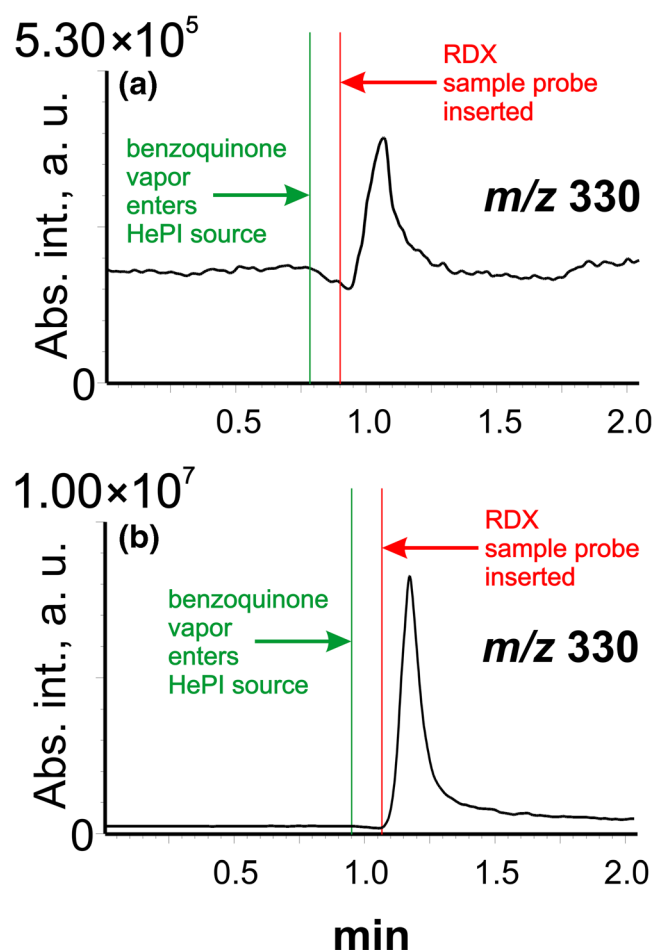


Figure 5. Selected-ion chromatogram recorded by an SIR HePI experiment from 0.5 pg (a) and 50 pg (b) samples of RDX desorbed at a 50 L h^{-1} desolvation gas flow at a heater temperature of $220 \text{ }^\circ\text{C}$, and exposed to benzoquinone vapor. The m/z 330 signal for the benzoquinone adduct of RDX was monitored

suppressed, because BQ is an excellent electron scavenger. In our early trials, we attempted introducing the dopant as a powder on a cotton swab and noted the above effect. Consequently, we revised the procedure to introduce only a small amount of BQ vapor delivered by PTFE tubing from a warmed-up external vial.

However, maintaining a constant supply of BQ to the ion source is not of paramount importance for sample analysis. Maintaining its supply for about 15 s while the sample desorbs from the probe is sufficient for it to afford analyte ionization without becoming a limiting reagent. Apparently, not only BQ scavenges electrons from the helium plasma very efficiently but also the resulting radical anion transfers electrons to the analytes very competently, rendering BQ a very powerful additive for detection of RDX and HMX.

To determine the reproducibility of the detection method, we performed an experiment of repeated insertion and withdrawal of glass probes with a freshly deposited residue of HMX (1.5 ng). The intensity of the m/z 404 peak for the adduct was monitored by a one-channel selected-ion recording (SIR) experiment. The time-intensity profile (*chronogram*) recorded showed that the intensities of peaks from three repetitive insertions and withdrawals were essentially the same (Figure 6) (one may notice that an analogous dip in signal as that noted for RDX, when BQ vapor was introduced to the source, was not obvious with the signal profile illustrated in Figure 5 for HMX. This is because a more improved technique was used for HMX. As soon as the heating of the BQ vial was started, the HMX sample was introduced. This procedure prevents the minor initial suppression of signal).

In a more rigorous experiment, probes with four different sample amounts ranging between 1 and 20 pg of RDX were repeatedly inserted to an enclosed HePI source, and the intensity of the m/z 330 peak was monitored by a SIR procedure. Figure 7 shows that the standard deviations are low and the sample-to-sample reproducibility is high when the samples are

