



Carbon and nitrogen isotope ratios of factory-produced RDX and HMX



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ABSTRACT

RDX and HMX are explosive compounds commonly used by the military and also occasionally associated with acts of terrorism. The isotopic characterization of an explosive can be a powerful approach to link evidence to an event or an explosives cache. We sampled explosive products and their reactants from commercial RDX manufacturers that used the direct nitration and/or the Bachmann synthesis process, and then analyzed these materials for carbon and nitrogen isotope ratios. For manufacturers using the Bachmann process, RDX ¹³C enrichment relative to the hexamine substrate was small (+0.9‰) compared to RDX produced using the direct nitration process (+8.2‰ to +12.0‰). RDX ¹⁵N depletion relative to the nitrogen-containing substrates (−3.6‰) was smaller in the Bachmann process than in the direct nitration process (−12.6‰ to −10.6‰). The sign and scale of these differences agree with theorized mechanisms of mass-dependent fractionation. We also examined the isotopic relationship between RDX and HMX isolated from explosive samples. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of RDX generally matched those of the HMX with few exceptions, most notably from a manufacturer known to make RDX using two different synthesis processes. The range in $\delta^{13}\text{C}$ values of RDX in a survey of 100 samples from 12 manufacturers spanned 33‰ while the range spanned by $\delta^{15}\text{N}$ values was 26‰; these ranges were much greater than any previously published observations. Understanding the relationship between products and reactants further explains the observed variation in industrially manufactured RDX and can be used as a diagnostic tool to analyze explosives found at a crime scene.

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1. Introduction

RDX and HMX are explosive compounds commonly used by the military and also occasionally associated with acts of terrorism. Yet there are few diagnostic approaches to distinguish chemically identical RDX and HMX explosives from each other. Forensic investigators are interested in linking evidence from an event or an explosives cache using quantitative observations collected from recovered explosive materials. These materials may take the form of unexploded chemicals, residues, and/or remains of devices; understanding the origin of each material or component can lead to the perpetrator. In order to link a material to its origin, investigators often collect quantitative data about the material and interpret that data against a set of previous observations on similar materials. Use of databases and models to predict the origin of a recovered sample given certain data, or conversely to predict distinctive characteristics of materials of known origin, are highly

useful for forensics investigations. Ehleringer and colleagues [1] provide an analytical and interpretative framework for using stable isotopes for these types of predictions in forensic studies.

The diagnostic approaches used to collect data for investigating origin are many and varied [2], but most rely on structural and chemical analyses to characterize and differentiate explosive materials. While chemical and structural characterization is very important, stable isotope ratio analyses can often provide additional characterization with the potential to differentiate explosives having identical chemical composition [3]. The first demonstration that explosive materials could be differentiated by isotopic analysis focused on trinitrotoluene (TNT) samples from several different countries [4]. Further studies on Semtex [5], cyclotrimethylene trinitramine ($\text{C}_3\text{H}_6\text{N}_6\text{O}_6$, RDX) [6–8], ammonium nitrate [9,10], black powder [11], TATP, [10,12], PETN [10,12], residues [13], and perchlorates [14] have shown forensic stable isotope analyses to be useful for discrimination and potential source identification (see review by Benson et al. [15] and chapter 15 in Mass Spectrometry Handbook [16]).

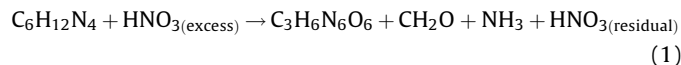
Isotope ratio analysis may be particularly useful in forensic investigations of manufactured materials because the isotope

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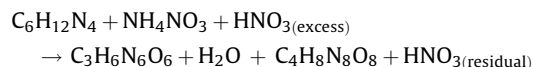
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'signal' recorded in a reactant is passed to the final product either unchanged or changed in a predictable way. This change (isotope fractionation) occurs when isotopes are partitioned unequally between two pools as a result of their subtle chemical differences. When a pool is enriched in a particular isotope, the other pool becomes depleted in that isotope. By understanding the fractionation factors associated with different processes and mechanisms, a forensic investigator may be able to infer a link between a product and a production method and/or reactant. The isotopic links between explosive products and reactants have been investigated for the peroxide explosive HMTD [17], urea nitrate [18], and RDX [19] produced in laboratory settings. However, to date there have been no stable isotope studies on explosives from commercial manufacturers who supply the marketplace.

Here we investigated stable isotope ratios and fractionation factors associated with factory-produced RDX, an important high explosive that has been in industrial-scale production since the middle of World War II [20]. RDX is heavily used in plastic explosives (such as C-4 and Semtex), boosters, and munitions produced by factories in several countries [21]. We examined two important industrial processes that synthesize RDX. First, the direct nitration process described by Hale [22] uses only hexamine ($C_6H_{12}N_4$) and nitric acid (HNO_3) as reactants, as shown in Eq. (1):



This reaction has two side-products in addition to the desired product RDX: formaldehyde (CH_2O) and ammonia (NH_3). The second most important manufacturing process for RDX, known as the Bachmann process [23], includes ammonium nitrate (NH_4NO_3) and acetic anhydride among the reactants in addition to hexamine and nitric acid. This reaction (Eq. (2)) simultaneously produces an additional explosive product ($C_4H_8N_8O_8$, HMX), at a concentration of 8–12% by weight in the overall explosive yield [24]. Acetic anhydride does not contribute any atoms to the final RDX product in the Bachmann process, so the equation can be described as



There is potential for carbon and nitrogen isotope fractionation in both the direct nitration and Bachmann processes because (1) carbon and nitrogen atoms from the reactants are partitioned into separate product pools and (2) not all of the reactant nitric acid is consumed. First, consider carbon isotope fractionation involving the heavy (^{13}C) and light (^{12}C) isotopes. Our hypothesis is that ^{13}C fractionation patterns differ between direct nitration and Bachmann processes due to different stoichiometry. In the nitrolysis mechanisms of the direct nitration process [25,26], breaking of C–N bonds in hexamine to form the carbon-containing products RDX and formaldehyde should result in ^{13}C enrichment of RDX, while formaldehyde becomes ^{13}C depleted (see the Supporting information for a proposed mechanism describing the incorporation of carbon and nitrogen into RDX). In the Bachmann process formaldehyde is not released as a side product, so there should be no ^{13}C enrichment of products relative to reactants; the only potential ^{13}C fractionation would be between the products RDX and HMX.

