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Improved accuracy and precision in $\delta^{15}\text{N}_{\text{AIR}}$ measurements of explosives, urea, and inorganic nitrates by elemental analyzer/isotope ratio mass spectrometry using thermal decomposition

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RATIONALE: Elemental analyzer systems generate N_2 and CO_2 for elemental composition and isotope ratio measurements. As quantitative conversion of nitrogen in some materials (i.e., nitrate salts and nitro-organic compounds) is difficult, this study tests a recently published method – thermal decomposition without the addition of O_2 – for the analysis of these materials.

METHODS: Elemental analyzer/isotope ratio mass spectrometry (EA/IRMS) was used to compare the traditional combustion method (CM) and the thermal decomposition method (TDM), where additional O_2 is eliminated from the reaction. The comparisons used organic and inorganic materials with oxidized and/or reduced nitrogen and included ureas, nitrate salts, ammonium sulfate, nitro esters, and nitramines. Previous TDM applications were limited to nitrate salts and ammonium sulfate. The measurement precision and accuracy were compared to determine the effectiveness of converting materials containing different fractions of oxidized nitrogen into N_2 .

RESULTS: The $\delta^{13}\text{C}_{\text{VPDB}}$ values were not meaningfully different when measured via CM or TDM, allowing for the analysis of multiple elements in one sample. For materials containing oxidized nitrogen, ^{15}N measurements made using thermal decomposition were more precise than those made using combustion. The precision was similar between the methods for materials containing reduced nitrogen. The %N values were closer to theoretical when measured by TDM than by CM. The $\delta^{15}\text{N}_{\text{AIR}}$ values of purchased nitrate salts and ureas were nearer to the known values when analyzed using thermal decomposition than using combustion.

CONCLUSIONS: The thermal decomposition method addresses insufficient recovery of nitrogen during elemental analysis in a variety of organic and inorganic materials. Its implementation requires relatively few changes to the elemental analyzer. Using TDM, it is possible to directly calibrate certain organic materials to international nitrate isotope reference materials without off-line preparation. Copyright © 2015 John Wiley & Sons, Ltd.

The introduction of the Coleman analyzer in 1960^[1] made routine the elemental analysis of nitrogen in organic compounds (e.g., those containing carbon). However, elemental analysis of many compounds with a large relative amount of nitrogen – including some nitrate salts, imidazoles, and pyrimidines – resulted in low recovery of nitrogen. Several solutions have been proposed and applied to reduce the quantity of nitrogen lost in elemental composition measurements using an elemental analyzer (EA). Addition of combustion aids such as V_2O_5 ,^[2] sugar,^[3,4] and charcoal^[5] to samples measured with automated analyzers, or graphite in off-line reactions,^[6] has resulted in near theoretical recovery of nitrogen for some compounds. Modifications of the reactor chemistry^[7] and the configurations^[8] of these analyzers have also improved the recovery of nitrogen. Yet there has been no consensus as to which among these

methods is best at recovering the theoretical amount of nitrogen from compounds with relatively large amounts of nitrogen relative to carbon.

Lower than expected recovery of nitrogen during elemental analysis is especially problematic for stable isotope analysis. This is because incomplete conversion of nitrogen into N_2 may be associated with isotopic fractionation, leading to potentially large errors in $^{15}\text{N}/^{14}\text{N}$ ratio measurements.^[9] This is particularly relevant to forensic isotopic analyses of explosives (e.g., ammonium nitrate, PETN, HMX, and RDX,) where investigators may be interested in distinguishing among explosive specimens with low C:N ratios.^[5,10–15]

In a recent publication,^[16] Gentile *et al.* addressed the problem of insufficient recovery of nitrogen by comparing the traditional combustion method, the traditional combustion method with the addition of combustion aids, and a modification to conventional elemental analyzer/isotope ratio mass spectrometry (EA/IRMS) techniques. They reported best results when the usual oxygen injection was suppressed during elemental analysis, especially for materials that may produce

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oxygen through decomposition. By not adding additional oxygen to the helium stream, the authors were able to improve repeatability and reproducibility in the measurements of both elemental composition and nitrogen-isotope ratio for a variety of inorganic compounds as compared to other variations of the combustion method. They concluded that this technique was preferable for inorganic materials but not for organic reference materials. In addition, Gentile *et al.* noted that the oxidation state of the nitrogen in analyzed materials is an important consideration in determining the applicability of the "no oxygen" analytical method.

