Isolation of components of plastic explosives for isotope ratio mass spectrometry

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Abstract
An improved method for the separation of the components of plastic explosives is described with the goal of stable isotope ratio analysis of each isolated component. The binder and plasticizer of a plastic explosive were extracted into cyclohexane, leaving the explosive components and other insoluble material. The plasticizers, oils, and additives were next extracted from the dried cyclohexane-soluble fraction into acetone, leaving the polymeric binder. Plasticizers, oils, and additives were identified by GC–MS and individual plasticizers, oils, dyes, and antioxidants were isolated by GC and/or flash chromatography free of interfering materials. The explosive components were extracted from the cyclohexane-insoluble fraction with acetone, and then quantitatively analyzed for individual explosive compounds via HPLC-UV/Vis spectroscopy. Individual explosive compounds were isolated via preparative HPLC. The separation process was validated by gravimetric, HPLC-UV/Vis, EA, GC–MS, TC/EA, and FTIR results consistent with the expected formulation of the plastic explosives. The isolated components were analyzed for component-specific stable isotope ratios. Control mixtures of previously characterized components of two common plastic explosive formulations were also separated and analyzed. These isolated components retained the isotope ratios prior to mixture, demonstrating the robustness and reliability of the technique. Two example C-4 explosives from different sources, with indistinguishable chemical composition and raw explosive $^{13}$C/$^{12}$C and $^{15}$N/$^{14}$N isotope ratios, were extracted and analyzed. The resultant binder and plasticizer $^2$H/$^1$H and $^{13}$C/$^{12}$C results were used to discriminate between the two C-4 samples that were otherwise apparently identical.

Introduction

Analytical chemists conduct a variety of analyses on explosives for intelligence and investigation purposes. The chemical makeup of an explosive or explosive residue is often a vital piece of information, and can differentiate sources of explosive material, whether that source is an environmental contaminant site, a stockpile diverted from a legitimate source, or a clandestine manufacturing facility [1]. Ideally, an explosive would have a characteristic, identifying “signature” that allows law enforcement and intelligence agencies to unambiguously identify its source – e.g., a particular block, package, batch, lot, or manufacturer.

The chemical properties of explosives and their residues are often the most characteristic features of a bomb scene, notwithstanding the physical construction of the bomb itself. Though there are a near-infinite variety of formulations to produce chemical explosives, the similarities between different manufacturers’ formulas, combined with the inherent variability in a single manufacturer’s formula, may lead an investigator to falsely equate two explosives from different sources that have similar chemical properties – i.e., a “false match” [3,4]. These false matches may not be due to poor analytical practices, but inherent variability in bulk measurements of a composite material, like an explosive.

Isotope ratio analysis of explosives—and more powerfully, isotope ratio analysis of individual explosive components—provides for discrimination that is not possible through chemical analysis alone [5–15]. This is especially true when extraneous contaminants may obscure the chemical profile of an explosive component [9,16–18], individual components from explosive residue extraction require compound-specific sourcing data [19–21], or links between an explosive precursor and product are part of the investigation [22–25]. In this paper, we demonstrate and validate methods in a framework described separately [26] that can be used to isolate multiple components from plastic explosives. We show that isolated components from mock C-4 and Semtex mixtures are
sufficiently pure to produce isotope ratios that reflect those of the original components. We also show how component-specific isotope ratio analysis of nonexplosive materials of a mixture can help discriminate explosive samples that were otherwise indistinguishable based on chemical composition analysis, isotope ratio analysis of the raw explosive, or analysis of the most abundant compound in C-4 (RDX).

Analysis of multiple components of an explosive is an example of using multiple orthogonal techniques, where significantly different approaches for matching and discriminating materials arrive at similar conclusions [18]. This approach supplements and validates explosive isoformic evidence in the criminal justice system, which has increasingly higher standards of data and method validation [27,28]. A statistical basis for evaluating component-specific evidence with relation to equating sources requires a background population dataset for the separate components, including a well-defined source level [29,30]. These statistical methods have been discussed elsewhere [31], and are applicable for explosives, as well [4]. Though providing background data are outside the scope of this paper, we demonstrate the first step to this goal—consistently good discrimination—by reliably and robustly separating and analyzing individual plastic explosive components.

