



Isotopic and elemental profiling of ammonium nitrate in forensic explosives investigations



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ABSTRACT

Ammonium nitrate (AN) is frequently encountered in explosives in forensic casework. It is widely available as fertilizer and easy to implement in explosive devices, for example by mixing it with a fuel. Forensic profiling methods to determine whether material found on a crime scene and material retrieved from a suspect arise from the same source are becoming increasingly important. In this work, we have explored the possibility of using isotopic and elemental profiling to discriminate between different batches of AN. Variations within a production batch, between different batches from the same manufacturer, and between batches from different manufacturers were studied using a total of 103 samples from 19 different fertilizer manufacturers. Isotope-ratio mass spectrometry (IRMS) was used to analyze AN samples for their ¹⁵N and ¹⁸O isotopic composition. The trace-elemental composition of these samples was studied using inductively coupled plasma-mass spectrometry (ICP-MS). All samples were analyzed for the occurrence of 66 elements. 32 of these elements were useful for the differentiation of AN samples. These include magnesium (Mg), calcium (Ca), iron (Fe) and strontium (Sr). Samples with a similar elemental profile may be differentiated based on their isotopic composition. Linear discriminant analysis (LDA) was used to calculate likelihood ratios and demonstrated the power of combining elemental and isotopic profiling for discrimination between different sources of AN.

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1. Introduction

Ammonium nitrate (AN) has applications in explosives in industry, such as mining and civil construction [1,2]. Its chemical stability and low sensitivity to shock and friction [1,3,4] make it relatively safe to produce and to handle in large quantities. Combined with its low costs these properties make AN a suitable ingredient for explosive devices. Explosive-grade ammonium

nitrate generally exists in the form of slurries, emulsions, or porous prills mixed with a fuel (ammonium nitrate fuel oil, ANFO) [1]. Obtaining explosive-grade AN for criminal abuse is difficult due to extensive regulations, but AN in the form of fertilizer prills or granules is widely available [1,3,4]. The European Commission prohibits the distribution of ammonium nitrate-containing fertilizers with a nitrogen percentage higher than 16% to private parties [5]. In addition, detonation tests should be performed on fertilizers with a nitrogen content of more than 28% [6]. Fertilizer prills have a higher density and a lower porosity than explosive-grade prills, reducing the sensitivity to detonate. However, fertilizer-grade ammonium nitrate can still detonate or be made to detonate [3,4]. Besides industrial applications of AN-based explosives, terrorist attacks involving the use of AN in improvised explosive devices (IEDs) have been a concern for many years. Afghanistan and Iraq are countries with a large number of attacks with AN-based IEDs, due to its low costs and ease of implementation.

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AN was also commonly used by the IRA, including in several bombings in London in the nineties [7]. Other examples of attacks involving fertilizer-based explosive devices are the bombings in Oklahoma City in 1995 [7] and Oslo in 2011.

In such cases of criminal use of AN in an IED, chemical profiling can be an important tool to investigate the origin of the material used.

In this work, we will examine the possibility of establishing relationships between AN retrieved from an IED and AN associated with a suspect. We will also investigate the possibility of tracing ammonium nitrate back to its production location. Product classification can yield important information especially for intelligence purposes and in the absence of leads and suspects. Chemical profiling of AN is especially challenging because of its inorganic nature and the bulk quantities in which it is produced. In this work the potential of profiling based on trace-elemental composition and isotope ratios has been investigated.

Ammonium nitrate is manufactured from ammonia and nitric acid [1,4,9]. Ammonia production occurs through the reaction of hydrogen with atmospheric nitrogen according to the Haber process [10]. Thereafter, nitric acid is formed by the oxidation of ammonia (the Ostwald process) [1,4,10]. Both the nitrogen and oxygen in ammonium nitrate are retrieved from the atmosphere. Although there is not much variation in the isotopic composition of atmospheric nitrogen and oxygen around the world [11], fractionation can occur during AN synthesis resulting in variation in both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values for different samples. Fertilizer prills or granules consist, besides ammonium nitrate, of various additives, such as gypsum, dolomite and magnesium nitrate. In addition, the prills are coated with a water-repellent material to prevent the prills from absorbing water [1–4,12]. These additives also contribute to the isotopic signature of the prills/granules. Moreover, the additives used during the manufacturing of AN-based fertilizers are rich in elements and therefore determine the elemental composition of the fertilizer prills. Two techniques that are, therefore, of special interest for profiling AN are isotope-ratio mass spectrometry (IRMS) and inductively-coupled plasma–mass spectrometry (ICP–MS). As part of the ICP–MS study also the application of laser-ablation ICP–MS (LA–ICP–MS) was investigated for element profiling of individual granules or prills. LA–ICP–MS could provide profiling options in forensic post-explosion investigations where only a limited number of granules or prills are found.

