

Rapid Commun. Mass Spectrom. 2014, 28, 1530–1534
(wileyonlinelibrary.com) DOI: 10.1002/rcm.6929

Isolation and stable nitrogen isotope analysis of ammonium ions in ammonium nitrate prills using sodium tetrphenylborate

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RATIONALE: Because of the threat of bombings using improvised explosives containing ammonium nitrate (AN), law enforcement and intelligence communities have been interested in stable isotope techniques for tracking and discriminating AN sources. Separate analysis of the AN component ions ammonium and nitrate would add discriminatory power to these techniques.

METHODS: Ammonium ions in dissolved AN solution were isolated from samples by precipitation using sodium tetrphenylborate solution. We tested the isolation of ammonium from nitrates using solutions of ammonium and nitrate salts with different ¹⁵N/¹⁴N isotope ratios. Ammonium tetrphenylborate and AN were separately analyzed for their ¹⁵N/¹⁴N isotope ratios using EA-ConFlo-IRMS, and the ¹⁵N/¹⁴N isotope ratios of the nitrate ions were calculated using mass balance. Ammonium and nitrate nitrogen isotope ratios were plotted as two separate variables.

RESULTS: Isolation of ammonium precipitate from solutions containing dissolved nitrates did not influence the nitrogen isotope ratios of test ammonium salts. A survey set of 42 AN samples showed that the ammonium and nitrate ¹⁵N/¹⁴N isotope ratios were not significantly correlated, and the paired mean differences were not statistically significant. Both ammonium and nitrate were depleted in ¹⁵N relative to their theoretical atmospheric sources.

CONCLUSIONS: Isolation of the ammonium ion from AN adds another dimension for the discrimination of forensic AN samples. This technique using sodium tetrphenylborate is robust and does not require specialized equipment. Our observations indicated that ammonium nitrogen and nitrate nitrogen have independent sources of isotopic variation. Copyright © 2014 John Wiley & Sons, Ltd.

While ammonium nitrate (AN) is an important fertilizer in modern agriculture, it can also be used in the production of explosives, mostly in mixtures with carbonaceous fuel sources such as coal, fuel oil, wood meal, and various nitro-compounds.^[1] Unfortunately, the wide availability of AN has implicated the material in events such as the Oklahoma City bombing in 1995,^[2] IRA bombing campaigns,^[3] and continued improvised explosive device use in Afghanistan.^[4,5] Given a need to trace AN origins in such cases, law enforcement and intelligence agencies have applied stable isotope analyses to characterize, compare, and discriminate explosive specimens containing AN, as has been done for high explosives.^[6,7] Beyond paired-sample comparisons of one explosive specimen with another, databases of isotope ratios of authentic explosive samples may provide clues to linking an unknown sample to a potential source.^[8]

In applying stable isotope analysis techniques to discriminate AN samples and identify potential AN sources, one must demonstrate both a range of potential isotope ratio values in the product of interest (variation) and the ability to accurately and precisely measure isotope ratios of a sample of interest so that two chemically identical samples can be

compared. The range of observed AN $\delta^{15}\text{N}$ values is much smaller than has been seen in other high explosives, such as the nitro-organic compounds PETN and RDX. Previous reviews^[9,10] showed that 80% of synthetic fertilizer nitrogen isotope ratios fell between -2% and $+2\%$. Benson *et al.*^[7] reported overall ranges of about 6% for $\delta^{15}\text{N}$ values. By contrast, the $\delta^{15}\text{N}$ values of the high explosives pentaerythritol tetranitrate (PETN) and cyclotrimethylene trinitramine (RDX) ranged over 50% .^[11–13] For this reason, the ability to discriminate among AN specimens is more reliant upon accurate measurements and/or combined isotope ratios of other elements as an additional discrimination dimension.

There is an additional variable for differentiating AN samples: nitrogen isotope ratio analysis of each component ion (ammonium and nitrate) within the samples. Separation and analysis of other explosives into component ions have been shown to add discriminatory power. For example, component ions of the explosive urea nitrate were shown to add forensic value,^[14] as the bulk nitrogen isotope ratio analysis obscured potential isotope ratio variation in both component ions. Similarly, AN has potential for independent $\delta^{15}\text{N}$ variation between its two ion components.