Here, we tested the hypothesis that the fraction of oxidized nitrogen determines whether a decomposition method or a combustion method (without the addition of combustion aids) is better suited to measuring nitrogen concentrations and isotope ratios of a variety of inorganic and organic materials. We refer to the traditional elemental combustion procedure as combustion method (CM) and the variant without added oxygen as thermal decomposition method (TDM). We specifically investigated whether TDM would produce more precise and accurate results than CM by analyzing inorganic compounds containing oxidized nitrogen and/or reduced nitrogen. We extended our investigation to organic compounds that contain oxidized and/or reduced nitrogen. We tested seven different material types related to previous explosives work,^[17–19] including urea, ammonium nitrate, nitro esters, and nitramine compounds.

EXPERIMENTAL

Material types

Materials analyzed in this study included: 6 ureas, 5 potassium nitrates, 2 ammonium nitrates, 1 cyclotrimethylene trinitramine (RDX), 1 cyclotetramethylene tetranitramine (HMX), 1 pentaerythritol tetranitrate (PETN), and 1 sodium nitrate.

Materials were analyzed for nitrogen elemental composition (w/w%) and ¹⁵N/¹⁴N isotope ratios. Stable isotope ratios are expressed as the deviation from an international standard: $\delta = (R_{SA} - R_{STD})/R_{STD}$, where R_{SA} and R_{STD} are the ratios of heavy to light molar abundances of carbon or nitrogen, ¹³C/¹²C or ¹⁵N/¹⁴N, of the sample and standard. The international standard for carbon is Vienna Pee Dee Belemnite (VPDB), and for nitrogen it is atmospheric N₂ (AIR). We present the stable isotope ratios, δ , in 'per mil' notation (‰).

We purchased potassium nitrates IAEA-N3 from the International Atomic Energy Agency (IAEA, Vienna, Austria) and USGS32, USGS34, and sodium nitrate USGS35 from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). The consensus values for these nitrate salts were obtained from the IAEA website^[20] and are expressed as the mean \pm 1 standard deviation (SD). We note that USGS32 is one of the IUPAC nominated materials defining the nitrogen-isotope normalization scale.

Urea #1, Urea #2, and Urea #3 were obtained from Arndt Schimmelmann (Indiana University, Bloomington, IN, USA); calibration of these materials was published in September 2009.^[21] The values reported here for these ureas are those obtained from the inter-laboratory comparison using combustion methods, with data normalized to the

internationally distributed reference materials USGS40 and USGS41 (glutamic acids). We chose to use these values because the ureas used for normalization in our study (e.g., URH1, URL1) were also calibrated using USGS40 and USGS41.

Ammonium nitrate (SAN) and ammonium sulfate (AmSu1) were purchased from Malinckrodt (St. Louis, MO, USA).

Organic explosives cyclotrimethylene trinitramine (RDX, 522R), cyclotetramethylene tetramine (HMX, 291H), and pentaerythritol tetranitrate (PETN, 544P) were obtained from previous studies at IsoForensics, Inc. (Salt Lake City, UT, USA). The purity of each of these nitrated explosive materials was determined to be greater than 99% by HPLC-UV-Vis analysis.

Laboratory reference materials URH1 and URL1 were produced in our laboratory using stock urea purchased from Sigma Aldrich (St. Louis, MO, USA), ¹³C-enriched and ¹⁵N-enriched urea purchased from Isotech Laboratories, Inc. (Champaign, IL, USA), and ¹³C-depleted and ¹⁵N-depleted urea purchased from Icon Isotopes (Summit, NJ, USA). The stock urea (URS1) was mixed in aqueous solutions with small quantities of enriched and depleted urea to form the laboratory reference materials URH1 and URL1, respectively, and precipitated in liquid nitrogen after Arndt Schimmelmann's method (personal communication).

The potassium nitrates KNit70 and KNit90 were produced in our laboratory by reaction of 70% (J.T. Baker, Phillipsburg, NJ, USA) and 90% (Fisher Chemical, Fair Lawn, NJ, USA) nitric acids with potassium hydroxide purchased from Sigma Aldrich. The method is described by Howa *et al.*^[18]

When presenting data for these materials in the tables, the material types are ordered first by fraction of oxidized nitrogen ($f N_{(ox)}$) found in the compounds then categorized as organic/inorganic. Published nitrogen-isotope ratio values are presented as 'outside information' for materials available for purchase (i.e., IAEA-N3, USGS32, USGS34, USGS35, Urea #1–3). The theoretical nitrogen elemental compositions were computed using the molecular mass for each material type, obtained from NIST, and the standard atomic weight of nitrogen, obtained from Atomic Weights of the Elements 2011 (IUPAC Technical Report),^[22] assuming the purity to be >99.9%.

