



## Short Communications

## Development of a methodological framework for applying isotope ratio mass spectrometry to explosive components

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## ABSTRACT

Isotope ratio mass spectrometry (IRMS) techniques have been used for decades to characterize explosives alongside traditional chemical analyses. We present here a broadly applicable framework for methodologically applying a variety of separation techniques to explosive mixtures and preparing different explosive components for stable isotope analysis. This framework allows an analyst to collect the most characteristic information possible from an explosive sample, by analyzing multiple components with independent isotope signatures to produce multivariate datasets for discrimination. A case illustration demonstrating the application of methods in the framework to plastic explosives (specifically C-4 and Semtex) has been prepared separately.

In developing this framework, we focused on explosives samples that may contain RDX, HMX, PETN, TNT, AN, and/or nitrocellulose along with various binders, plasticizers, oils, and other additives. This paper describes the theory and processes used to develop a component-specific approach to prepare explosives samples for isotope ratio analysis, focusing specifically on optimization of solvent extraction methods. Other methods used in framework development include gravimetric analysis and HPLC.

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## 1. Introduction

Following an explosive attack or thwarted bombing attempt, investigators are concerned with determining the responsible party (or parties). Characteristics of the explosive may provide clues about those who were responsible, whether they were involved in other events, and the source of materials they used. Chemical analyses play a central role in these investigations, supplying the tools to characterize explosives and their residues [1–3].

Most analyses focus on describing chemical features of the explosive. For example, plastic explosives can be characterized based on moisture content, acidity, explosive content (e.g., RDX, HMX), and non-explosive component identity and quantity (e.g., plasticizer content). Techniques used to measure these characteristics include chromatography, mass spectrometry, and spectroscopy [4,5]; spectroscopic techniques such as FTIR have also proven useful to identify non-explosive components [6,7]. Within the last decade, mass spectrometry has been further used to characterize oils found in the non-explosive portion of an explosive [8].

Isotope ratio mass spectrometry (IRMS) is a powerful analytical tool for characterizing explosives and discriminating samples, even

those having identical chemical formulations. Benson et al. [9] published the first review paper describing forensic applications of IRMS to explosive characterization. That review was followed by a recent publication by Gentile et al. [10], who described the use of IRMS for sourcing, including specific case examples on source attribution for explosives. Using these contributions as foundations, we can broadly summarize the approaches used to date in the application of IRMS techniques to the isotopic characterization of explosives.

Previously published methods using stable isotopes to characterize explosives can be categorized into one of three approaches. First and rudimentarily, the analyst can apply IRMS methods to a “bulk” explosive [11–13], thereby considering all components contained within together in a single measurement. Second, the analyst can focus on measurement of an explosive recovered as a pure material, which requires no preparation or cleanup [14–20]. Finally, the investigation can consider analysis of explosive components [5,21] that have been isolated for isotope ratio measurement – for example, RDX extracted from a plastic explosive. In this approach, any other components, such as binders or plasticizers, are not isolated or considered for isotope ratio analysis. Of these three approaches for applying IRMS techniques to explosives, we contend that the most explicit and reproducible approaches, such as component-specific analytical techniques, are preferable and

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most likely to be allowed as evidence in the judicial system [22]. In their recent review, Gentile and colleagues [10] suggested evaluation of compound-specific isotope analysis (CSIA) for explosive source attribution.

In this short communication, we introduce a methodological framework for preparing different explosive components for stable isotope analysis. The methods included in the framework allow analysts to isolate and then characterize a variety of components using chemical and isotopic analyses. We first describe the overall concept of the process and then describe the steps taken to optimize one method used in the framework, namely solvent extraction of explosive materials. Finally, we present the framework in a graphical format. An example application of the framework to plastic explosives—including component isolation and subsequent stable isotope analysis for discrimination purposes—has been prepared as a separate manuscript [23].

## 2. Considerations for component-specific separation and analysis

An explosive is a chemical mixture whose purpose is to shatter or destroy surrounding objects by a rapid expansion of gases. Common explosives include RDX (cyclotrimethylene trinitramine), HMX (cyclotetramethylene tetranitramine), PETN (pentaerythritol tetranitrate), TNT (2,4,6-trinitrotoluene), ammonium nitrate (AN), and nitrocellulose. Explosive mixtures often contain these components in various combinations, in addition to small quantities of other components. Binders can be added to bind components together and decrease the sensitivity of the explosives. Two common binders found in plastic explosives include styrene-butadiene rubber (SBR) and polyisobutylene (PIB). The addition of plasticizers and oils such as *bis*(2-ethylhexyl) adipate (BEHA), *bis*(2-ethylhexyl) sebacate (BEHS), diisobutyl phthalate (DIBP), and tributyl citrate can make an explosive easier to mold and safer to handle. Oil can act as a release agent while additives such as metal or wood can increase blast effects. In some cases, explosives may also contain very small amounts of antioxidants, dyes, and/or taggants.