Materials and methods

Chemicals

Optima-grade acetone, cyclohexane, and dichloromethane were obtained from Fisher Scientific (Tustin, CA, USA). HPLC-grade methanol, water, and acetonitrile were purchased from VWR Scientific Products (South Plainfield, NJ, USA). Standard explosive solutions of HMX, RDX, and PETN for the creation of a UV spectral library and calibration of HPLC working standards were purchased from Accustandard, Inc. (New Haven, CT, USA). Isofocens, Inc. provided the C-4 explosive samples labeled “1", “4", and “1261" and pure explosive material used for control mixtures and method development. RDX (identifier 522), HMX (identifier 291), and PETN (identifier 544) reference materials for elemental analysis, extraction controls, and IRMS quality control were characterized according to a previously published method [32]. C18 resin (BakerBond® Octadex 40 μm Prep LC packing) for flash chromatography was obtained from VWR (cat #J7025-00, lot J2687). Mineral oil for method development was obtained from Mallinckrodt (cat #6358, lot 6358 A06833). Other commercially available chemicals used as reference materials were purchased from Sigma-Aldrich (Saint Louis, MO, USA); these were styrene-butadiene rubber (branched copolymer, 21 w/w% styrene, catalog #432474-100G, lot 017088), polyisobutylene (cat #181455-100G, lot MB982131), bis(2-ethylhexyl) adipate (cat #02140, lot 1319532 @010732), N-phenyl-2-naphthaleneamine (cat #17055-25G, lot 050609HV), and Sudan I (cat #013624-G, lot 050609). Alkanes used for retention time indices and isotope ratio normalization included docosane (cat #134457-100G, lot 07404ATA), dodecane (D221104-100ML, lot 17320TA), dotriacanone (cat #D233107-5G, lot 08225AE), eicosane (cat #21927-5G, lot 02812EE), hexadecane (cat #296317-100ML, lot 00728BC), hexatriacontane (cat #H12552-25G, lot 10818PC), octacosane (cat #0504-25G, lot 06725AD), octadecane (cat #0052-25G, lot 17119MD), tetracosane (cat #TB752-25G, lot 18101EE), and tetracosane (cat #172456-100G, lot 10011B8). All drying and manipulation of volatile organic substances took place in a fume hood or properly vented area.