Reagents and gases

High-purity gases purchased for use with the elemental analyzer and isotope ratio mass spectrometer included helium UHP grade (purity greater than 99.999%) as carrier gas, oxygen UHP grade (purity greater than 99.999%) as oxidizer, and nitrogen UHP grade (purity greater than 99.999%) as isotope reference gas. All gases were supplied by Airgas (Salt Lake City, UT, USA). Chromium(III) oxide (Cr₂O₃) on alumina, silvered cobaltous-cobaltic oxide, quartz wool, quartz chips, reduced copper wire, quartz glass inserts, and magnesium perchlorate were purchased from Costech Analytical (Valencia, CA, USA).

Sample preparation

Samples and reference materials were weighed into 3.5 \times 5 mm tin capsules (Costech Analytical) to produce a theoretical yield of 140 \pm 14 μ g total nitrogen. All samples in an individual

analytical sequence were weighed and analyzed on the same day with sample mass recorded to 2- μg precision. Identical sample sequences were analyzed at least twice using each of the methods, CM and TDM. The method treatments were paired such that the CM or TDM sequences were analyzed the day following its comparative treatment. Individual samples were arranged within a sequence in a mirror image to preclude order effects; i.e., the second half of the sequence had the same samples as the first but in reverse order. The numbers (capsules) of each sample in a sequence ranged from 2–8 and were run consecutively in only a few cases. For instance, PETN samples, 6–8 samples per sequence, were analyzed consecutively in blocks of 3–4 samples in order to detect memory effects if they existed, but none were observed.

Instrumentation

Analyses were performed with a 4010 elemental analyzer (Costech Analytical) coupled to the Conflo IV interface of a MAT 253 isotope ratio mass spectrometer (ThermoFinnigan, Bremen, Germany). The sample capsules were introduced into the EA with a zero-blank autosampler. The EA parameters were 1.2 bar helium, flow rate 95 mL/min, 1.0 bar oxygen, oxidation reactor at 980°C, reduction reactor at 650°C, sample delay 8 s, sample stop 9 s, oxygen stop 30 s, and run time 60 s. The timing of the sample delay was set so the sample would drop in the hot zone ~1–2 s before the oxygen pulse. The oxidation reactor was packed to the manufacturer's specifications with Cr_2O_3 on alumina and silvered cobaltic oxide. The reduction reactor was packed with 310 mm of reduced copper centered between 60 mm of quartz wool on both ends.

Instrument methods

Two different methods were used to analyze samples. For the combustion method (CM), oxygen was introduced using the semi-micro loop (5 mL). A magnesium perchlorate trap was used to remove water from the reaction in the helium carrier stream. The product N_2 and CO_2 gases were separated using a 3-m $\frac{1}{4}$ " PoraPak Q column (Costech Analytical) held at 40°C. For the thermal decomposition method (TDM), the same reactor, traps, and columns were employed but the oxygen injection was suppressed by selecting the 'O2' analysis mode. Because the 'O2' analysis mode does not use the Sample Delay parameter, the sample drop timing was adjusted 8 s, from 42 to 50 s, through the IsoDat 3.0 software (ThermoFinnigan) to maintain identical chromatographic timing between the two methods. No significant differences were observed in the retention times of N_2 peaks for material types containing reduced nitrogen analyzed using CM versus TDM. Significantly later retention times (1-tailed t -test, $p < 0.0010$) and tailing of the nitrogen peak were observed for nitrate salts and nitro ester compounds when analyzed by the CM.

All samples were analyzed alongside the urea laboratory reference materials URH1 and URL1. Each of these two reference materials were analyzed at least as frequently as one in ten sample capsules; no less than two of each were included in any individual sequence. These reference materials were used to correct for potential memory, time, and size bias in individual analytical sequences. URH1 and

URL1 were used to normalize measured isotope ratios to the international isotope scales. Values measured for URS1 were used to check the normalizations by comparison of corrected isotope ratios within the sequence with previously measured values.