Second, consider nitrogen isotope ratios ($^{15}N/^{14}N$). The isotope ratio difference between the products and reactants will be dependent upon the mechanism by which nitrogen is transferred from the reactants to the products. RDX and HMX have two nonexchangeable pools of nitrogen: the 'amine' nitrogen from hexamine and the 'nitro' nitrogen from nitric acid. The release of

ammonia as a side product in the direct nitration process may result in fractionation between amine ^{15}N in the reactant hexamine and amine ^{15}N in the product RDX. In the Bachmann process, all of the amine nitrogen from hexamine ends up in either RDX or HMX and thus no ^{15}N fractionation should occur between hexamine nitrogen and the amine nitrogen in RDX and HMX. In both production methods, a fractionation involving the nitronium (NO_2^+) species [24,25,27] from nitric acid should preferentially incorporate ^{14}N nitro nitrogen into RDX and/or HMX, leaving the residual nitric acid ^{15}N enriched.

We expected greater ^{13}C and ^{15}N fractionation between products and reactants in the direct nitration process than in the Bachmann process, as the Bachmann process does not release formaldehyde and ammonia. Since HMX and RDX are synthesized using a similar mechanism in the Bachmann process, we expected HMX and RDX produced together in the same batch would be isotopically similar [28]. By determining the potential synthesis fractionation factors and the known isotopic ranges of reactants, we may be able to predict the isotope ratio ranges of RDX and HMX products among industrial manufacturers. Once these isotopic parameters are established, isotope ratio analyses of RDX and/or HMX from an unknown source may be used to constrain the isotopic ranges of the reactants and determine which of the two processes was used to synthesize the RDX.

We collected samples of reactants that were used to make explosives in a Bachmann process batch at one manufacturer and in direct nitration batches at two additional manufacturers. We also collected products and side-products associated with those production batches and other pure RDX samples from earlier batches at the same factories. These data were important for establishing within-batch isotopic variation. A comparison of within-batch variation to (1) within-sample variation (heterogeneity) and (2) sample measurement uncertainty allowed us to infer the overall "within-source" isotopic variation for a suspect sample. Here, we present within-source isotopic variation as uncertainty associated with batches and samples, accounting for measurement uncertainty. Together with RDX purified from other industrially produced explosive materials, we surveyed 12 different manufacturers to determine ranges in RDX carbon and nitrogen stable isotope ratios from these different sources. We present between-source isotopic variation as ranges of measured isotope ratios encompassing samples of different source.

2. Materials and methods

2.1. Sample collections from factories

We use the term 'explosive sample' to identify a substance containing the explosive compounds RDX and/or HMX. Some samples were obtained through visits to manufacturing facilities, whereas the US Government provided other samples to us (GFM). The types of explosive samples included, but were not limited to: C-3 and C-4 plastic explosives, plastic-bonded explosives (PBX), cast HMX/RDX/TNT explosives such as Composition B, and RDX/PETN explosives such as Semtex.

Hexamine reactant, nitric acid reactant, and explosive product (RDX and/or HMX) were collected from three industrial-scale manufacturers. The association between reactants (hexamine and nitric acid) and products (RDX, HMX) was noted (see Tables 1 and 2). None of the factories are identified by name, but each is a registered explosives manufacturer known to the US Government. As available, samples were also taken from archives representing prior production runs at the factories. Samples were stored in borosilicate glass vials (1-dram) with PTFE cap liners. A pure sample of RDX from one of the factories (manufacturer C), was measured in 2009 and again 4 years later; measurements were not

Table 1
 $\delta^{13}\text{C}$ values for reactants (hexamine) and RDX produced at three different factories using two different processes. Batches 1–4 RDX and hexamine were sampled three times each; each sample was analyzed two times. Results shown are the batch means and SD of the mean $\delta^{13}\text{C}$ values obtained for each sample. For batches 3 and 4 (produced on the same day), the same hexamine source was used. For batches 5–10, one sample each was collected and analyzed two times. Results shown are the sample means and SD. Batches 5 and 6 were produced on the same day. Batches 7–10 were from prior productions (a span of 4 years), but the archived hexamine sources were identified and sampled alongside the RDX.

Factory	$\delta^{13}\text{C}_{\text{Hexamine}}$ (‰ vs. VPDB)	Process	Batch	$\delta^{13}\text{C}_{\text{RDX}}$ (‰ vs. VPDB)	ϵ_a (‰)
A	-48.7 ± 0.2	Bachmann	1 ^a	-47.8 ± 0.2	+0.9
B	-50.7^*	Direct nitration	2 ^b	-43.0 ± 0.2	+8.2
	-48.1 ± 0.2		3 ^b	-40.1 ± 0.3	+8.3
C	-48.1 ± 0.2	Direct nitration	4 ^b	-39.9 ± 0.1	+8.6
	-51.5 ± 0.1		5 ^b	-43.6^*	+8.3
	-51.4 ± 0.1		6 ^b	-43.5^*	+8.2
	-45.8 ± 0.1		7 ^c	-37.6^*	+8.6
	-37.4 ± 0.1		8 ^c	-29.5^*	+8.2
	-37.6 ± 0.1		9 ^c	-29.2 ± 0.1	+8.7
	-48.3^*		10 ^c	-36.9 ± 0.4	+12.0

* SD < 0.1

^a RDX was from a slurry in 60% acetic acid.

^b Crude RDX (pre-crystallization).

^c RDX (post-crystallization).

found to be significantly different for $\delta^{13}\text{C}$ values (t -test, $t = 0.369$, $df = 25$, $P = 0.715$) or $\delta^{15}\text{N}$ values (t -test, $t = 0.293$, $df = 28$, $P = 0.772$), suggesting the pure explosives were stable under these storage conditions.

2.2. Stock chemicals

Standard explosive solutions of RDX, HMX, TNT, and PETN were purchased from AccuStandard Inc. (New Haven, CT, USA) for calibration of the HPLC working standard and creation of a UV spectral library. A calibrated working standard was used for daily HPLC/UV normalization and consisted of samples collected from various factory sources. The working standard contained four explosive compounds mixed at the following concentrations: HMX, 152.66 $\mu\text{g}/\text{mL}$; RDX, 610.76 $\mu\text{g}/\text{mL}$; TNT, 560.82 $\mu\text{g}/\text{mL}$; PETN, 514.78 $\mu\text{g}/\text{mL}$. The working standard was dissolved in 1:1 methanol:acetonitrile and stored in sealed glass ampules at 4 °C. Methanol, water, acetonitrile, acetone, methylene chloride, and hexanes for HPLC and component separation were HPLC grade and purchased from Fisher Scientific (Tustin, California, USA). Sodium bicarbonate for sample neutralization and potassium hydroxide for conversion of nitric acid to potassium nitrate were purchased from VWR Scientific Products (South Plainfield, New Jersey, USA).