1.1. Forensic applications of IRMS and ICP–MS

Most of the analytical techniques conventionally used in forensic science are not able to determine whether samples with the same chemical identity have a common source. IRMS can in principle be used to study the source of samples based on their isotopic composition. In the field of explosives, IRMS was previously used to discriminate between different sources of Semtex [13], triacetone triperoxide (TATP) [14], pentaerythritol tetranitrate (PETN) [14,15], black powder, flash powder, nitromethane, plastic explosive no. 4 (PE4) [16], trinitrotoluene (TNT) [15–17], urea nitrate [18], and ammonium nitrate [15,19]. With one exception [19] these were all preliminary studies with either a small sample set or limited information on the origin of the materials. In addition to the ability to examine the source of explosive samples, IRMS has also been used to study relationships between precursors and the explosive product for urea nitrate [18], cyclotrimethylenetrinitramine (RDX) [20] and hexamethylene triperoxide diamine (HMTD) [21]. Benson et al. [19] attempted to correlate the isotopic composition of post-explosion AN to the isotopic composition of the intact AN, but without success. Therefore, we did not consider the analysis of post-explosion AN

residues in the present project. In addition, we did not consider explosive mixtures of AN (e.g. with a fuel or sugar), because this requires isolation of the AN from the mixture.

ICP–MS is capable of detecting and quantifying multiple elements and thus of producing trace-elemental signatures. Samples can be introduced in the plasma either by nebulization (liquids or solutions) or by laser ablation (LA–ICP–MS). When sufficient evidence material is available, spraying from solution will provide the most accurate quantitative analysis as it allows for homogenization of the material. However, the use of laser ablation allows for trace-element profiling of small amounts of material and for studying the spatial distribution of the trace elements (2D and 3D profiling). Elemental profiles obtained using ICP–MS have been used to discriminate between different sources of glass [22–24], paint [25], tapes [26], white cotton fibers [27], beer [28], bullets [29], methylamphetamine [30], human bones and teeth [31], and in the detection of art forgeries [32]. The combination of IRMS and ICP–MS may result in complementary information on the origin of a material and has shown to be powerful in discriminating between different sources of document paper [33].

1.2. Challenges for IRMS of nitrates

Stable-isotope analysis of nitrogen-containing samples and nitrates in particular poses some challenges. Meier-Augenstein et al. [34] reported on the influence of N_2 gas formed during high-temperature reduction of nitrogen-rich compounds on the analysis for ^2H isotope abundance. Partial overlap of the N_2 and H_2 peaks after GC separation resulted in inaccurate and imprecise $\delta^2\text{H}$ values, either due to dilution of the H_2 peak or to ionization competition between H_2 and N_2 gas. Mimicking nitrogen-rich samples by adding silver nitrate to benzoic acid samples resulted in a shift of roughly 5‰ toward more negative $\delta^2\text{H}$ values for an N:H ratio of one compared to ‘nitrogen-free’ benzoic acid.

Analysis of $^{18}\text{O}/^{16}\text{O}$ isotope ratios is performed by conversion of elemental oxygen in the sample to carbon monoxide (CO) using high-temperature conversion (HTC) in a reactor packed with glassy carbon. The IRMS is then used to measure the amounts of m/z 28 ($^{12}\text{C}^{16}\text{O}$) and m/z 30 ($^{12}\text{C}^{18}\text{O}$) to determine $^{18}\text{O}/^{16}\text{O}$ ratios in a sample. Conversion of oxygen in inorganic samples to CO has proven to be challenging. Powdered [35] or nickelized carbon [36–39] has been added either to the reactor or directly to the capsules containing the samples. Farquhar et al. [40] used a reactor packed with nickelized carbon only instead of glassy carbon. Nickel acts as a catalyst, enhancing the conversion to CO and allowing the use of lower reaction temperatures. The use of nickelized carbon resulted in more precise $^{18}\text{O}/^{16}\text{O}$ determinations.

The hygroscopic nature of AN is another point of concern. For prills or granules, water absorption is minimized by coating with an inert, hydrophobic material [1–4,12]. However, sample preparation for IRMS requires grinding of the prills or granules, causing interaction with atmospheric water. Exchange of oxygen was not observed for KNO_3 and NaNO_3 reference materials (USGS34, IAEA-NO-3 and USGS35) [36,41]. In addition, $\delta^{18}\text{O}$ values of these dried nitrate standards were not affected by repeated sorption and desorption of H_2O [35]. This suggests that oxygen exchange should not be an issue for ammonium nitrate, if a suitable drying and storage procedure is used to prevent absorption of water.

During high-temperature conversion, nitrogen in a sample is converted to N_2 , which is isobaric to CO (m/z 28). Although N_2 and CO can be separated using a 5-Å molecular-sieve GC column, the presence of small traces of oxygen may result in formation of NO^+ at the hot filament of the ion source. Whereas the signals of m/z 28 ($^{14}\text{N}_2$) and m/z 29 ($^{14}\text{N}^{15}\text{N}$) quickly diminish after elution of the N_2 peak, NO disappears slowly from the ion source, resulting in a long

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