The urea laboratory reference materials were previously calibrated against USGS40 and USGS41. The calibrated $\delta^{13}\text{C}_{\text{VPDB}}$ values for URH1, URL1 and URS1 were -7.92% , -65.06% and -32.85% , respectively, when the certified values of -26.39% and $+37.63\%$ were used for USGS40 and USGS41, respectively. The calibrated $\delta^{15}\text{N}_{\text{AIR}}$ values for URH1, URL1 and URS1 were $+41.41\%$, -66.37% and $+0.15\%$, respectively, when the recommended values -4.52% and $+47.57\%$ were used for USGS40 and USGS41, respectively.^[23]

Statistical analyses were completed using Prism for Macintosh (version 5.0f, GraphPad Software Inc., La Jolla, CA, USA). Normalized analytical results were used in the tests. The significance level for the all the statistical tests was set at $\alpha = 0.05$.

RESULTS AND DISCUSSION

The mean $\delta^{13}\text{C}_{\text{VPDB}}$ values obtained by the thermal decomposition method (TDM) were compared with those obtained by the combustion method (CM) for each of the four relevant organic material types studied [Urea (URS1), RDX, HMX, and PETN; Table 1]. No significant difference was found except for PETN (t -test with Welch's correction, $p = 0.0057$). However, the difference between the mean $\delta^{13}\text{C}_{\text{VPDB}}$ values for PETN measured using CM and TDM was less than 0.1%. The remainder of our study focuses on nitrogen.

The nitrogen elemental composition and isotope ratio analyses of six different material types by CM and TDM are summarized in Tables 2 and 3. As noted previously, the materials are first sorted by the fraction of oxidized nitrogen and then categorized as organic/inorganic. The measured mean nitrogen compositions (%N) of most of the materials containing oxidized nitrogen were significantly lower when analyzed via CM than via the TDM (t -test; see statistical results in Table 2). We did not observe a significant difference in the %N measurements of materials containing only reduced nitrogen between CM and TDM in contrast to the differences observed by Gentile *et al.*^[16] for ammonium sulfate. The EA cycle timing – especially the sample drop time in relation to the oxygen pulse arrival time – used in the CM of the two studies may explain the observed differences. The cycle timing for CM used in this study resulted in samples arriving just before the O_2 pulse, which does not result in the reduction of recovered nitrogen as frequently observed in the previous study for ammonium sulfate. If the conditions in our study were near ideal for the conversion of ammonium sulfate N into N_2 in the CM, then results from analysis using the TDM would not show an improvement.

The mean $\delta^{15}\text{N}_{\text{AIR}}$ values obtained by TDM were compared with those obtained by CM for urea, ammonium sulfate, nitramines, ammonium nitrate, PETN, and nitrate salts. The $\delta^{15}\text{N}_{\text{AIR}}$ values produced via TDM for materials containing oxidized nitrogen were significantly different from those produced by the combustion method (see Table 3 for results). In general, the measured $\delta^{15}\text{N}_{\text{AIR}}$ values were lower when measured via CM than via TDM. Unpaired t -tests using

Table 1. Summary of the carbon-isotope ratio data collected for materials examined in this study. Fraction oxidized nitrogen ($fN_{(ox)}$), means, and standard deviations (SD) of $\delta^{13}C_{VPDB}$ values of individual samples included all measurements (n) in the statistical comparisons between methods (t -test with Welch's correction and F -test for unequal variances)

Material type	ID	$fN_{(ox)}$	Thermal decomposition		Combustion		p value t -test	p value F -test
			n	$\delta^{13}C, \text{‰}$ (Mean \pm 1SD)	n	$\delta^{13}C, \text{‰}$ (Mean \pm 1SD)		
Urea	URH1	0	28	-7.90 ± 0.06	24	-7.90 ± 0.18	na	na
	URL1		28	-65.11 ± 0.07	26	-65.11 ± 0.20	na	na
	URS1		34	-32.84 ± 0.08	32	-32.82 ± 0.11	0.4342	0.0981
Nitramine	RDX	0.5	18	-29.19 ± 0.14	16	-29.17 ± 0.16	0.7946	0.7402
	HMX		14	-49.14 ± 0.18	4	-49.25 ± 0.09	0.1310	0.2689
Nitroester	PETN	1	23	-38.20 ± 0.06	24	-38.12 ± 0.11	0.0057 ^a	0.0100

^aThe difference is less than 0.1‰; na = not applicable

Table 2. Summary of the %N results for materials examined in this study. Calculated %N values of compounds from outside sources are included along with fraction oxidized nitrogen ($fN_{(ox)}$) and description 'organic' (o) vs 'inorganic' (i). Mean, standard deviation (SD), and count of analyses (n) for individual materials are summarized by method. Statistical tests of comparisons between methods are by unpaired t -test with Welch's correction and F -test for unequal variances