2.3. Sample preparation

Nitric acid and explosive material in acidic substrates were processed according to procedures outlined below within a week of sample acquisition. Hexamine samples were prepared for stable isotope analysis without further processing.

Explosive samples that contained ~1 g of RDX and/or HMX, water, residual nitric acid, and other impurities were tested for acidity with standard pH paper and neutralized with saturated sodium bicarbonate solution. The explosive material was separated from the aqueous phase by centrifugation, washed twice with deionized water, dried under an air stream, and extracted from the dried sodium bicarbonate and other acetone-insoluble contaminants by successive dissolution and centrifugation of the solution in acetone. After the solution was filtered and air-dried, it was analyzed for purity and explosive component composition by HPLC/UV.

Nitrate in nitric acid was precipitated as potassium nitrate for subsequent stable isotope analyses. To prepare potassium nitrate from the nitric acid, an aliquot of the sample nitric acid (0.25 mL) was placed in a piece of borosilicate tubing that was sealed at one end (9 mm OD, standard wall thickness, 20 cm length). The sealed end of the tube was frozen in liquid N_2 . A slight stoichiometric

Table 2
 $\delta^{15}\text{N}$ values for reactants (hexamine and nitric acid) and RDX produced at three different factories using two different processes^a. Batches 1–4 RDX and hexamine were sampled three times each; each sample was analyzed two times. Results shown are the batch means and SD of the mean $\delta^{15}\text{N}$ values obtained for each sample. For batches 3 and 4 (produced on the same day), the same hexamine source and nitric acid source was used. For batches 5–10, one sample each was collected and analyzed two times. Results shown are the sample means and SD. Batches 5 and 6 (produced on the same day) used the same nitric acid source, which was sampled twice; each sample was analyzed twice. Batches 7–10 were from prior productions (a span of 4 years). The nitric acid was not stored for batches 7–10 and therefore not sampled, precluding a computation of the apparent nitrogen enrichment factor.

Factory	$\delta^{15}\text{N}_{\text{Hexamine}}$ (‰ vs. air)	$\delta^{15}\text{N}_{\text{Nitric acid}}$ (‰ vs. air)	$\delta^{15}\text{N}_{\text{Reactants}}$ (‰ vs. air)	Process	Batch	$\delta^{15}\text{N}_{\text{RDX}}$ (‰ vs. air)	ϵ_a (‰)
A	-0.4 ± 0.2	-1.0 ± 0.4	-0.7	Bachmann	1 ^b	-4.3 ± 0.2	-3.6
B	$+0.8 \pm 0.3$	$+7.8 \pm 0.1$	+4.3	Direct nitration	2 ^c	-6.3 ± 0.4	-10.6
	-0.4 ± 0.1	$+13.7 \pm 0.1$	+6.7		3 ^c	-5.8^*	-12.4
C	-0.4 ± 0.1	$+13.7 \pm 0.1$	+6.7	Direct nitration	4 ^c	-6.0 ± 0.2	-12.6
	$+0.3 \pm 0.2$	-9.1^*	-4.4		5 ^c	-17.4 ± 0.3	-13.0
	$+0.2^*$	-9.1^*	-4.5		6 ^c	-17.2^*	-12.8
	-1.9 ± 0.1	-	-		7 ^d	-17.3^*	-
	0.5 ± 0.1	-	-		8 ^d	-16.1 ± 0.1	-
	-1.8 ± 0.1	-	-		9 ^d	-17.3^*	-
	$+0.4^*$	-	-		10 ^d	-16.7 ± 0.1	-

* SD < 0.1.

^a $\delta^{15}\text{N}_{\text{Reactants}}$ is calculated as $(\delta^{15}\text{N}_{\text{Hexamine}} + \delta^{15}\text{N}_{\text{Nitric acid}})/2$ and assumes for Factory A that: $\delta^{15}\text{N}_{\text{Ammonia}} = \delta^{15}\text{N}_{\text{Hexamine}}$ and $\delta^{15}\text{N}_{\text{Nitrate}} = \delta^{15}\text{N}_{\text{Nitric acid}}$ (see Eq. (2)).

^b RDX was from a slurry in 60% acetic acid.

^c Crude RDX (pre-crystallization).

^d RDX (post-crystallization).

excess of concentrated potassium hydroxide solution (14.4 M, 0.5 mL) was pipetted into a separate, smaller piece of borosilicate tubing that was also sealed at one end (6 mm OD, standard wall thickness, 6 cm length). The contents of the smaller tube were frozen in liquid N₂. The tube was shortened to near the top of the liquid level and placed in the 9-mm tubing on top of the frozen acid. The entire reaction vessel was then frozen in liquid N₂ and sealed under vacuum. Care was taken to properly anneal the top of the sealed vessel. Once annealed, the tube was allowed to equilibrate to room temperature and then inverted in a beaker of ice water (4 °C). Manual shaking facilitated the reaction, which was determined to be complete when no more heat was generated and precipitate was observed in the reaction vessel (~10 min). The reaction vessel was scored, opened, and the contents immediately tested with pH paper to assure the precipitated sample was basic. Potassium nitrate product was successively centrifuged and washed with methanol until the supernatant tested neutral with pH paper.

Explosive materials in nonexplosive matrices, such as the explosive formulation C-4, were subsampled to approximately 6 mg and the actual weight was recorded to 1-μg precision using a Sartorius MC-5 microbalance (Sartorius AG, Göttingen, Germany). Subsamples were extracted twice with hexanes (2 mL each) and both hexane-soluble and hexane-insoluble fractions were dried under an air stream. The hexane-soluble fraction was archived. The hexane-insoluble fraction was extracted twice with acetone (2 mL each) and the extract was filtered using a 13-mm diameter, 0.2-μm pore size GHP Acrodisc syringe filter (Pall Gelman Laboratory, Ann Arbor, Michigan, USA). The acetone-soluble fraction was dried under an air stream and subsequently dissolved in acetonitrile (1.00 mL). A 100-μL aliquot of the solution was diluted to 1/100 of its original concentration in a 4:5 ratio mixture of methanol:water in preparation for HPLC/UV analysis. Cast explosives, such as B-4, and pure explosive compounds, such as RDX and HMX crystals, were dissolved in acetone, then filtered, diluted, and analyzed via HPLC/UV as above without hexane extraction.

