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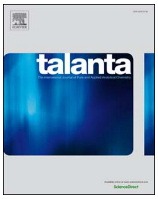

TATP isotope ratios as influenced by worldwide acetone variation

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ABSTRACT

Isotope ratio analysis has been shown to discriminate samples of forensic interest and to link many synthesized and natural materials to their precursors when traditional chemical and physical analyses cannot. Successful application of stable isotope analysis to chemicals of interest requires a background of likely variations in stable isotope ratios; often, this background population can be generated from analysis of possible precursors and the relationships of stable isotopes of precursor(s) to product(s), which may depend on synthesis techniques. Here we measured the carbon ($^{13}C/^{12}C$) and hydrogen ($^{2}H/^{1}H$) isotope ratios of the oft-illicitly manufactured explosive triacetone triperoxide, TATP, and one of its precursors, acetone. As acetone is the sole source of carbon and hydrogen to TATP, a survey of acetone from 12 countries was conducted to explore the breadth of $^{13}C/^{12}C$ and $^{2}H/^{1}H$ variation in the precursor, and therefore, its product. Carbon and hydrogen isotope ratios were measured using continuous flow isotope ratio mass spectrometry (IRMS) techniques. We observed greater ranges in both C and H isotope ratios of acetone than previously published; we also found that country-of-purchase was a large contributing factor to the observed variation, larger than acetone grade and brand. Following clandestine production methods, we observed that the stable isotope ratios of TATP retained the stable isotope signatures of acetone used in synthesis. We confirmed the robustness of TATP carbon isotope ratios to both recrystallization and time-dependent sublimation, important considerations when faced with the task of practical sampling of potential unexploded TATP from a crime scene.

1. Introduction

The powerful high explosive triacetone triperoxide (TATP) can be made from household chemicals—acetone, hydrogen peroxide, and strong acids—easily obtained at hardware and beauty supply stores. Nicknamed "the mother of Satan," this primary explosive is shock-sensitive, sublimates, and is potentially unstable, making it unsuitable for legitimate uses [1], but perfect for the terrorist's toolbox. Its use in improvised explosive devices, alongside other peroxide-based explosives such as hexamethylene triperoxide diamine (HMTD), is becoming more prevalent, as seen in recent high-profile incidents such as the "shoe" and "underwear" bombers, the July 2005 London transit bombings, and the 2016 Brussels airport attack [2]. As the use of homemade explosives, such as TATP, in improvised explosive devices becomes more prevalent, the ability of law enforcement to link a precursor, such as acetone, to a clandestine lab or possibly to the explosive itself is of forensic interest.

When examined as a pure crystalline material, traditional chemical analyses cannot unequivocally link a particular batch of TATP to a bomb or cache of precursors; however, stable isotope ratio analysis provides forensic chemists a reliable technique to distinguish among chemically identical materials by their stable isotope ratios [3,4], and has been shown to be useful for discriminating among explosives, including TATP [5,6]. In many circumstances, the precursors of manufactured explosives, even those made using improvised methods, can be related to the final product by their isotope ratios [7–10].

By the reaction mechanism to produce TATP [6], all oxygen atoms originate from the hydrogen peroxide, and all carbon and hydrogen atoms originate from acetone. The oxygen atoms in TATP are likely related to the peroxide oxygen in hydrogen peroxide solutions, which have been surveyed extensively by Barnette et al. [11] and, on a smaller scale, by Bezemer et al. [6]. The carbon and hydrogen isotope ratios of TATP are strongly related to that of the acetone precursor, as shown by Bezemer et al. [6] over different reaction conditions. When TATP yield is high with respect to acetone, we would expect the carbon and hydrogen isotope ratios of the precursors to match the product closely, as demonstrated previously for the explosive pentaerythritol tetranitrate (PETN) made using high-yield methods [10]. Thus, a survey of acetone may be a good proxy for the expected variation of isotope ratios in TATP in the course of investigations.

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As discussed in recent literature [4,12,13], interpretation of forensic data beyond "intelligence gathering" requires a sufficient characterization of the background variation within and between "sources," no matter the definition of "source" used for the interpretation. Methods for analyzing isotope ratios of acetone have been published alongside results from samples found in laboratories [14] and encountered in casework [6], but no systematic survey of acetone has been conducted to date.

Here we present an isotopic survey of acetone of several different grades from 12 countries, with a major focus on the United States. The relationship between carbon and hydrogen isotope ratios was examined, as they were expected to co-vary in a fashion similar to their petrochemical sources. Various factors such as acetone grade ("hardware", "nail", "scientific", and "unspecified"), brand, and country of purchase were examined to determine their influence on the overall variation of carbon and hydrogen isotope ratios. Isotope ratios of TATP synthesized from several of these acetone samples were compared to that of the acetone. To confirm the robustness of practical collection methods as it applies to isotope ratio analysis of TATP and its precursors, we examined the effects of evaporation of acetone as well as the effects of sublimation and recrystallization of TATP on their respective isotope ratios.