Material type	$fN_{(ox)}$	Theoretical Wt %N	Thermal decomposition		Combustion		p value t -test	p value F -test
			n	Measured %N (Mean \pm 1SD)	n	Measured %N (Mean \pm 1SD)		
Urea (o)	0	46.65	113	46.51 ± 0.93	84	46.65 ± 0.87	0.2593	0.4899
Ammonium sulfate (i)		21.20	4	21.11 ± 0.14	7	21.11 ± 0.21	0.9442	0.5501
Nitramine (o)	0.5	37.84	33	37.80 ± 0.57	20	36.93 ± 0.94	0.0009	0.0129
Ammonium nitrate (i)		35.00	6	35.32 ± 0.47	9	33.00 ± 1.28	0.0008	0.0445
Nitro ester (o)	1	17.72	23	17.49 ± 0.24	24	15.89 ± 0.51	<0.0001	0.0010
Nitrate salt (i)		13.85	45	13.63 ± 0.23	29	12.59 ± 0.37	<0.0001	0.0033

Welch's correction of the method comparisons for specific compounds were significant except for RDX, which had a difference of less than 0.1‰.

Thermal decomposition method is precise

The variances of measured %N and $\delta^{15}N_{AIR}$ values obtained by TDM were compared with those obtained by CM for each of the materials containing oxidized nitrogen (i.e., all but urea and ammonium sulfate). TDM produced significantly more precise measurements (F -test; see results in Tables 2 and 3) and confirmed the observations of Gentile *et al.*^[16] for nitrate salts. TDM analysis of urea and ammonium sulfate did not produce significantly more precise $\delta^{15}N_{AIR}$ measurements than the CM, in contrast to the observations of Gentile *et al.*^[16] for ammonium sulfate. We note that measured %N values of the ammonium sulfate analyzed via CM were not significantly different from its theoretical value and the standard deviations in $\delta^{15}N_{AIR}$ values for this compound measured by either method were less than 0.2‰.

Thermal decomposition method is accurate

Nitrogen recoveries nearer to theoretical quantities should result in more accurate nitrogen-isotope ratio measurements since incomplete conversion reactions have the potential to

discriminate between heavy and light isotopes. We tested this hypothesis using materials of known %N (see Table 2 for all material types) and nitrogen-isotope ratios (see Table 3 for ureas and nitrate salts having published nitrogen-isotope ratio values).

Elemental compositions

When compared with the theoretical nitrogen elemental composition, the mean %N for the samples containing oxidized nitrogen (nitramines, ammonium nitrate, PETN, and nitrate salts) and analyzed via TDM was nearer to – and in most cases within 1 SD of – the theoretical %N value than when the materials were analyzed by CM (Table 2). The measured %N values for urea and ammonium sulfate, which contained only reduced nitrogen, were not significantly different from the theoretical values. These observations are consistent with those made earlier by Gentile *et al.*^[16] for ammonium sulfate.

Nitrogen-isotope ratios

The accuracy of an isotope ratio measurement is dependent upon the capability to compare results in a run to measurements of materials of a known isotope ratio. Among the materials that were analyzed using TDM were

Table 3. Summary of the $\delta^{15}\text{N}_{\text{AIR}}$ results for materials examined in this study. Published $\delta^{15}\text{N}_{\text{AIR}}$ values of compounds from outside sources are included along with fraction oxidized nitrogen ($f\text{N}_{(\text{ox})}$) and description 'organic' (o) *vs* 'inorganic' (i). Mean, standard deviation (SD), and count of analyses (n) for individual materials are summarized by method. Statistical tests of comparisons between methods are by unpaired t -test with Welch's correction and F -test for unequal variances