2.4. HPLC conditions

HPLC separations were conducted using a Waters Delta 600 solvent delivery system connected to a Waters 996 photodiode array detector (Waters Corporation, Milford, MA, USA). Data storage and analysis was performed with Waters Millennium chromatography software. For component quantification and identification, the analytical column consisted of a 8 mm × 100 mm radial compression module (Waters, WAT082887) equipped with a C18, 4-μm particle size Radial-Pak 5 mm × 100 mm cartridge (Waters, WAT025843). Solvent conditions were isocratic at 60% methanol in water with a flow rate of 0.8 mL/min. Chromatogram channels were set at 220 nm with a spectral acquisition between 210 and 340 nm. For preparative separations, the column consisted of a PrepLC 25 mm radial compression module (Waters, WAT015814) equipped with a C18, 6-μm particle size PrepPak 25 mm × 100 mm cartridge (Waters, WAT038510). A gradient was held between 33% and 80% methanol in water with a flow rate of 9.8 mL/min. Chromatogram channels were set at 220 nm with a spectral acquisition between 210 and 270 nm. Explosives components were identified by spectrum and retention time using a library created from commercially acquired standard explosive solutions. Explosive fractions were collected using the Waters Fraction Collector II with HMX, RDX, TNT, and PETN eluting at approximate apex retention times of 6.0, 10.8, 15.6, and 17.6 min, respectively, and with peaks resolving in less than 1.9 min. Peaks were baseline resolved. We collected the entire peak of each eluted explosive component and verified the amount

that was injected matched the amount collected gravimetrically. We also verified the purity of the eluted explosive components by elemental analysis. This method of HPLC separation of samples of pure explosives HMX and RDX should not affect the carbon and nitrogen isotope ratios of the compounds.

2.5. Stable isotope analysis

HPLC-purified explosive components HMX and RDX, as well as reagent hexamine, prepared potassium nitrate, and explosive samples that were considered pure (>95%) by analytical HPLC were loaded in duplicate, where possible, into 3 mm × 5 mm tin capsules (Costech Analytical, Valencia, California, USA) at a weight of 2.0 mg (±10%) for combined carbon and nitrogen isotope ratio analysis. Isotopic analysis was performed at the SIRFER facility at the University of Utah in Salt Lake City, Utah, USA on a Thermo Finnigan Delta S isotope ratio mass spectrometer (Bremen, Germany), operated in continuous flow mode, attached to an elemental analyzer (EA) with an autosampler (Carlo Erba, Milan, Italy). The quartz EA oxidation reactor was loaded according to manufacturer's specifications with silvered cobaltous/cobaltic oxide, chromium oxide, and quartz wool and operated at 1020 °C. The quartz EA reduction reactor tube, maintained at 650 °C, was packed with reduced copper wire filled between the bottom 40 mm of the tube and the top 30 mm of the tube to maintain a high temperature throughout the copper. Resultant water was removed by a magnesium perchlorate trap and product N₂ and CO₂ gases were separated by a 3-m 1/4" PoraPLOT Q packed column (Costech Analytical) at 40 °C. Helium flow rates were set at 95 mL/min. The mass spectrometer and ConFlo interface were configured to analyze both gases produced from a single capsule; N₂ and CO₂ gases were ~80% diluted by helium at the interface.

Stable isotope contents are expressed in 'delta' (δ) notation as values in ‰ (per mil), where $\delta = (R_A/R_{Std} - 1) \times 10^3$ (‰) and R_A and R_{Std} are the ratios of the rare to abundant isotope (e.g., ¹³C/¹²C) in the sample and the standard, respectively. The international standard used for carbon is Vienna Pee Dee Belemnite (VPDB) and the standard for nitrogen is atmospheric N₂ (air).

Samples were analyzed alongside an in-house laboratory reference material consisting of imidazole, which was used to normalize sample δ¹³C and δ¹⁵N data to international isotope scales. Imidazole was chosen to analyze alongside the explosive samples as it also contains a large amount of nitrogen relative to carbon (41% nitrogen and 53% carbon as compared to 38% nitrogen and 16% carbon for RDX). In addition, we included two pure nitramine explosive samples (HMX and RDX) that were chosen as quality control reference materials to monitor long-term instrument stability and estimate analytical uncertainty. The C/N ratio (by weight) of the explosives and reference materials were monitored to assess reactor conditions; a C/N value between 0.43 and 0.49 for both HMX and RDX inferred complete elution of N₂ gas. The reduction column was replaced after one third of the copper was oxidized (~200 samples) to maintain the required reductive capacity needed for samples with large amounts of nitrogen (unpublished data).

We later adopted two-point normalization for δ¹³C and δ¹⁵N data using the glutamic acid reference materials USGS40 and USGS41 (available from nist.gov as SRM8573 and SRM8574) [29,30]. Imidazole and the prior analyses were normalized using these reference materials. We estimated analytical uncertainty for analyses of RDX and HMX samples using the long-term standard deviations of a reference material (a pure RDX sample from Factory C, batch 9), which were 0.15‰ (n = 67) and 0.23‰ (n = 58) for δ¹³C and δ¹⁵N measurements, respectively.