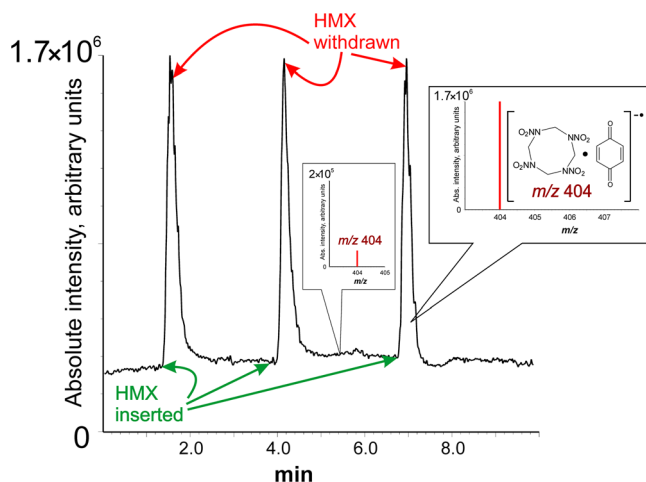


Figure 6. A selected-ion chromatogram recorded for m/z 404, the HMX-benzoquinone adduct. The probe containing a solid HMX sample (1.5 ng) was inserted to an open source that was exposed to benzoquinone vapor. The probe was kept in for 5 s and withdrawn. The procedure was repeated two more times with the same probe. Desolvation gas flow, 50 L h^{-1} ; desorption heater temperature, $250 \text{ }^\circ\text{C}$

introduced through an orifice in the cover of an enclosed HePI source engulfed with nitrogen. These data were better than the signals obtained under open-source conditions. An exemplar of the chromatograms obtained to construct the histogram is presented in Supplementary Figure S3. Based on these findings, we estimated the detection limit for RDX by the method to be 1 pg (Figure 7).

Although the mechanism was not investigated in the current study, the interaction of the radical anion of 1,4-benzoquinone with RDX or HMX for the electron transfer occurs presumably

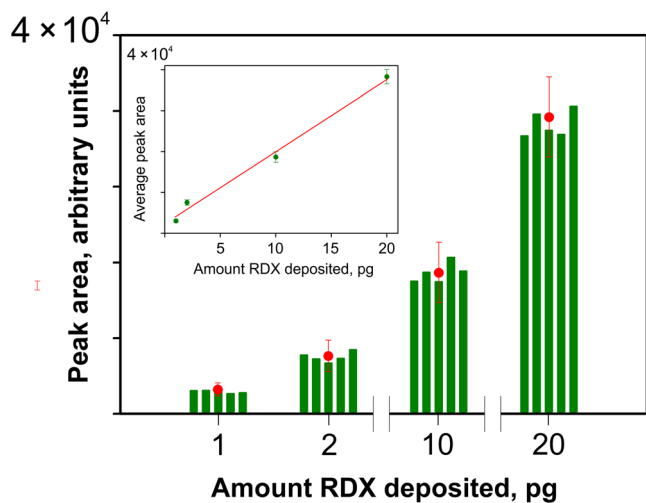


Figure 7. A histogram showing the integrated signal intensities from benzoquinone-RDX adducts obtained by SIR monitoring of the m/z 330 ion. Five samples of four different amounts of RDX (1 pg, 2 pg, 10 pg, and 20 pg) were inserted consecutively into the HePI source infused with benzoquinone vapor. Inset: a plot of the average integrated area of the SIR-monitored m/z 330 signal vs. RDX amount deposited ($N = 5$, $R^2 = 0.9918$)

by the formation of a transition complex in which the two oxygen atoms of BQ form bidentate bonds with the hydrogen atoms of the nitramines in a manner similar to that proposed by Usmanov et al. [41] for the interaction of the nitrate ion with RDX and HMX.

Conclusions

A helium-plasma ionization source fitted to a compact single-quadrupole mass spectrometer provides an improved platform for the direct and ultra-low-level detection of nitramine explosives. Radical anions generated from an electron-capturing dopant are employed to ionize neutral analyte molecules by adduct formation. Minimum sample preparation is required. Because a low amount of the 1,4-benzoquinone additive is needed and its vapor is delivered directly to an enclosed ion source, the operator is practically not exposed to its noxious fumes. Furthermore, the amount of benzoquinone delivered to the source can be controlled by varying the temperature of its externally placed enclosing vessel. Moreover, our approach eliminates the need of thermally dissociating the analyte or the dopant, as required by many existing procedures, and provides a method for rapid, specific, and sensitive determination of nitramine explosives. Although the ionization approach was only tested on a HePI source at ambient conditions and with solid samples of a particular nature, we envisage that benzoquinone is potentially an excellent additive for other plasma ionization-MS techniques and is applicable in this capacity to a wide range of analytes. Finally, while benzoquinone is clearly an excellent dopant for nitramine detection, it should, by no means, be presumed that it is unique. There are many other excellent electron-capturing chemicals, such as anthracene, tetracyanoethylene, and tetracyanoquinodimethane that may perform as the electron donor. In order to ascertain the most practical dopant for this kind of application, properties of the additives such as ionizability, volatility, adductability, and safety must be evaluated and compared.

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