Material type	Outside information		Thermal decomposition		Combustion		p value t -test	p value F -test	
	ID	$f\text{N}_{(\text{ox})}$	$\delta^{15}\text{N}$, ‰ (Mean \pm 1SD)	n	$\delta^{15}\text{N}$, ‰ (Mean \pm 1SD)	n			$\delta^{15}\text{N}$, ‰ (Mean \pm 1SD)
Urea (o)	URH1	0		29	41.41 \pm 0.09	25	41.41 \pm 0.14	na	na
	URL1			29	-66.37 \pm 0.05	27	-66.37 \pm 0.13	na	na
	URS1			34	0.14 \pm 0.11	32	0.14 \pm 0.11	0.9494	0.9168
	Urea #1		0.10 \pm 0.19	7	0.22 \pm 0.08			nd	nd
	Urea #2		20.39 \pm 0.29	7	20.51 \pm 0.08			nd	nd
	Urea #3		41.11 \pm 0.31	7	41.21 \pm 0.11			nd	nd
Ammonium sulfate (i)	AmSul1	0		4	-4.81 \pm 0.19	7	-4.93 \pm 0.14	0.3564	0.5031
Nitramine (o)	RDX	0.5		18	-17.52 \pm 0.24	16	-17.59 \pm 0.41	0.5389	0.0377
	HMX			15	-0.57 \pm 0.10	4	-1.08 \pm 0.32	0.0489	0.0020
Ammonium nitrate (i)	AN	0.5		6	21.26 \pm 0.23	9	20.15 \pm 0.66	0.0010	0.0310
Nitro ester (o)	PETN	1		23	-13.68 \pm 0.07	24	-15.10 \pm 0.60	<0.0001	<0.0001
Nitrate salt (i)	USGS32	1	180 \pm 1	6	181.37 \pm 0.38	1	179.06	nd	nd
	USGS34		-1.8 \pm 0.2	10	-1.71 \pm 0.07	6	-2.74 \pm 0.47	0.0030	<0.0001
	IAEA-N3		4.7 \pm 0.2	9	4.78 \pm 0.08	6	3.95 \pm 0.37	0.0027	0.0003
	KNit70			10	3.13 \pm 0.07	8	2.11 \pm 0.37	0.0001	<0.0001
	KNit90			10	-1.86 \pm 0.04	8	-2.82 \pm 0.44	0.0005	<0.0001
	USGS35		2.7 \pm 0.2	4	2.77 \pm 0.04			nd	nd

na = not applicable; nd = not determined

four nitrate salts and three ureas that have published nitrogen-isotope ratio values. The known nitrogen-isotope ratios of these materials are summarized in Table 3 as "outside information".

The $\delta^{15}\text{N}_{\text{AIR}}$ values of the four nitrate salts measured via TDM were nearer to the known values than the measurements made on these materials using CM (Table 3). The differences between the measured means made using TDM in this study and the reported values were +0.09, +0.08 and +0.07‰ for USGS34, IAEA-N3 and USGS35, respectively (Table 3), within 1 SD of the known values. The difference for USGS32 was +1.37‰, within 2 SD of the defined value of +180‰. The values obtained for Urea #1, Urea #2, and Urea #3 using TDM were all within 0.12‰ (<1 SD) of the published values.^[21]

TDM allows normalization of explosives and urea directly to international reference materials using EA/IRMS

Accurate and precise measurement of stable isotope ratios requires that the principle of identical treatment^[24–26] is followed during the analysis of both unknowns (samples) and reference materials. The accuracy of the preparative and analytical methods of analysis should be robust across the compositions of materials to be tested. Thus they should not show a bias where chemically dissimilar materials are being measured. This is especially important during the calibration of laboratory reference materials. The IUPAC recommended normalization reference materials for the atmospheric nitrogen isotope scale are USGS32, an inorganic nitrate salt, and IAEA-N1, an

inorganic ammonium sulfate.^[23] These international reference materials are often used in turn to calibrate a variety of organic reference materials (e.g., urea, glutamic acid).^[21,27] Until recently, the only preparative and analytical methods available to treat these material types identically and without bias had been in-tube combustion, off-line preparation, and analysis of the purified N_2 gas by dual-inlet IRMS.^[28] Drawbacks to this approach include the increased labor and time required to prepare and analyze samples. An increasing number of laboratories analyze samples exclusively using traditional on-line systems because they lack: (1) the additional equipment to convert these solid reference materials to gas off-line, and (2) the capacity to analyze pure gas samples.

Using the TDM, inorganic materials (e.g., nitrate salts, ammonium sulfates) and tested organic materials, like nitramines, nitro esters, and ureas, can be analyzed using the principle of identical treatment while also generating more precise measurements. Materials with vastly different chemical compositions (i.e., inorganic *vs* organic) can be measured or calibrated directly to the IUPAC recommended normalization reference materials^[23] and the calibrations can be verified with other internationally distributed materials.^[29] Isotope ratio analysis using an elemental analyzer is no longer restricted to the analysis and calibration of materials that are chemically similar to the international reference materials. Any laboratory with the capacity to analyze inorganic or organic material by EA/IRMS can accurately and precisely analyze samples amenable to TDM alongside internationally distributed reference materials with a few simple changes to the EA system.