2.6. Calculation of enrichment factors

We calculated the apparent fractionation factor, α_a , as

$$\alpha_a = \frac{\delta_{\text{Products}} + 10^3}{\delta_{\text{Reactants}} + 10^3}$$

and the apparent enrichment factor, ε_a , as

$$\varepsilon_a = (\alpha_a - 1) \times 10^3$$

For $\delta^{13}\text{C}$ enrichment factors in both Eq. (1) (direct nitration process) and Eq. (2) (Bachmann process), $\delta_{\text{Products}} = \delta^{13}\text{C}_{\text{RDX}}$ and $\delta_{\text{Reactants}} = \delta^{13}\text{C}_{\text{Hexamine}}$. For $\delta^{15}\text{N}$ enrichment factors, $\delta_{\text{Products}} = \delta^{15}\text{N}_{\text{RDX}}$, but $\delta_{\text{Reactants}}$ cannot be calculated directly from $\delta^{15}\text{N}_{\text{Hexamine}}$, as hexamine is only one of several possible sources of nitrogen in Eqs. (1) and (2). Nitrogen in RDX has two nonexchangeable oxidation states as amine and nitro groups in equal proportion. In direct nitration (Eq. (1)), all of the amine groups are derived from hexamine and all of the nitro groups are derived from nitric acid. So for direct nitration, we calculated:

$$\delta^{15}\text{N}_{\text{Reactants}} = \frac{\delta^{15}\text{N}_{\text{Hexamine}} + \delta^{15}\text{N}_{\text{Nitric acid}}}{2}$$

assuming that the contribution of nitrogen to the RDX is equal for both the amine and nitro nitrogen pools because RDX contains an equal amount of reduced and oxidized nitrogen atoms. In the Bachmann process, the amine groups are derived from a combination of hexamine and ammonium ions from ammonium nitrate. The nitro groups are derived from a combination of nitric acid and nitrate ions from ammonium nitrate. In this study, the relative contributions from hexamine, ammonium nitrate, and nitric acid were unknown, and the isotope ratio of ammonium nitrate used in the Bachmann process samples was not measured. Here we assumed the $\delta^{15}\text{N}$ values of ammonium ions in the ammonium nitrate and hexamine were identical at the manufacturer; likewise, we assumed that the $\delta^{15}\text{N}$ values of nitrate ions in the ammonium nitrate and nitric acid were identical. Validating this approach, we note that the $\delta^{15}\text{N}$ values of both the hexamine and nitric acid collected in this survey (see Table 2) were within the $\delta^{15}\text{N}$ range also shared by a vast majority of ammonia and nitrate sources (between -2% and $+2\%$, [31,32] as well as various hexamine sources (between -2.5% and $+1.1\%$) [17,19]. This allowed us to use the same formula for $\delta^{15}\text{N}_{\text{Reactants}}$ for both the direct nitration and Bachmann process models.

Statistical analyses were completed using Prism 5.0c software for Mac OS X (GraphPad Software, Inc., San Diego, California, USA). Paired *t*-tests were two-tailed and assumed normality, as δ -values are considered continuous over the ranges studied. Tests for significance used an α value of 0.05.

3. Results

3.1. Isotopic relationship between RDX and its reactants in factory samples

Where it was possible to collect reactant hexamine and the product RDX for production runs at the three visited factories, we present $\delta^{13}\text{C}_{\text{Hexamine}}$, $\delta^{13}\text{C}_{\text{RDX}}$, and the associated apparent enrichment factor ε_a (Table 1). For the direct nitration batches at Factories B and C, ε_a ranged from $+8.2$ to $+12.0\%$ (Table 1). For these reactions, $\delta^{13}\text{C}_{\text{Hexamine}}$ was equivalent to $\delta^{13}\text{C}_{\text{RDX}}$ with a constant offset. The best fit for the model was the line $\delta^{13}\text{C}_{\text{RDX}} = 0.99 \times \delta^{13}\text{C}_{\text{Hexamine}} + 8.2\%$ ($r^2 = 0.96$, $F_7 = 157.1$, $P < 0.0001$). For the

Bachmann process batch at Factory A, ε_a was $+0.9\%$. To determine if ε_a associated with the Bachmann process was different from ε_a associated with direct nitration, we performed a one-sample *t*-test comparing the available Bachmann sample to the population defined above for direct nitration. The calculated ε_a associated with the Bachmann process sample was significantly more negative relative to the mean ε_a associated with the direct nitration samples by 7.9% ($t = 19.40$, $P < 0.0001$, $df = 8$).

Where it was possible to collect both hexamine and nitric acid reactants used to produce RDX, we calculated $\delta^{15}\text{N}_{\text{Reactants}}$ from $\delta^{15}\text{N}_{\text{Hexamine}}$ and $\delta^{15}\text{N}_{\text{Nitric acid}}$. Together with these values, we present $\delta^{15}\text{N}_{\text{RDX}}$ and the associated enrichment factor ε_a calculated from $\delta^{15}\text{N}_{\text{Reactants}}$ and $\delta^{15}\text{N}_{\text{RDX}}$ in Table 2. For the direct nitration batches at Factories B and C, ε_a ranged between -13.0% and -10.6% (Table 2). For these reactions, $\delta^{15}\text{N}_{\text{Reactants}}$ was equivalent to $\delta^{15}\text{N}_{\text{RDX}}$ with a constant offset. The best fit for the model was the line $\delta^{15}\text{N}_{\text{RDX}} = 1.06 \times \delta^{15}\text{N}_{\text{Reactants}} - 12.4\%$ ($r^2 = 0.98$, $F_3 = 138.4$, $P = 0.0013$). For the Bachmann process batch at Factory A, ε_a was -3.6% . To determine if ε_a associated with the Bachmann process was different from ε_a associated with direct nitration, we performed a one-sample *t*-test comparing the available Bachmann sample to the population defined above for direct nitration. The calculated ε_a associated with the Bachmann process sample was significantly more positive by 8.7% ($t = 20.10$, $P < 0.0001$, $df = 4$).

Within-batch variation, assessed by the standard deviations of three samples each taken from four different batches, was 0.1 – 0.3% for $\delta^{13}\text{C}_{\text{RDX}}$ and 0.1 – 0.4% for $\delta^{15}\text{N}_{\text{RDX}}$, combining for a pooled standard deviation of 0.18% and 0.19% , respectively.