2. Materials and methods

2.1. Sample collection

Acetone samples were collected from 13 different locations in 11 countries outside the US as well as from 63 locations within 27 states of the US (see Fig. 1). The entire survey consisted of 96 acetone samples in different grades categorized as "scientific," "hardware," and "nail," with a fourth "unspecified" grade, and were obtained from hardware, grocery, beauty, and scientific suppliers. Brand name, e.g., "Ace," "J. T. Baker," etc. was also recorded (31 different brands). Acetone samples collected by the authors were stored at room temperature in their original container. Other samples were obtained from colleagues by mail. Shipped samples were subsampled to 1.5 mL, stored in 4-mL borosilicate glass vials, and kept at 4 °C after receipt. The glass vials were sealed with caps including PTFE-lined septa, and the caps secured with Parafilm.

TATP was synthesized in six batches from four different acetones that had measured δ^{13}C and δ^{2}H values. *Warning: TATP is a primary explosive sensitive to friction and impact. The storage, handling, and synthesis of TATP are hazardous activities that require safety considerations for handling high explosives.* The particular synthesis method used was chosen as it was of practical and popular use in the clandestine "literature." Samples were synthesized at two separate locations. Samples from batches "E" through "I" were received in crystalline form; three additional samples of TATP from these syntheses were received following recrystallization from organic solvents. Four additional synthesized TATP samples (batches "A" through "D") were synthesized from acetone that was not collected for isotope ratio analysis, and used to examine heterogeneity and the effects of sublimation; these samples were also received in crystalline form (see Table 1).

Table 1
Key for matching product TATP to acetone and hydrogen peroxide IDs in syntheses. Sample IDs refer to samples and analyses given in Supplementary Information. Synthesis batches refer to data points in Fig. 3; IDs 71–74 were used in the sublimation experiment (Fig. 4).

Synthesis batch	Raw TATP ID	Recrystallized TATP ID	Acetone ID	Peroxide ID	Peroxide conc. (w/w%)
A	–	71	–	–	–
B	–	72	–	–	–
C	–	73	–	–	–
D	–	74	–	–	–
E	88	89	104	–	50
F	90	91	104	–	35
G	92	93	104	–	20
H	94	–	100	–	–
I	95	–	102	–	–
J	254	255	18	12	35

Synthesis was conducted by slowly adding hydrogen peroxide to chilled (5 °C) acetone while stirring with a magnetic stir bar, keeping the reaction temperature below 11.5 °C. Hydrogen peroxide was of concentrations between 20% and 50%. The amount of acetone used was adjusted to keep a constant acetone: peroxide molar ratio, maintaining acetone as a limiting reagent. After 30 min, sulfuric acid (50%) was slowly added to the reaction vessel, keeping reaction temperature below 13 °C. After crystals formed and the solution thickened, the solution was allowed to crystallize overnight at 4 °C. (*Warning: at this point, the material is at risk for explosion.*) Water was used to wash the crystals, transfer the slurry onto filter paper, and filter. After the crystals were allowed to air dry, they were transferred to a storage vessel. Raw TATP was stored at room temperature in 1-dram borosilicate glass vials sealed with Parafilm.

2.2. Sublimation/evaporation experiments

To examine the effect of sublimation on the carbon isotope ratios of TATP, samples from each of synthesis batches "A" through "D" were loaded in duplicate at a target weight of 1.2 mg into tin capsules used for EA-IRMS (see below) and allowed to sublimate on a laboratory benchtop for 0, 3, 7, and 14 days. The material remaining in capsules was analyzed immediately following the designated elapsed time. To examine the effect of evaporation on carbon isotope ratios of acetone, four vials of a single stock acetone (ID 17; see Supporting Information) were weighed to ~15 g in 20-mL scintillation vials and capped with a permeable nylon mesh to avoid contamination with airborne dust. Vials were allowed to evaporate in a fume hood at ambient temperature (~ 21 °C) while weighing and subsampling each vial (~ 0.3 mg) at 0, 5.5,

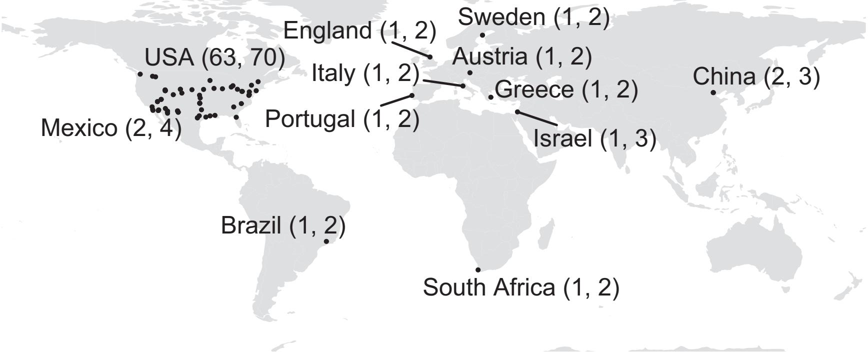

Fig. 1. Map of locations from the worldwide survey of acetone in this study. Following the country label are two numbers (a, b) corresponding to: (a) the number of locations from which samples were collected in that country, and (b) the total number of samples collected in that country.