Where a bias is observed, %N measurements can be used to correct measured isotope ratios

As demonstrated previously by Gentile *et al.*^[16] and here in this study, traditional combustion EA analysis of materials containing oxidized nitrogen can lead to lower than expected recovery of nitrogen. This in turn can lead to nitrogen-isotope ratio measurements that are more negative by as much as 0.9‰ on average and as much as ~4‰ on an individual analysis basis from the known values, depending on the condition of the EA reactor.

We have been analyzing nitro-organic and nitrate salts using combustion EA for more than 15 years.^[17–19] As part of our regular quality assurance/quality control procedures, we analyze laboratory quality control (QC) materials with identical or nearly identical chemical composition alongside samples. We regularly observed a high frequency of $\delta^{15}\text{N}_{\text{AIR}}$ QC failures in RDX, HMX, PETN and ammonium nitrate that correlated to a lower than expected nitrogen elemental composition. We thus considered these types of materials as difficult to analyze and often reanalyzed samples. Prior to the publication by Gentile *et al.*^[16] we had not found a solution to reduce the failure rate of QC materials containing oxidized nitrogen.

When QC failures occurred, samples and reference material data were rejected and samples were reanalyzed when possible. Although the $\delta^{15}\text{N}_{\text{AIR}}$ values from failed analytical sequences were rejected and not used in data interpretations or publications,^[17–19] we collected the $\delta^{15}\text{N}_{\text{AIR}}$ and weight percent data in our Laboratory Information Management System. One such QC reference material with 5+ years of data is a pure PETN sample highlighted in a recently published study.^[19]

Based on results of this current work, a correction to measured nitrogen-isotope ratios may be possible using the relationship between %N and $\delta^{15}\text{N}_{\text{AIR}}$ values. Differences between the measured and theoretical %N ($\Delta\%N$) and the $\delta^{15}\text{N}_{\text{AIR}}$ values measured using the CM and the TDM ($\Delta\delta^{15}\text{N}$) for the six material types were calculated. The slopes of $\Delta\delta^{15}\text{N}$ as a function of $\Delta\%N$ for each material type are presented in Table 4 and Fig. 1(a). These slopes may be used to calculate a correction for individual sample analyses. To test this hypothesis, we applied the slope determined for PETN ($m = 0.7866$) in our current study to produce a correction factor of $0.7866 \times \Delta\%N$ to previous measurements of PETN made over a 5-year period. Previously measured $\Delta\delta^{15}\text{N}$ values and those values with the added correction factor are presented in Fig. 1(b).

Table 4. Linear relationships between the difference in the measured and theoretical %N ($\Delta\%N$) and the difference in the $\delta^{15}\text{N}_{\text{AIR}}$ values measured using the combustion method and the thermal decomposition method ($\Delta\delta^{15}\text{N}$). The calculated slopes $\pm 95\%$ CI, p -value for significance test of slope different than zero, and the correlation coefficient r are provided along with the fraction of oxidized nitrogen ($f N_{(\text{ox})}$) for each material type and description 'organic' (o) *vs* 'inorganic' (i)

Material type	$f N_{(\text{ox})}$	Combustion		
		Slope($\Delta\delta^{15}\text{N}$ vs $\Delta\%N$) (Slope \pm 95% CI)	p value slope	r
Urea (o)	0	0.0186 \pm 0.0256	0.1525	0.1566
Ammonium sulfate (i)	0	0.1753 \pm 0.7803	0.6024	0.219
Nitramine (o)	0.5	0.1191 \pm 0.1550	0.1244	0.3461
Ammonium nitrate (i)	0.5	0.5128 \pm 0.1465	<0.0001	0.9437
PETN (o)	1	0.7866 \pm 0.0832	<0.0001	0.9712
Nitrate salt (i)	1	0.8214 \pm 0.0753	<0.0001	0.9731