A key consideration in explosive characterization using chemical and isotopic analyses is the careful separation of different components contained within the mixture. This is important for accurate quantification of the constituent components. It is also crucially important for component-specific stable isotope analysis as splitting a component into multiple pools or a loss in yield may be associated with isotopic fractionation effects.

A schematic of the components contained within explosive mixtures is presented in Fig. 1. The schematic considers a variety of components: explosive material(s), binders, plasticizers, oils, and other additives such as dyes, metal, wood, etc. In developing a methodological framework for separating these components for isotopic analysis, we considered mixtures that may contain the explosive materials RDX, HMX, PETN, TNT, AN, and/or nitrocellulose.

## 3. Materials and equipment used in framework development

We used a variety of explosive materials during methods development, procured as follows. A single sample each of RDX (identifier 522), HMX (identifier 291), PETN (identifier 544), and AN (identifier SAN) came from materials previously investigated by us [5,18,21]. A single sample of TNT (identifier 268) was provided by the U.S. Government. Nitrocellulose was made in-house by nitrating a cellulose (laboratory) reference material [24]. Standard concentration solutions of RDX, HMX, PETN, and TNT for HPLC/UV

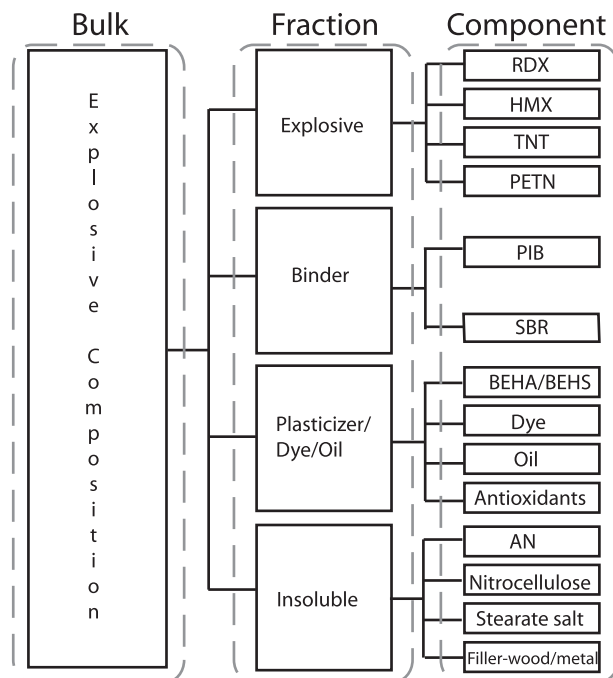


Fig. 1. A schematic representation of the breakdown of the bulk explosive into components contained within explosive mixtures, which include explosive material (s), binders, plasticizers, oils, and other additives.

analysis were purchased from AccuStandard, Inc. (New Haven, CT, USA) and prepared as described by Howa et al. [5].

Non-explosive materials used in method development included the polymeric binders SBR and PIB; plasticizers BEHA, BEHS, and DIBP; mineral oil; an antioxidant (N-phenyl-2-naphthylamine); and Sudan I dye. The mineral oil was purchased from Malinkrodt. All other non-explosive materials were purchased from Sigma-Aldrich.

Solvents were Optima-grade and included acetone, chloroform, cyclohexane, hexanes, and methanol; all solvents were purchased from Fisher Scientific. Samples were dried under a stream of purified air at room temperature using a Pierce evaporator. HPLC/UV analyses were completed using a Waters HPLC system as described by Howa et al. [5]. Gravimetric analysis was conducted in 1-dram vials (mass ~4.5 g) using a Sartorius MC-5 microbalance (Bradford, Massachusetts, USA).

## 4. Methodological framework development and results

### 4.1. Solvent selection for initial extraction

A variety of analytical methods have been published for the chemical characterization of explosive mixtures and most begin with an extraction to separate binders, plasticizers, and oils from the explosive(s), salts, and any fillers. The solvent most commonly used for initial extraction is chloroform, followed by an acetone extraction of both fractions [4,6,7,25]. For subsequent spectroscopic and spectrometric examination, explosive material is typically collected from the chloroform-insoluble, acetone-soluble fraction while binders are collected from the chloroform-soluble, acetone-insoluble fraction; plasticizers and oils are collected from the chloroform-soluble, acetone-soluble fraction. However, previous studies have noted the presence of explosives in the spectra of binders and plasticizers (e.g., [7]), suggesting that initial chloroform extraction partially extracts explosives as well, leading to incomplete separation.

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