Control mixtures

Control mixtures, mimicking the compositions typical of C-4 and Semtex, were produced to demonstrate the robustness and reliability of the fraction separation techniques. The relevant isotope ratios and elemental compositions of individual “source” components used in the mixtures were previously measured (Table 1). The relative amount of each component in the mixtures are also listed in Table 1. To prepare the mixtures, the listed amounts of each explosive component (HMX and RDX for C-4, PETN and RDX for Semtex) were added in crystalline form to the vials, mixtures of the nonexplosive components dissolved in cyclohexanes were added, and the completed mixtures dried under an oil-free air stream. The nonexplosive mixtures were composed of bis(2-ethylhexyl) adipate, mineral oil, and polyisobutylene for C-4; mineral oil, N-phenyl-2-naphthaleneamine, Sudan I, and styrene-butadiene rubber for Semtex. Four separate aliquots of each control mixture were prepared. Additional aliquots of each nonexplosive mixture were processed alongside the explosive mixtures as controls.
Table 1
Gravimetric, HPLC-UV/Vis, $\delta^{13}$C, $\delta^{2}$H, and $\delta^{15}$N data for components isolated from control mixtures of C-4 and Semtex compared to theoretical component composition and known isotope ratios of the individual components prior to mixture. Analysis of true C-4 sample 1261 is shown for comparison. Delta ($\delta$) values are in “permil” (ppm), or parts per thousand. Values in italics are calculated from the sum of total components measured. Four of each type of control mixture were prepared. Gravimetric data were aggregated by mixture type (C-4 or Semtex). Relative error for gravimetric measurements was 1–3% except for the oil fraction of Semtex, which was 25%. Relative error for HPLC data was 4–10%. Isolated components from each of the 8 mixture vials were measured for isotope ratios 1–2 times each where possible; listed values for each component are aggregated as mean ± SD for that mixture type (C-4 or Semtex).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fraction/component</th>
<th>Target amount (mg)</th>
<th>Theor. w/%</th>
<th>$\delta^{13}$C, source</th>
<th>$\delta^{2}$H, source</th>
<th>$\delta^{15}$N, source</th>
<th>Component isolated w/w% (gravi-metric)</th>
<th>w/w% (HPLC)</th>
<th>$\delta^{13}$C, isolated</th>
<th>$\delta^{2}$H, isolated</th>
<th>$\delta^{15}$N, isolated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control mix C-4</td>
<td>RDX</td>
<td>40.900</td>
<td>90.0%</td>
<td>$-29.70 \pm 0.04$</td>
<td>$-16.16 \pm 0.03$</td>
<td>RDX</td>
<td>88.4%</td>
<td>85.8%</td>
<td>$-29.70 \pm 0.05$</td>
<td>$-16.20 \pm 0.05$</td>
<td></td>
</tr>
<tr>
<td>n = 4</td>
<td>HMX</td>
<td>4.100</td>
<td>8.2%</td>
<td>$-51.03 \pm 0.09$</td>
<td>$-1.93 \pm 0.18$</td>
<td>HMX</td>
<td>77.8%</td>
<td>8.0%</td>
<td>$-50.82 \pm 0.08$</td>
<td>$-2.13 \pm 0.06$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Binder (PIB)</td>
<td>1.300</td>
<td>2.6%</td>
<td>$-25.83 \pm 0.04$</td>
<td>72.5 ± 2.5</td>
<td>Binder</td>
<td>2.7%</td>
<td>6.5%</td>
<td>$-25.88 \pm 0.03$</td>
<td>72.5 ± 2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oil</td>
<td></td>
<td>7.4%</td>
<td>$-30.65 \pm 0.07$</td>
<td>159.9 ± 2.9</td>
<td>BEHA</td>
<td>5.6%</td>
<td>1.8%</td>
<td>$-30.61 \pm 0.07$</td>
<td>159.7 ± 1.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BEHA</td>
<td>2.800</td>
<td>0.900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Mineral oil</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control mix Semtex</td>
<td>Explosive</td>
<td>20.775</td>
<td>81.6%</td>
<td>$-37.43 \pm 0.35$</td>
<td>$-16.62 \pm 0.07$</td>
<td>RDX</td>
<td>35.5%</td>
<td>71.2%</td>
<td>$-37.43 \pm 0.12$</td>
<td>$-16.66 \pm 0.05$</td>
<td></td>
</tr>
<tr>
<td>n = 4</td>
<td>RDX</td>
<td>20.775</td>
<td>41.6%</td>
<td>$-46.53 \pm 0.44$</td>
<td>$-10.96 \pm 0.28$</td>
<td>PETN</td>
<td>35.7%</td>
<td>10.87 ± 0.1</td>
<td>$-46.49 \pm 0.17$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Binder (SBR)</td>
<td>4.500</td>
<td>9.0%</td>
<td>$-26.61 \pm 0.11$</td>
<td>$-33.1 \pm 3.1$</td>
<td>Binder</td>
<td>8.6%</td>
<td>9.8%</td>
<td>$-26.60 \pm 0.03$</td>
<td>33.8 ± 1.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oil***</td>
<td>3.450</td>
<td>6.9%</td>
<td>$-27.97 \pm 0.01$</td>
<td>$-136.4 \pm 1.1$</td>
<td>Mineral oil</td>
<td></td>
<td></td>
<td>$-27.95 \pm 0.09$</td>
<td>136.7 ± 2.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dye</td>
<td>0.250</td>
<td>0.5%</td>
<td>$-27.41 \pm 0.13$</td>
<td>147.0 ± 1.2</td>
<td><strong>Sudan I</strong></td>
<td></td>
<td></td>
<td>$-27.33 \pm 0.21$</td>
<td>150.8 ± 1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Antioxidant</td>
<td>0.250</td>
<td>0.5%</td>
<td>$-26.99 \pm 0.05$</td>
<td>$-186.1 \pm 5.8$</td>
<td><strong>2NPA</strong></td>
<td></td>
<td></td>
<td>$-27.00 \pm 0.09$</td>
<td>183.6 ± 1.4</td>
<td></td>
</tr>
<tr>
<td>True C-4 (1261)</td>
<td>Explosive</td>
<td>90.0%</td>
<td>81.8%</td>
<td>$-46.69 \pm 0.08$</td>
<td>$-2.39 \pm 0.58$</td>
<td>RDX</td>
<td>88.9%</td>
<td>86.3%</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>n = 8</td>
<td>RDX</td>
<td></td>
<td>8.2%</td>
<td>$-49.08 \pm 0.24$</td>
<td>$-3.01 \pm 0.46$</td>
<td>HMX</td>
<td>77.7%</td>
<td>8.7%</td>
<td>$-28.25 \pm 0.12$</td>
<td>$-87.2 \pm 1.0$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Binder (PIB)</td>
<td>2.6%</td>
<td>2.6%</td>
<td>$-28.25 \pm 0.12$</td>
<td>$-87.2 \pm 1.0$</td>
<td>PIB</td>
<td>6.7%</td>
<td>1.8%</td>
<td>$-29.14 \pm 0.08$</td>
<td>122.6 ± 1.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oil</td>
<td>7.4%</td>
<td>7.4%</td>
<td>$-29.14 \pm 0.08$</td>
<td></td>
<td>BEHA</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BEHA</td>
<td>5.6%</td>
<td>5.6%</td>
<td>$-122.6 \pm 1.6$</td>
<td></td>
<td>Process oil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bold: Significantly different at the $\alpha = 0.05$ level.
Dye is Sudan I; antioxidant is 2-naphthylphenylamine.
* By HPLC.
** By GC-IsoLink or GC–MS.
*** Only 3 of this fraction was further processed.
the cyclohexane-insoluble fraction, dried and weighed, then prepared for HPLC (the “explosive” fraction). Any cyclohexane-insoluble, acetone-insoluble material (the “insoluble” fraction)—typically a very small amount (C-4)—was also dried and weighed. Preparative HPLC was used to isolate the individual explosive compounds HMX, RDX, and PETN from the cyclohexane-insoluble, acetone-soluble fraction.