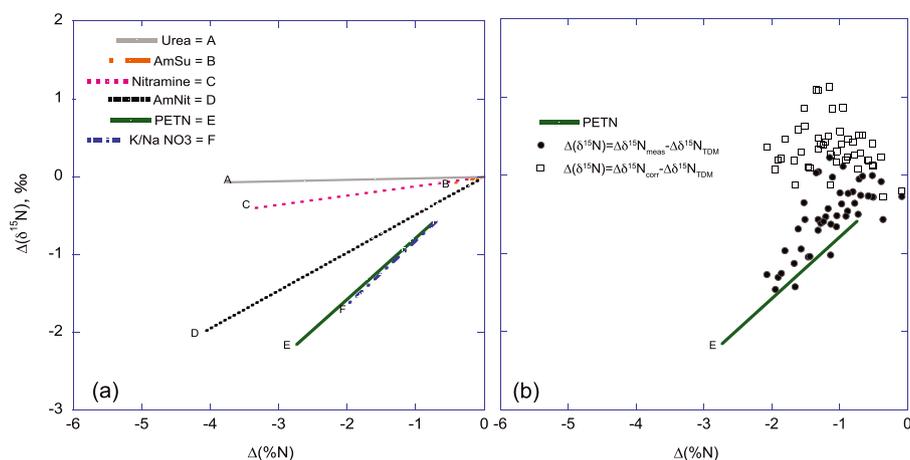


Figure 1. (a) Linear relationships between the difference in the measured and theoretical %N ($\Delta\%N$) and the difference in the $\delta^{15}\text{N}_{\text{AIR}}$ values measured using the combustion method and the thermal decomposition method ($\Delta\delta^{15}\text{N}$). (b) Individual analyses of PETN reference material previously analyzed by the CM (circles, ●) and corrected (squares, □) using slope from line E ($m = 0.7866$).

Comparison of the original measured and newly corrected $\delta^{15}\text{N}_{\text{AIR}}$ values for PETN shows significant differences in the variances and means. A test of unequal variances shows significantly smaller variances in the corrected $\delta^{15}\text{N}$ values (SD = 0.31‰) than in the original dataset (SD = 0.43‰; one-tailed *F*-test, *p* = 0.0325). The mean corrected value for PETN (−13.32) is nearer the mean value measured via TDM in this study (−13.68, Table 3) than the original, uncorrected mean value (−14.20). The corrected $\delta^{15}\text{N}_{\text{AIR}}$ values are significantly more positive than the uncorrected values (paired *t*-test; *p* < 0.0001, *n* = 47). This exercise demonstrates the possibility of correcting previously biased data collected using the CM by accounting for the dependence of $\delta^{15}\text{N}$ values on low nitrogen recovery, although we note that it requires either pure compounds or materials with a well-known %N.

CONCLUSIONS

We tested a thermal decomposition method proposed by Gentile *et al.*^[16] for the elemental analysis of a variety of inorganic and organic materials containing both oxidized and reduced nitrogen. The carbon-isotope ratios were not adversely affected in materials measured in this study by the thermal decomposition method (TDM). In the materials types that we tested, the $\delta^{13}\text{C}_{\text{VPDB}}$ values of the materials containing carbon differed by less than 0.15‰ and in most cases by less than 0.1‰. One advantage to analyzing materials using an EA/IRMS system and the TDM is that multiple elements (i.e., C and N) can be measured from one sample.

We hypothesized that the fraction of oxidized nitrogen is the determinant factor for applying the TDM or the traditional combustion method (CM). In general, we found that the TDM produced significantly more precise and accurate %N and $\delta^{15}\text{N}_{\text{AIR}}$ values than the CM for materials containing oxidized nitrogen, including both inorganic (e.g., nitrate salts) and organic (e.g., nitramine, nitro ester) materials. The measurement precision was similar for materials containing only reduced nitrogen that were analyzed via TDM and CM. The %N values acquired by TDM were near theoretical for all tested materials whereas for materials containing oxidized nitrogen, %N acquired by CM were significantly lower than theoretical. Analysis of the inorganic nitrate reference materials analyzed by the TDM and normalized to our urea reference materials produced $\delta^{15}\text{N}_{\text{AIR}}$ values not significantly different from the published ("known") values. Using the TDM for analysis, the scale defining reference materials USGS32 and IAEA-N1 for $\delta^{15}\text{N}_{\text{AIR}}$ measurements can be used directly to normalize certain organic materials on an EA/IRMS system without the additional time or cost associated with off-line preparation.

Implementation of the TDM as a part of routine EA/IRMS analysis is straightforward. Most elemental analyzers are equipped with the capacity to eliminate added oxygen with a simple switch. With oxygen suppressed, subtle timing changes may be required to accommodate a sample peak timing shift. The associated time and cost requirements to change to the TDM are negligible.

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