3.2. Relationship between HMX and RDX collected from the same explosive sample

HMX was isolated from 44 explosive samples that contained RDX. The pooled standard deviations of 14 duplicate HMX analyses (30 samples were analyzed only once) were 0.68% and 0.74% for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values, respectively. Scatterplots of $\delta^{13}\text{C}_{\text{HMX}}$ as a function of $\delta^{13}\text{C}_{\text{RDX}}$ and $\delta^{15}\text{N}_{\text{HMX}}$ as a function of $\delta^{15}\text{N}_{\text{RDX}}$ are presented in Fig. 1. For all factories except Factory B, the data points generally fit along a 1:1 line; i.e., the RDX isotopically matched the HMX over a range of isotope ratios. These ranges were -49.52% to -31.32% for $\delta^{13}\text{C}_{\text{RDX}}$ values and -12.0% to -0.49% for $\delta^{15}\text{N}_{\text{RDX}}$ values. We calculated a linear regression for both relationships for the set of all samples excluding Factory B: $\delta^{13}\text{C}_{\text{HMX}} = 0.92 \times \delta^{13}\text{C}_{\text{RDX}} - 4.9\%$ ($r^2 = 0.88$, $F_{37} = 270.9$, $P < 0.0001$), and $\delta^{15}\text{N}_{\text{HMX}} = 0.97 \times \delta^{15}\text{N}_{\text{RDX}} - 0.86\%$ ($r^2 = 0.95$, $F_{37} = 689.4$, $P < 0.0001$). The two equations had slopes not significantly different from 1; however, the intercepts were significantly different from 0. By paired *t*-tests, we found that for this set of samples, $\delta^{13}\text{C}_{\text{HMX}}$ was significantly more negative than $\delta^{13}\text{C}_{\text{RDX}}$ by 1.16% ($t = 6.58$, $P < 0.0001$, $df = 38$), and $\delta^{15}\text{N}_{\text{HMX}}$ was significantly more negative than $\delta^{15}\text{N}_{\text{RDX}}$ by 0.68% ($t = 6.07$, $P < 0.0001$, $df = 38$).

3.3. Carbon and nitrogen isotope ratios of RDX

Paired $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of RDX from factory collections and RDX extracted and purified from manufactured explosive products are plotted in Fig. 2. Data represent 100 samples from 12 different factories. The range spanned by $\delta^{13}\text{C}_{\text{RDX}}$ values was -49.5% to -16.6% ; the range spanned by $\delta^{15}\text{N}_{\text{RDX}}$ values was -17.4% to $+8.5\%$. Each point on the scatterplot represents the mean of two measurements, where possible. The pooled standard deviations of 81 duplicate RDX analyses (19 samples were analyzed only once due to limited material) were 0.20% and 0.18% for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values, respectively. Standard deviations for samples analyzed in duplicate ranged from less than 0.01% to 1.8% for $\delta^{13}\text{C}$, and

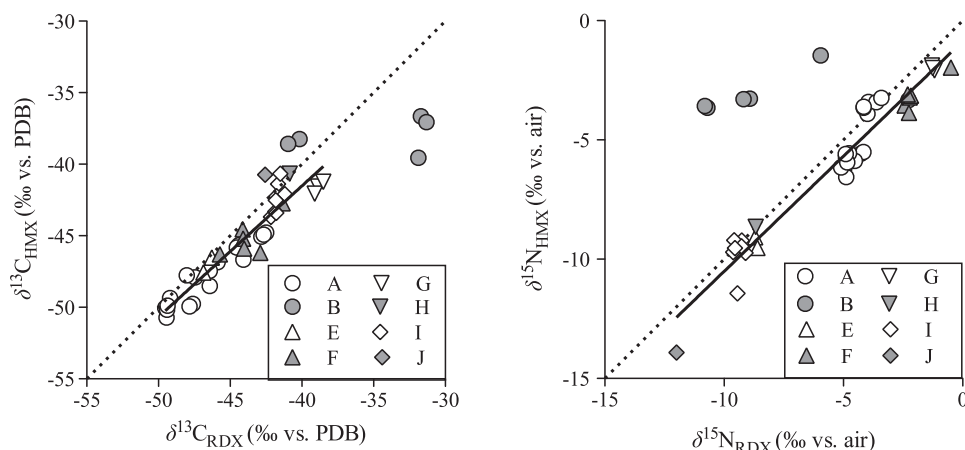


Fig. 1. Left: scatterplot of $\delta^{13}\text{C}$ of HMX vs. $\delta^{13}\text{C}$ of RDX from the same explosive sample. Right: scatterplot of $\delta^{15}\text{N}$ of HMX vs. $\delta^{15}\text{N}$ of RDX from the same explosive sample. Each of the 44 data points in each plot represents single samples distinguished by the factory (A through J) that produced them. Dotted lines represent a theoretical 1:1 relationship between RDX and HMX isotope ratios. Solid lines represent linear regressions between RDX and HMX for the set of samples excluding Factory B. Samples were analyzed in duplicate, where possible; data points represent means of replicate analyses of a single sample. Estimated analytical uncertainty based on the long-term standard deviations of a reference material were 0.15‰ ($n = 67$) and 0.23‰ ($n = 58$) for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements, respectively.

between 0.01‰ and 0.5‰ for $\delta^{15}\text{N}$. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of the 100 samples were not significantly correlated (Spearman $r = 0.019$, $P = 0.7876$), indicating that they can be used as independent variables. We do not have equivalent sample numbers for each manufacturer, as sampling was mostly opportunistic; some manufacturers were sampled 25 times, while others were sampled once. Moreover, this dataset represents samples from a range of timescales between manufacturers. Thus, we do not attempt to define within-manufacturer isotope ratio variation or variation associated with time.

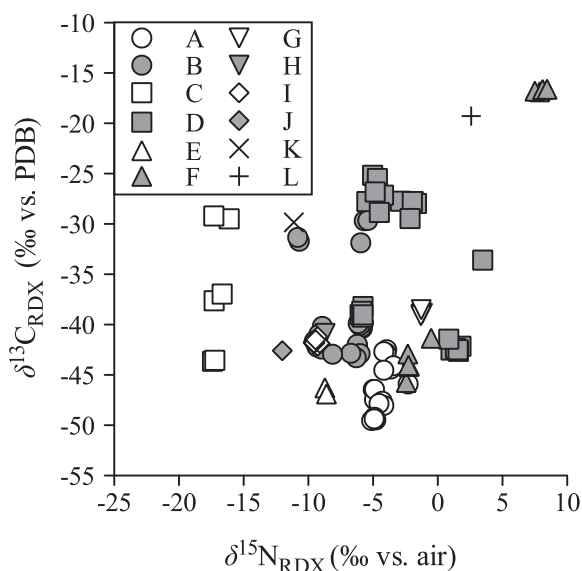


Fig. 2. Scatterplot of pairwise $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of RDX from factory collections and RDX extracted and purified from authentic manufactured explosive products. Each of the 100 data points represents single samples distinguished by the factory (A through L) that produced them. Samples were analyzed in duplicate, where possible; data presented are means of replicate analyses. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were not significantly correlated. Estimated analytical uncertainty based on the long-term standard deviations of a reference material were 0.15‰ ($n = 67$) and 0.23‰ ($n = 58$) for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements, respectively.