**Instrumentation and instrument methods**

HPLC-UV/Vis analysis and isolation of individual explosive compounds from the explosive fraction was conducted according to a previous publication [33]. $^{13}C$/C and $^{2}H$/H analysis of RDX, HMX, and PETN was conducted using a modification of EA-IRMS (thermal decomposition) according to a previously published method [32] on a Costech ECS 4010 EA (elemental analyzer, Costech, CA, USA) attached to a Thermo Finnigan MAT 253 via a Conflo IV interface. Both raw, unpurified explosive compounds as well as HPLC-purified materials were used to calculate the $^{13}C$ and $^{2}H$ values of the source material. Explosive component $^{13}C$ values were corrected for blank as determined by excess carbon.

$^{13}C$/C analysis of the binder samples, raw explosive, and RDX of the example C-4 (samples 1 and 4) was conducted using conventional EA methods (including oxygen pulse). Oil samples were loaded into 3.5 g 9 mm tin capsules via hexanes and dried prior to folding the capsules. Isotope ratios were “stretch-shift” corrected using two previously characterized urea reference materials [32]. Quality control was verified using polyisobutylene, RDX, and styrene-butadiene rubber reference materials. A Thermo TC/EA (high-temperature conversion elemental analyzer) was used to convert binder and bulk oil samples into H$_2$ gas for $^{2}H$/H measurements at 1400 °C in a glassy carbon reactor. Samples and reference materials (0.08 mg) were loaded into 3.2 × 4.0 mm silver capsules and dropped into the reactor via zero-blank autosampler. Oil samples were loaded into 3.2 × 4.0 mm silver boats via hexanes and allowed to dry prior to analysis. Isotope ratios were corrected using previously calibrated tetracosane and octacosane reference materials [34], and verified using polyisobutylene and styrene-butadiene rubber.