AN is usually synthesized on a plant scale in a continuous process, by mixing equimolar quantities of ammonia and nitric acid.^[15] Typically, these two nitrogen species are made from the same natural resource – atmospheric N_2 . When ammonia is produced in a closed system under high

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temperatures and pressures, there should be little fractionation between the reactants (N_2) and the products (NH_3); however, Freyer and Aly^[16] suggested that ammonia nitrogen produced in this manner would be ^{15}N depleted (they reported a range of $\delta^{15}N$ values between -3.5% and $+1.6\%$). Synthetic fertilizers containing only ammonium nitrogen in a study by Bateman and Kelley^[9] had $\delta^{15}N$ values that varied between -1.2% and $+0.8\%$ with a single ammonium sulfate sample at $+6.6\%$. Macko and Ostrom^[10] reported a $\delta^{15}N$ range for ammonium nitrogen between -7% and $+5\%$. We expect the nitrogen isotope ratio of ammonium in synthesized ammonium nitrate to likewise span this range, with a hypothetical mean similar to the atmospheric value of 0% .

In most modern factories, nitric acid is synthesized by oxidation of ammonia with atmospheric oxygen under pressure and heat.^[17] Freyer and Aly^[16] showed that nitrates produced in this reaction have the potential for nitrogen isotope fractionation, as sodium nitrate produced from waste gases was shown to be ^{15}N depleted relative to the product. Their study on synthetic fertilizers showed that nitrate was 4% more ^{15}N enriched than ammonium. In a review by Macko and Ostrom,^[10] nitrate isotope ratios in fertilizers covered a range of $\delta^{15}N$ values between -8% and $+7\%$, illustrating the possibility for greater nitrate isotope ratio variation than in AN. We hypothesize that the nitrate nitrogen isotope ratios from synthesized ammonium nitrate will have a greater range than the ammonium and will be ^{15}N enriched relative to ammonium.

Many hydrology and environmental studies have analyzed ammonium and nitrate ions separately,^[9,10,16,18] however, methods for separating and analyzing the ions are often lengthy and require extensive equipment and experience for nitrate reduction, steam distillation of ammonia, and subsequent conversion into N_2 gas,^[16,19] or collection on acidified filters, a process which carries its own problems.^[20] Other methods focus on the reduction of nitrates to N_2O via denitrifying bacteria.^[21] We used a solution of sodium tetrphenylborate to precipitate ammonium ions, as demonstrated in prior quantitative methods.^[22] This method is amenable to quick online elemental analyser/isotope ratio mass spectrometry (EA/IRMS) methods using an autosampler-enabled elemental analyzer, which can analyze ~ 80 samples in a 24-h period without supervision. We used the principle of mass balance to calculate the nitrogen isotope ratios of the nitrate ions and present ammonium and nitrate isotope ratios as two separate variables. This method was applied to a set of AN pills obtained from a survey of 42 different AN sources.

EXPERIMENTAL

AN samples.

A survey set of 42 authentic AN pill samples from different sources was obtained for demonstration of the method.

Ammonium and nitrate salts

Three analytical reagent grade ammonium salts were selected from materials on hand: ammonium sulfate dibasic (Mallinckrodt, St. Louis, MO, USA), ammonium chloride (Mallinckrodt) and ammonium phosphate dibasic (Mallinckrodt). Analytical reagent grade AN (Mallinckrodt) was also selected as a quality control

material. Two stock nitrate salts, calcium nitrate (analytical reagent grade, Mallinckrodt) and potassium nitrate (ACS grade, EMD Chemical, Billerica, MA, USA), were selected to test the effectiveness of separating the ammonium and nitrate pools using the sodium tetrphenylborate method. These nitrates necessarily had to have $\delta^{15}N$ values different from those of their ammonium salt pairings (see Table 1). The ammonium chloride salt $\delta^{15}N$ value was more positive than that of the nitrate ($t = 19.05$, $df = 5$, $P < 0.0001$); the ammonium sulfate salt $\delta^{15}N$ value was more negative than that of the nitrate salt ($t = 13.53$, $df = 4$, $P = 0.0002$).

Isolation of the ammonium ion fraction

Stock ammonium salts (30–100 mg) were dissolved in 0.1 mL deionized water in a 13×100 mm borosilicate test tube. Aqueous sodium tetrphenylborate solution (0.16 g/mL) was added to the ammonium salt solutions in 25% molar excess to ensure complete precipitation of the ammonium ions. The mixture was stirred and left to stand for 30 min. The ammonium tetrphenylborate precipitate was separated by filtration using a Whatman #1 55 mm paper filter (Cole-Parmer, Vernon Hills, IL, USA) in a Büchner funnel. The precipitate was then washed twice with 5 mL deionized water. The filter and precipitate were dried for 2 h at $70^\circ C$ in a drying oven. The precipitate was gently removed from the paper filter, ground using a ceramic mortar and pestle, and placed into a 1-dram glass vial for storage.