4. Discussion

4.1. RDX products from the direct nitration process become enriched in ^{13}C compared to reactants

For the direct nitration process samples obtained from two factories, we observed a relatively consistent ^{13}C enrichment factor between RDX and hexamine of $\sim 8.2\%$, with RDX enriched relative to hexamine (Table 1). These enrichment factors observed in factory samples were similar to that observed in small-batch direct nitration by Lock et al. using the Woolwich process in a laboratory (+8.69‰; [19]). In contrast, the observed ϵ_a value for the Bachmann sample at Factory A (+0.9‰) was significantly smaller than those observed for reactants and products in the direct nitration process. These results support the pattern we expected based on the equations describing the direct nitration process (Eq. (1)) and the Bachmann process (Eq. (2)). Based on whether the Bachmann process or direct nitration process was used to synthesize the explosives (determined possibly by the presence/absence of HMX or acetic acid residues), a forensic scientist may infer the $\delta^{13}\text{C}$ value of the hexamine used to produce a recovered RDX sample—it will either be greatly (~ 8 – 9%) or subtly ($\sim 1\%$) depleted relative to the RDX. Conversely, one may infer the possible $\delta^{13}\text{C}$ values of a produced RDX sample given a known synthesis method and the $\delta^{13}\text{C}$ values of a recovered hexamine reactant. Information about carbon isotope fractionation may be used to exclude or infer potential origins of an explosive, as it supplies information to an investigation about the synthesis process and the reactants.

4.2. RDX products from both the direct nitration and the Bachmann processes become isotopically depleted in ^{15}N compared to reactants

Despite a limited number of factory-collected samples, we found that the apparent enrichment factors associated with $\delta^{15}\text{N}_{\text{Reactants}}$ and $\delta^{15}\text{N}_{\text{RDX}}$ were consistently different between the two processes. For batches 2–6, which used direct nitration processes, we observed significantly more negative ϵ_a values than in batch 1, which used the Bachmann process (Table 2).

There are two probable mechanisms that may contribute to the more negative ϵ_a in direct nitration as opposed to the Bachmann process. The first mechanism is similar to that

described for ^{13}C enrichment during the direct nitration process. As a result of the first broken C–N bond in nitrolysis (see the Supporting information), depleted nitrogen becomes preferentially incorporated into RDX instead of being released as ammonia. This mechanism would not apply in the Bachmann process, where there is no ammonia side-product. The second mechanism involves the contribution to $\delta^{15}\text{N}_{\text{RDX}}$ from nitric acid. Direct nitration requires stronger nitric acid than in the Bachmann process [26]. The more negative ϵ_a values observed in direct nitration processes are consistent with the expectation that a smaller proportion of the initial nitric acid is incorporated into RDX in direct nitration than in the Bachmann process. In addition, the higher reaction temperature (75 °C as opposed to 25–38 °C [25]) in the Bachmann process may also reduce the apparent fractionation between $\delta^{15}\text{N}_{\text{Nitric acid}}$ and $\delta^{15}\text{N}_{\text{RDX}}$, as ϵ_a values tend to approach zero at higher temperatures [33].

Using these fractionation factors, a forensic scientist may hypothesize a link between a set of reactants of known $\delta^{15}\text{N}$ and a suspect RDX sample, since the reactants also suggest the method used to produce the RDX or RDX/HMX. Though the inference of reactant $\delta^{15}\text{N}$ by way of the reaction mechanism and fractionation factors may not be as straightforward as it is for $\delta^{13}\text{C}$ due to multiple sources of nitrogen, a forensic scientist may infer the $\delta^{15}\text{N}$ value of one of the reactants if the others are known; for example, the $\delta^{15}\text{N}$ of a suspect hexamine may be inferred given the $\delta^{15}\text{N}$ of a recovered RDX, nitric acid, and other traces that allow one to infer the process used. Likewise, information about nitrogen isotope fractionation may be used to exclude or infer potential origins of an explosive.

4.3. HMX and RDX in samples have a predictable isotopic relationship

As expected, paired RDX and HMX δ -values from the same explosives sample generally fit a 1:1 line. However, three samples from Factory B had $\delta^{13}\text{C}_{\text{HMX}}$ values 4–8‰ more negative than $\delta^{13}\text{C}_{\text{RDX}}$, and six samples from Factory B had $\delta^{15}\text{N}_{\text{HMX}}$ values 4–7‰ more positive than the $\delta^{15}\text{N}_{\text{RDX}}$ values. As Factory B employed a direct nitration process to produce RDX, it is possible the samples may be a mixture of HMX and/or RDX produced with the Bachmann process combined with RDX produced by the direct nitration process. Post-production mixing would theoretically result in HMX with a lower $\delta^{13}\text{C}$ value than the RDX and a higher $\delta^{15}\text{N}$ value than the RDX given the same hexamine and nitric acid reactants.

Due to its explosive power and compatibility with RDX, HMX is an accepted and established side-product at 8–12% of the total nitramine mass in what is called “Type B RDX” [24] or “Type II RDX”, which is required to contain 4–17% HMX by military specification [34]. To comply with these military standards, manufacturers may blend RDX produced by one process with HMX and/or RDX that is produced by another to attain the required RDX:HMX ratio. An isotopic comparison of RDX to HMX may indicate that this mixing happened post-synthesis, since the general pattern for RDX/HMX manufacturers shows significant but small depletions in HMX relative to RDX in both ^{13}C (1.16‰) and ^{15}N (0.68‰) content. A forensic scientist may be interested in evaluating the evidence provided by relative differences in isotope ratios between HMX and RDX with regards to two competing hypotheses: (1) HMX and RDX within the sample were produced in one reaction, and (2) HMX and/or RDX within the sample were produced in separate reactions and later combined (as in Factory B). Such an approach may have direct applications to RDX-containing explosives of unknown origin recovered in caches. Here, distinguishing among the practices of manufacturing facilities has direct applications to forensic and intelligence-related investigations.