FTIR analyses were performed on Nicolet 510 FT-IR spectrometer collecting wavelengths between 400 and 4000 cm$^{-1}$. Samples were loaded directly onto the diamond ATR (attenuated total reflectance) plate. Gravimetric analyses were conducted on a Mettler Toledo AT265 microbalance (resolution ± 1 μg) in preweighed 1-dram vials. Due to drift and environmental factors, the estimated propagated error of measurements of 80% for a gravimetric measurement (0.04 g) was ±46 μg.

Gas chromatography-mass spectrometry (GC-MS) was conducted on a Thermo Trace GC 2000 coupled to a Thermo Finnigan Trace quadropole MS. Samples (1 μL) were injected into a split/splitless injector held at 280°C in “splitless with surge” mode. The surge was at 23.4 psi and held for 30 s. The helium carrier was held at a constant flow of 1.3 mL/min after the injection surge. Compounds were separated using a J&W DB-5 fused silica column (30 m × 0.25 mm, 0.25 mm film thickness, Agilent, California, USA) using the following temperature program: initial temperature 102°C, hold time 4 min, ramp to 300°C at 18°C/min, hold for 8 min, ramp to 320°C at 20°C/min, hold for 2 min (total run time of 26 min). The IsoLink interface was in backflush between 0–350 s and 1580–1680 s. For combustion into carbon dioxide, the combustion reactor was maintained at 1030°C for high-temperature conversion into hydrogen gas, the high-temperature conversion reactor was maintained at 1400°C. Chromatographic peaks from combustion or high-temperature conversion were recorded on 2-thyethylene adipate, N-phenyl-2-naphthalenamine, and Sudan I were detected at their Kovats indices relative to n-alkane reference materials. The alkanes for normalization of GC-based compound-specific $^{13}C$/C data were octadecane (n-C18, $^{13}C$VSMOW = −33.35 ± 0.14‰) and octacosane (n-C28, $^{13}C$VSMOW = −28.90 ± 0.04‰). We used tetracosane (n-C24, $^{2}H$/HSMOW = −36 ± 4‰) and the same octacosane (n-C28, $^{2}H$/HSMOW = −250 ± 5‰) for $^{2}H$/H data.

Stable isotope ratios are expressed in this paper as the difference between rare and abundant isotope ratios of a sample and an internationally accepted isotope standard relative to the standard; e.g., $^{13}C$/C$_{\text{VSMOW}}$ = (R$_{\text{sample}}$ − R$_{\text{VSMOW}}$)/R$_{\text{VSMOW}}$, where R$_{\text{sample}}$ and R$_{\text{VSMOW}}$ are the $^{13}C$/C ratios of the sample and standard, respectively. Delta (δ) values are presented in “permil” (‰), or parts per thousand. For $^{13}C$/C, the standard is Vienna Pee Dee belemnite; the other isotope ratios used in this work are $^{2}H$/H (VSMOW scale) and $^{2}H$/H (AIR scale).

Hydrogen isotope ratios of n-alkane standards used for normalization of sample $^{2}H$/H data were previously calibrated to the VSMOW scale using the defined $^{2}H$/H values of VSMOW (0‰, exactly) and SLAP (−428‰, exactly), with an error of 3‰ [34]. The values of the $^{13}C$/C normalization reference materials were likewise calibrated to the VPDB scale using the internationally available isotope reference materials NBS22 (−30.03 ± 0.04‰), FEP-1 (−32.15 ± 0.05‰), USGS54 (−26.39 ± 0.08‰), and USGS41 (37.63 ± 0.05‰). Calibration of the urea reference materials for EA-IRMS was described previously [32]. The use of δ-notation and reference materials calibrated to international isotope scales complies with current IUPAC recommendations [35] as well as best practices adopted by the Forensic Isotope Ratio Mass Spectrometry (FIRMS) Network [36].