EA/IRMS

Stock ammonium salts, stock nitrate salts, sample AN and precipitated ammonium tetrphenylborate were analyzed for nitrogen isotope ratios using a model 1108 elemental analyzer (Carlo Erba, Milan, Italy) equipped with a zero-blank autosampler (Costech Analytical, Valencia, CA, USA) interfaced to a Delta S isotope ratio mass spectrometer via a ConFlo interface (both from Finnigan MAT, Bremen, Germany). The EA reactors were packed according to the manufacturer's recommendations using chromium oxide and silver cobaltous/cobaltic oxide in the oxidation reactor and reduced copper wire in the reduction reactor. Magnesium perchlorate was used to remove water upstream from a 3-m $\frac{1}{4}$ " packed gas chromatography (GC) column (catalog #051082, Costech Analytical) used to separate N_2 and CO_2 gas.

All samples and reference materials were weighed into 3.5×5 mm tin capsules (Costech Analytical) at a target mass of 80 ± 8 μg of nitrogen. Laboratory reference materials, imidazole and yeast, which were calibrated against international glutamic acid isotope standards USGS40 ($\delta^{15}N = -4.5 \pm 0.1\%$) and USGS41 ($\delta^{15}N = 47.6 \pm 0.2\%$), were interspersed among samples within an analytical sequence. For the analysis of ammonium salts, nitrate salts, and ammonium nitrate, imidazole ($\delta^{15}N = -0.47 \pm 0.15\%$, $n = 22$) was used for normalization and yeast was used for quality control (QC). For the analysis of ammonium tetrphenylborate samples, yeast ($\delta^{15}N = -1.00 \pm 0.10\%$, $n = 15$) was used for normalization and imidazole as the QC material. Ammonium nitrate, ammonium salt, and nitrate salt samples were analyzed in triplicate, and ammonium tetrphenylborate samples were analyzed in duplicate. The elemental analysis results (in percent by weight) for ammonium nitrate and ammonium tetrphenylborate were consistent with expected results for the pure compounds.

Table 1. $\delta^{15}\text{N}$ values of test ammonium salts and precipitates. Ammonium salts were precipitated with and without the addition of nitrate salts. Measured $\delta^{15}\text{N}$ values of the added nitrate are shown on the bottom row. Nitrate salts each had different $\delta^{15}\text{N}$ values from their respective test ammonium salts. Each ammonium salt $\delta^{15}\text{N}$ value was not different from its precipitated ammonium tetraphenylborate $\delta^{15}\text{N}$ value with or without mixing with nitrate salts

Sample	Salt only	Ammonium tetraphenylborate precipitate		
		Salt only	Salt + $\text{Ca}(\text{NO}_3)_2$	Salt + KNO_3
	$\delta^{15}\text{N} \bar{x} \pm \text{SD} (\text{‰}), n$			
NH_4Cl	$1.78 \pm 0.23, 3$	$1.53 \pm 0.19, 8$	$1.8 \pm 0.19, 4$	
$(\text{NH}_4)_2\text{SO}_4$	$-3.1 \pm 0.66, 3$	$-2.84 \pm 0.18, 8$		$-2.76 \pm 0.14, 4$
$(\text{NH}_4)_2\text{HPO}_4$	$-0.97 \pm 0.41, 3$	$-1.14 \pm 0.16, 8$		
nitrate salt			$-4.39 \pm 0.52, 4$	$2.3 \pm 0.21, 3$

Isolation method validation

To validate that the method sufficiently separated ammonium and nitrate ions, ammonium sulfate and ammonium chloride salts were mixed in 1:1 molar ratios with potassium nitrate and calcium nitrate, respectively. The mixture was then processed according to the described method to isolate the ammonium fraction. The nitrogen isotope ratios of the tetraphenylborate precipitate from each ammonium/nitrate salt mixture were compared with those of the original ammonium salt and the tetraphenylborate precipitate of that salt without the nitrate.