4.4. Observed isotope ratios vary between and within factories

Both variations in process and in isotope ratios of the reactants likely contribute to the wide ranges in $\delta^{13}\text{C}_{\text{RDX}}$ and $\delta^{15}\text{N}_{\text{RDX}}$ shown in Fig. 2. As Lock et al. have shown previously, a range of $\delta^{13}\text{C}_{\text{Hexamine}}$ (–46.18‰ to –34.51‰) could contribute to an offset range of $\delta^{13}\text{C}_{\text{RDX}}$ (–38.34‰ to –26.23‰) as a result of a consistent fractionation factor. Assuming that a manufacturer maintains a consistent synthesis method, we may infer that changes in $\delta^{13}\text{C}_{\text{RDX}}$ and $\delta^{15}\text{N}_{\text{RDX}}$ are likely due to changes in reactant isotope ratios. These changes in isotope ratio of reactants may be due to a change in supplier or the supplier's raw materials. Our samples from one manufacturer (Factory C) showed that the $\delta^{13}\text{C}_{\text{Hexamine}}$ varied over the span of several years, and $\delta^{13}\text{C}_{\text{RDX}}$ was related to $\delta^{13}\text{C}_{\text{Hexamine}}$ by the process-specific enrichment factor of ~8.2‰. Conversely, since Factory C had consistent $\delta^{15}\text{N}_{\text{Hexamine}}$ and $\delta^{15}\text{N}_{\text{Nitric acid}}$, $\delta^{15}\text{N}_{\text{RDX}}$ varied little over two production runs (see Table 2). These relative differences in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ variation may suggest similar patterns in certain manufacturers such as Factory A and I (Fig. 2), where $\delta^{13}\text{C}_{\text{Hexamine}}$ varies along with source, whereas nitric acid sources and/or $\delta^{15}\text{N}_{\text{Hexamine}}$ and $\delta^{15}\text{N}_{\text{Nitric acid}}$ remain relatively constant. Other factories (B and D) produced RDX that varied in both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, suggesting they used a range of both hexamine and nitric acid sources. A source of ^{15}N -enriched nitric acid, and hence $\delta^{15}\text{N}_{\text{Nitric acid}}$ variation, could be an explosives manufacturer that recycles its own residual nitric acid.

Our survey (Fig. 2) includes RDX with more positive carbon and nitrogen isotope ratios than any previously reported, with $\delta^{13}\text{C}_{\text{RDX}}$ values > –20‰ and $\delta^{15}\text{N}_{\text{RDX}}$ values > +5‰ (e.g., Factory F, Fig. 2). We also observed $\delta^{13}\text{C}_{\text{RDX}}$ values less than –45‰, more negative than any values previously reported. Each of these highly ^{13}C depleted samples (from Manufacturers A, E, and F) also contained 5–10% HMX. The negative $\delta^{13}\text{C}_{\text{RDX}}$ observations were probably associated with relatively depleted hexamine and the small apparent enrichment factor associated with the Bachmann process.

Very little published isotopic data on RDX from varying sources are available for comparisons. Several other studies have reported isotope ratios of control RDX for the purpose of monitoring RDX degradation in the environment. Gelman et al. [6] and Bernstein et al. [35] both reported $\delta^{13}\text{C}_{\text{RDX}}$ and $\delta^{15}\text{N}_{\text{RDX}}$ within the ranges reported by Lock et al. [5]. In comparison, the range of $\delta^{13}\text{C}_{\text{RDX}}$ values in our survey was 33‰; the range of $\delta^{15}\text{N}_{\text{RDX}}$ values was 26‰. These larger ranges are likely due to a more extreme set of reactant stable isotope ratio values combined with RDX produced by two different methods. These ranges, considered as a measure of between-source variation, are very large compared to within-batch variation, within-sample variation, and the standard deviation of a pure RDX reference material (approximately 0.2‰ for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$). These data illustrate the powerful selectivity of comparative isotope ratio measurements of two RDX samples.

Military grade explosives containing RDX and HMX have been used in terrorism events (e.g., improvised explosive devices) and are likely to be used again in the future by domestic or foreign terrorists. Applying the isotope analysis approach described here to explosives containing RDX and/or HMX has direct application to terrorism-related studies, especially in the direct link between explosives recovered at a scene and explosives recovered elsewhere. Whereas comparisons of relative chemical composition and trace chemical analyses have been useful comparative tools in the past, the analyses of stable isotopes greatly increase the likelihood of distinguishing or linking explosives recovered at a scene and elsewhere because the evidence must be consistent both in terms of chemical composition and in multiple isotopes in order for two samples to share a common origin. The dataset presented here has application in isotope forensics by defining the possible

combinations of paired $\delta^{13}\text{C}$ – $\delta^{15}\text{N}$ values for RDX and RDX/HMX explosives, as well as providing a possible background dataset for evaluation of isotopic evidence. Using the reactant–product relationships explored above, an investigator may also evaluate the evidence including $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ RDX and HMX values obtained from an explosive sample of unknown origin with regards to the following hypotheses: (1) Was the sample produced using a particular suspect hexamine source? (2) Was the sample produced using a particular set of hexamine and nitric acid reactants? (3) Was the sample mixed from explosives produced using the Bachmann method and the direct nitration method separately? (4) Was the sample from a particular manufacturer as opposed to another?

4.5. Future work

Several additional efforts will help improve our understanding of isotope fractionation in RDX and extend its applicability in isotope forensics. Though ^{13}C fractionation between RDX and its reactants may be well characterized for direct nitration processes, the fractionation factors for the Bachmann process should be further explored through additional observations at factories with known production methods. In addition, $^2\text{H}/^1\text{H}$ analyses could help to match a hexamine reactant with that of the RDX product irrespective of synthesis method, as only secondary isotope effects would be expected through the currently understood mechanism. We should deconvolve the fractionation factors associated with the amine and nitro nitrogen by developing a method to measure $\delta^{15}\text{N}$ values of the groups separately, which could allow inference of reactant nitric acid and hexamine independently. The hypothesized effect of temperature and nitric acid concentration on nitric acid fractionation in RDX synthesis should also be examined. Analyses of $^{18}\text{O}/^{16}\text{O}$ isotope ratios may elucidate fractionation factors associated with nitrolysis, as the oxygen isotope signal is directly related to the nitric acid source and is not dependent upon oxygen in any other reactant. Finally, more purified RDX from samples of known manufacturer as well as time of production should be added to the body of stable isotope literature. By better understanding the extent of both within-source variation and between-source variation of isotope ratios in explosives, we increase the predictive power of models that infer a source based on chemical and isotopic characteristics of an unknown sample.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.forsciint.2014.04.013>.

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