Statistical analysis was performed using the open-source statistical programming language R, available via the Internet at http://cran.r-project.org. Tests for significant differences between two groups were conducted using 2-sample Student’s t-test with Welch's correction, and had a Type 1 error (α) set at 5%. Long-term expanded uncertainty for δ-values was defined as the combined standard uncertainty of a single measurement (estimated by the standard deviation of multiple analyses of a reference material in conditions of reproducibility) times a coverage factor [37]. The coverage factor was chosen to provide an interval corresponding to a 95% confidence level. These values are available as Supplemental Data (Table S1).

**Results and discussion**

**Validation of separation method using control mixtures**

Table 1 contains the gravimetric analysis, HPLC-UV/Vis analysis, and $^{13}C$/C, $^{2}H$/H, and $^{2}H$/H results of the two control mixtures made to mimic plastic explosives typical of C-4 and Semtex. Also listed is the analysis of the repeated processing (n = 8) of a true C-4 sample. The columns on the left list the theoretical amount of each fraction (i.e., “explosive,” “binder,” and “oil”) and component, as well as the isotope ratios of the materials prior to mixing and subsequent isolation. No significant differences were found between the $^{13}C$/C and $^{2}H$/H results of isolated explosive components and those of the original material, except for HMX, which was slightly different from the original material (−0.21% in $^{13}C$/C, p = 0.005; +0.20% in $^{2}H$/H, p = 0.044). This demonstrates that the process of isolating each explosive component was complete (i.e., there was no contamination). Few significant differences between the source material and the isolated components were shown in the nonexplosive materials. The polyisobutylene $^{13}C$/C value was very slightly more negative than the original material (0.06‰, p = 0.02). The dye $^{2}H$/H values were slightly more negative in the extracted material than in the original source (3.7‰, p = 0.04). These differences in both explosive and nonexplosive components were small relative to long-term analytical uncertainty (at the level of reproducibility).
The relatively small amount of error in each gravimetric, HPLC-UV/Vis, and isotope ratio measurement demonstrates the reliability of the measurements over several distinct samples ($n = 4$ for each control mixture, $n = 3$ for the real C-4 sample).

For the most part, the gravimetric results of the control mixtures confirmed the amount of material originally added. A discrepancy in the amount of explosive material recovered in the control Semtex mixture (78% gravimetric, 71% HPLC versus the theoretical amount of 83%), combined with a larger-than-expected amount of material in the oil fraction (9.8% gravimetric versus the theoretical amount of 7.9%) suggests that some of the explosive material was co-extracted into the oil fraction. However, the isolated explosive compounds (after preparative HPLC) were not isotopically different from the original materials, demonstrating that no measurable isotopic fractionation took place during co-extraction.

### Examples using true C-4

The gravimetric results of the true C-4 sample confirmed the theoretical amount of material in each fraction, based on previous measurements as well as results from the literature [38–40]. The carbon, hydrogen, and nitrogen elemental analysis of the isolated components also confirmed their purity and the accuracy of the technique for separating components of plastic explosives like C-4 and Semtex. The identity and purity of individual compounds that were analyzed by GC–MS and HPLC-UV/Vis were also confirmed by retention time indices (see Supplemental Data, Table 1).

### Table 2
Gravimetric and HPLC data for samples 1, 4, and 1261. Sample 1261 was analyzed 8 separate times. Using the analytical uncertainty of sample 1261 as a guide, Samples 1 and 4 are indistinguishable by gravimetric and HPLC analysis, and are very similar in composition to Sample 1261. Fractions measured are the binder fraction, oil fraction, explosive fraction ($xf$), and insoluble fraction; the explosive fraction was further analyzed for the components RDX and HMX by HPLC. Weights (wt) are in mg.