Calculation of isotope ratios

Stable isotope ratios are expressed in 'delta' (δ) notation in ‰ (per mil) relative to a standard, where $\delta = (\text{R}_A - \text{R}_{\text{Std}}) / \text{R}_{\text{Std}}$ and R_A and R_{Std} are the ratios of the rare to abundant isotope (e.g., $^{15}\text{N}/^{14}\text{N}$) in the sample and the standard, respectively. The international standard used for nitrogen is atmospheric N_2 (Air). The nitrogen isotope ratio of the nitrate fraction of AN was calculated using mass balance. We assumed that equimolar amounts of ammonium and nitrate existed in all of the AN samples, such that:

$$\delta^{15}\text{N}_{\text{NO}_3} = 2 \times \delta^{15}\text{N}_{\text{NH}_4\text{NO}_3} - \delta^{15}\text{N}_{\text{NH}_4}$$

Statistical analyses

Statistical hypothesis testing was performed using Prism 5.0c (GraphPad Software, Inc., San Diego, CA, USA) at the $\alpha = 0.05$ level and all tests were two-tailed. We tested the statistical equivalence of a group of data and a theoretical mean, or the equivalence of means of two groups of data by *t*-test; tests were paired where appropriate. We tested statistical equivalence of more than two groups of data by one-way analysis of variance (ANOVA). We tested correlation of variables by Pearson's method. We tested for differences in variance by a right-handed *F*-test.

RESULTS AND DISCUSSION

Method validation

We found no statistically significant differences in $\delta^{15}\text{N}$ values between the means of the stock ammonium chloride salt, the ammonium tetraphenylborate precipitated from

the salt, and the ammonium tetraphenylborate precipitated from the salt mixed with calcium nitrate (ANOVA, $F = 3.308$, $P = 0.0718$). Likewise, we saw no statistically significant differences between the means of the stock ammonium sulfate salt, the ammonium tetraphenylborate precipitated from the salt, and the ammonium tetraphenylborate precipitated from the salt mixed with potassium nitrate (ANOVA, $F = 1.190$, $P = 0.3377$). We also saw no statistically significant difference between the means of the stock ammonium phosphate salt and the ammonium tetraphenylborate precipitate (*t*-test, $t = 1.069$, $df = 9$, $P = 0.3128$). These results provided assurance that the isolation method is appropriate for measuring the $\delta^{15}\text{N}$ values of ammonium without fractionating ammonium isotopes, and the method isolates the ammonium $\delta^{15}\text{N}$ signal from the nitrate $\delta^{15}\text{N}$ signal in AN.

Ammonium $\delta^{15}\text{N}$ values from AN samples

The paired analysis of ammonium $\delta^{15}\text{N}$ and nitrate $\delta^{15}\text{N}$ values calculated via mass balance is shown in Fig. 1. The ammonium $\delta^{15}\text{N}$ analysis can be considered independent of the nitrate $\delta^{15}\text{N}$ analysis, and therefore useful for discrimination purposes, as we observed no statistically significant correlation between the ammonium and nitrate $\delta^{15}\text{N}$ values (Pearson $r = 0.24$, $P = 0.1270$). The range in ammonium $\delta^{15}\text{N}$ values of -4.5‰ to $+0.7\text{‰}$ (between-sample variation) was much larger than the within-sample variation as estimated by the pooled standard deviation (SD) of the samples (0.16‰ , $n = 42$, 2 repeated measurements). The pooled SD was comparable with the SD of the $\delta^{15}\text{N}$ analyses of the isotopic reference materials ($0.13\text{--}0.24\text{‰}$).

The range of our measured $\delta^{15}\text{N}$ values agreed with the reported $\delta^{15}\text{N}$ values of ammonium from synthetic sources (range between -7‰ and $+5\text{‰}$ ^[9,10]). The mean value of the ammonium $\delta^{15}\text{N}$ distribution (-0.8‰) was less than the theoretical value of 0‰ ($t = 5.655$, $df = 41$, $P < 0.0001$), rejecting the hypothesis that there is no isotope ratio difference between atmospheric N_2 and the mean NH_4 in AN. We suggest alternative hypotheses that fractionation occurs due to: (1) incomplete conversion and kinetic isotope effects in the synthesis of N_2 into NH_3 , or (2) loss of ^{15}N -enriched residues during distillation prior to AN synthesis, or (3) incomplete reactions and/or side products during AN synthesis.

