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Isolation of components of plastic explosives for isotope ratio mass spectrometry

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ARTICLE INFO

Article history:

Received 10 June 2016

Received in revised form 12 July 2016

Accepted 13 July 2016

Available online 16 July 2016

Keywords:

Plastic explosive

Isotope ratio

Component separation

Compound-specific

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 $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ isotope ratios, were extracted and analyzed. The resultant binder and plasticizer $^2\text{H}/^1\text{H}$ and $^{13}\text{C}/^{12}\text{C}$ results were used to discriminate between the two C-4 samples that were otherwise apparently identical.

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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

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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 isotopic 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). IsoForensics, 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® Octadecyl 40 µm Prep LC packing) for flash chromatography was obtained from VWR (cat #JT7025-00, lot J25087). Mineral oil for method development was obtained from Malinckrodt (cat #6358, lot 6358 A08638). Other commercially available chemicals used as reference materials were obtained from Sigma-Aldrich (Saint Louis, MO, USA); these were styrene-butadiene rubber (branched copolymer, 21 w/w% styrene, catalog #432474-100G, lot 01708BJ), polyisobutylene (cat #181455-100G, lot MKBK8213V), bis(2-ethylhexyl) adipate (cat #02140, lot 1319382 @0107326), N-phenyl-2-naphthaleneamine (cat #178055-25G, lot 05609HJV), and Sudan I (cat #103624-25G, lot S50809). Alkanes used for retention time indices and isotope ratio normalization included docosane (cat #134457-100G, lot 07404TA), dodecane (D221104-100ML, lot 17320TA), dotriacontane (cat #D223107-5G, lot 08220AE), eicosane (cat #219274-5G, lot 02812EE), hexadecane (cat #296317-100ML, lot 00742BC), hexatriacontane (cat #H12552-25G, lot 10818PC), octacosane (cat #0504-25G, lot 06725AD), octadecane (cat #0652-25G, lot 17119MD), tetracosane (cat #T8752-25G, lot 18101EE), and tetradecane (cat #172456-100G, lot100118HB). 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), then compared to those of the same components after they were isolated from the control mixtures. The relative amounts 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.

Overview of explosive fraction separation scheme

The goal of the fraction separations described in this paper is the quantitative isolation of individual components of plastic explosives in sufficient purity for isotope ratio analysis of each component. A scheme for the complete separation is shown in Fig. 1. In summary, the binder and plasticizer of a plastic explosive were extracted into cyclohexane, separating them from explosive components and other insoluble material. The plasticizers, oils, and additives were then extracted with acetone from the dried cyclohexane-soluble fraction, leaving the polymeric binder. The explosive components were extracted from the cyclohexane-insoluble fraction with acetone. Dyes and antioxidants were separated from other aliphatic material in the cyclohexane-soluble, acetone-soluble fraction using a column of non-encapped C18 resin. Preparative HPLC was used to isolate the explosive compounds according to a previously published method [33]. Purified explosive compounds, polymeric binders, and bulk oil fractions were analyzed using EA-IRMS for carbon and nitrogen isotope ratios; the binder and oil fractions were analyzed using TC/EA-IRMS for hydrogen isotope ratios. GC-IRMS methods provided hydrogen and carbon compound-specific isotope ratios of the plasticizers, dyes, and the antioxidant.

Cyclohexane-soluble fractions

Plastic explosive material (50–60 mg) was weighed into an ashed, labeled, and pre-weighed 1-dram glass vial. The weight of the explosive was recorded to 0.001 mg (for gravimetric analysis). Optima-grade cyclohexane (2 mL) was added and the vial shaken for 16–24 h on a benchtop shaker. If the shape of the sample was not disrupted overnight, the sample was placed back on the shaker for several more hours. The vial was then spun using a low-speed, tabletop centrifuge to clarify the solution of any suspended insoluble particles. The supernatant was transferred via Pasteur pipet to another ashed, labeled, and pre-weighed 1-dram vial. This is the “cyclohexane-soluble” fraction. An additional 2-mL aliquot of cyclohexane was used to extract the remainder of oils, additives, plasticizers, and binders from the original sample vial (shaken for 1 h) and added to the cyclohexane-soluble fraction. Both cyclohexane-soluble and cyclohexane-insoluble fractions were dried under an oil-free air stream and weighed.

A 2-mL aliquot of Optima grade acetone was added to the cyclohexane-soluble fraction. In samples containing 1–2% binder (typical of C-4-like compositions) the insoluble binder was released from the side of the vial and was visible as a colorless film suspended in the solvent. The vial was shaken for 1 h on the benchtop shaker, and then shaken on a Vortex mixer for 10 s. The insoluble binder coalesced into a small (~1–2 mm) ball. The acetone-soluble fraction was removed via Pasteur pipet and transferred to another ashed, labeled, pre-weighed 1-dram glass vial. The acetone extraction was repeated (2 mL) on the cyclohexane-soluble fraction and the supernatant combined with the previously acquired acetone-soluble fraction (the “oil” fraction). Both fractions were dried and weighed. The cyclohexane-soluble, acetone-insoluble fraction containing the polymeric binder (the “binder” fraction) was then ready for analysis by FTIR, EA-IRMS, and TC/EA-IRMS.

The cyclohexane-soluble, acetone-soluble fraction was prepared for GC-MS for compound identification and quantification, and then processed if necessary to remove interfering compounds prior to GC-IRMS. Samples were dissolved into 0.5–1.8 mL hexanes to a nominal concentration of 200 µg/mL per resolved compound. A retention time standard, consisting of *normal*-alkanes of carbon length 14, 16, 18, 20, 22, 24, 28, 32, and 36 was also prepared in advance for calculation of Kovats indices, normalization of isotope ratio data, and assessment of quality control. Compounds were identified by Kovats index and comparison of fragmentation patterns to the mass spectral library supplied with the Excalibur software. Samples containing resolved peaks (antioxidant, dyes, plasticizers) were analyzed for $^2\text{H}/^1\text{H}$ by GC-IRMS at 20 ng hydrogen per resolved compound per injection. Samples were diluted to produce 20 ng carbon per resolved compound per injection for $^{13}\text{C}/^{12}\text{C}$ analysis by GC-IRMS.

For the control mixture mimicking a Semtex sample, separation of the antioxidant and dye from the relatively large amounts of oil was necessary, as the oil co-eluted from the GC column in the form of an unresolved complex mixture. This flash chromatography separation step was conducted using a short pipet column containing 0.2 g of C18 resin (described above) loaded with hexanes. The column was conditioned with 2 mL of dichloromethane, followed by 2 mL hexanes. The sample, dissolved in 0.5 mL of hexanes, was loaded onto the column and followed by a 0.5-mL rinse of the sample vial (also hexanes). The remainder of the first fraction, containing aliphatic hydrocarbons, was eluted with an additional 0.5 mL of hexanes. The second fraction, containing the antioxidant and dye, was eluted using three 0.5-mL aliquots of dichloromethane. A final third fraction was eluted using 0.5 mL of acetone. Fractions were dried under an oil-free air stream prior to dissolution in hexanes for GC (as above). No significant differences between the original oil and the oil prepared via flash chromatography were found in $^2\text{H}/^1\text{H}$ or $^{13}\text{C}/^{12}\text{C}$ isotope ratios.

Cyclohexane-insoluble fractions

The cyclohexane-insoluble fractions were treated in a fashion similar to the hexane-insoluble fractions from a previously described method [33]. Briefly, two 2-mL aliquots of acetone were used to extract the explosive components from

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