<table>
<thead>
<tr>
<th>ID</th>
<th>Subsample</th>
<th>statistic</th>
<th>Raw wt</th>
<th>Binder wt</th>
<th>Oil wt</th>
<th>xf wt</th>
<th>Insoluble wt</th>
<th>Binder w/w %</th>
<th>Oil w/w %</th>
<th>xf w/w %</th>
<th>Insoluble w/w %</th>
<th>RDX by HPLC</th>
<th>HMX by HPLC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>55.393</td>
<td>1.417</td>
<td>3.524</td>
<td>49.739</td>
<td>0.154</td>
<td>2.6%</td>
<td>6.4%</td>
<td>89.8%</td>
<td>0.3%</td>
<td>83.6%</td>
<td>9.1%</td>
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<td></td>
</tr>
<tr>
<td>4</td>
<td>51.297</td>
<td>1.194</td>
<td>3.651</td>
<td>45.713</td>
<td>0.191</td>
<td>2.3%</td>
<td>7.1%</td>
<td>89.1%</td>
<td>0.4%</td>
<td>82.0%</td>
<td>9.5%</td>
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</tr>
<tr>
<td>1261</td>
<td>46.100</td>
<td>1.162</td>
<td>3.308</td>
<td>40.567</td>
<td>-0.100</td>
<td>2.5%</td>
<td>7.2%</td>
<td>88.0%</td>
<td></td>
<td>***</td>
<td>*** 9.1%</td>
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</table>

* Below detection limit.
** Not determined.
*** Mean of 3 measurements.
Table S2 and Figs. S1–S7), UV–Vis spectra (see Supplemental Data, Figs. S1–S3), and EI-mass spectra (see Supplemental Data, Figs. S8–S10) by comparison to reference materials. The identity and purity of the polysobutylene binder isolated from C-4 was confirmed by comparison to reference material via FTIR spectroscopy (see Supplemental Data, Fig. S11).

As an example of the utility of this fraction separation approach to add valuable forensic data to the analysis of an explosive sample, we present the results from two C-4 samples from different sources; these explosives were separated in manufacturing date by 11 years. These samples are indistinguishable by the δ13C and δ15N values of the raw (pre-separation) material (see Fig. 2A), as well as gravimetric and HPLC-UV/Vis analysis (see Table 2). These two additional examples also have very similar δ13C and δ15N values in their RDX component, precluding their discrimination by isolation of this component alone (see Fig. 2B). However, δ13C and δ18O analysis of the binder components and bis(2-ethylhexyl) adipate (Fig. 2C and D) clearly demonstrated that the samples can be discriminated by analysis of these minor components. The combination of multiple isotope ratio analyses of multiple components provides further information on explosive samples of forensic interest, and also discriminates samples of similar composition, even in cases where isotope ratios of the largest component are indistinguishable.

Conclusions

The method for separation of components of plastic explosives described here successfully partitions the components into 3–4 fractions based on their solubility: binder, oil, explosive, and insoluble. These fractions can be further separated into components using HPLC and/or GC to produce isotope ratios of individual compounds, such as RDX and HMX for the explosive fraction, and Sudan I and N-phenyl-2-naphthalamine for the oil fraction. The addition of isotopic analysis of nonexplosive materials (e.g., binder) allows for discrimination between chemically indistinguishable C-4 samples that cannot be differentiated by δ13C and δ15N analysis of raw material or only the RDX component. Using these separation techniques, the isolated components are sufficiently pure to produce isotope ratios that are both consistent and accurately reflect the isotope ratios of the components prior to fraction separation. Though the additional evidence gained from component-specific analysis clearly can help distinguish explosives with similar characteristics, the problem of evaluating the evidence given source propositions, such as an explicit link between a known and a recovered explosive, requires additional background data. We propose that surveys examining the δ13C and δ18O signatures of binders and plasticizers from plastic explosives be undertaken to provide background population data so that investigations into explosive source can be conducted in a consistent manner acceptable to the forensic community and the judicial system. These kind of data would also be invaluable to intelligence as a way to track shifting supplies or suppliers of plastic explosives.

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.jorc.2016.07.003.

References

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