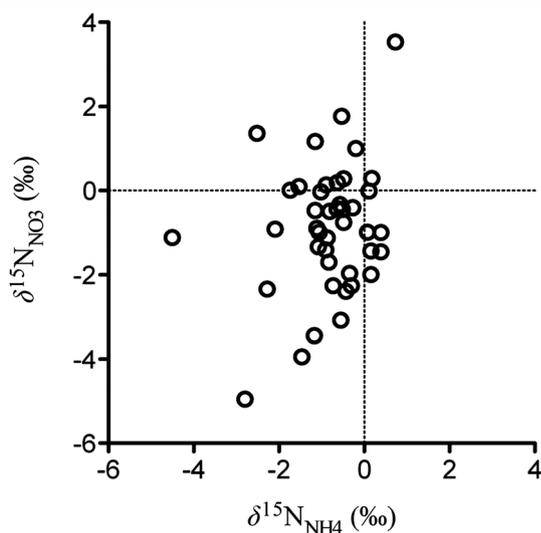


Figure 1. Scatterplot of $\delta^{15}\text{N}$ values of ammonium (NH_4^+) ions versus $\delta^{15}\text{N}$ values of nitrate (NO_3^-) ions in 42 ammonium nitrate samples from the survey. Nitrate $\delta^{15}\text{N}$ values were calculated from the ammonium $\delta^{15}\text{N}$ values and the $\delta^{15}\text{N}$ values of the bulk AN by the mass balance equation, where $\delta^{15}\text{N}_{\text{AN}} = (\delta^{15}\text{N}_{\text{NO}_3} + \delta^{15}\text{N}_{\text{NH}_4})/2$. Each point represents the paired means of two measurements of ammonium tetraphenylborate and three measurements of AN. Propagated uncertainties for $\delta^{15}\text{N}$ measurements of ammonium and nitrate were 0.16‰ and 0.38‰, respectively. The means of both distributions were more negative than the theoretical value of 0‰ (marked by the dotted lines), and the two variables were not correlated.

Nitrate $\delta^{15}\text{N}$ values from bulk AN analysis and mass balance calculations

The nitrate $\delta^{15}\text{N}$ values were calculated from the AN and ammonium tetraphenylborate values by mass balance. The pooled SD of the ammonium nitrate sample $\delta^{15}\text{N}$ analysis (0.25‰, $n = 42$, 3 repeated measurements) indicated variance greater than that of isolated NH_4 (F -test, $P = 0.0009$). The higher measurement precision of the analysis of ammonium tetraphenylborate may be due to its chemical makeup, which is more amenable to EA/Conflo techniques than AN due to the presence of carbon.^[23] The range of nitrate $\delta^{15}\text{N}$ values (-5.0‰ to +3.5‰) was roughly twice that of the ammonia $\delta^{15}\text{N}$ values, and the propagated uncertainty of the nitrate $\delta^{15}\text{N}$ values, in terms of SD, was 0.38‰ – roughly twice the SD of the ammonia $\delta^{15}\text{N}$ values. Although the uncertainty was greater, nitrate $\delta^{15}\text{N}$ analysis by this method still has discriminatory power due to the larger range in nitrate $\delta^{15}\text{N}$ values.

The distribution of measured nitrate $\delta^{15}\text{N}$ values in this study was consistent with literature values (range between -8‰ and +7‰).^[10] The mean value (-0.9‰) was also less than the atmospheric $\delta^{15}\text{N}$ value of 0‰ ($t = 3.625$, $df = 41$, $P = 0.0008$) suggesting that nitrogen isotope fractionation occurs between the atmospheric source and the nitrate ion in AN. These sources of fractionation may be the same as those affecting the ammonium ion, as discussed above. Paired ammonium and nitrate $\delta^{15}\text{N}$ values had a mean difference that was not statistically significant (paired t -test, $t = 0.093$, $df = 41$, $P = 0.926$), contrasting with the results from Freyer and Aly^[16] that showed ^{15}N enrichment of NO_3^-

relative to NH_4^+ in fertilizers with both forms of nitrogen. These results show that amine and nitrate nitrogen isotope ratios in ammonium nitrate are independent and both contribute discriminatory power for forensic analysis, and that the tetraphenylborate isolation method is conducive to obtaining these new variables.

Additional discrimination of samples was provided by separate analysis of the AN component ions ammonium and nitrate. Although a robust statistical analysis of discriminatory power is outside the scope of this study, we can demonstrate the utility of this method by comparing the nitrogen isotope ratios of each of the 42 samples of different sources against every other sample. A simple test considers samples 'different' if the measured isotope ratios differ by more than 1.96 SD. Of the 861 ($42 \times 41 \times 0.5$) comparisons of ammonium nitrate $\delta^{15}\text{N}$ values (as bulk AN), 433 (50%) were not different. When we considered the $\delta^{15}\text{N}$ values of ammonium and nitrate component ions separately, only 42 of the 861 comparisons (5%) were not different. Separate component ion $\delta^{15}\text{N}$ analysis improves the discriminatory power over bulk analysis, and additional isotopes of ammonium nitrate may further be of use to the forensic scientist.

Acknowledgements

IsoForensics, Inc. provided funding for this project. We thank Lesley Chesson and James Ruff for comments on the manuscript.

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