B56 Assessment of the Forensic Utility of the Carbon, Nitrogen, and Oxygen Isotope Variability in a Suite of RDX-Based Explosives

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The goal of this presentation is to summarize the methodologies used in stable isotope analyses of nitrated high explosive, demonstrates substantial variations in the carbon, nitrogen, and oxygen isotope composition of high explosives, and discusses how these data can be used in forensic analysis of explosive devices.

This presentation will impact the forensic community by providing an initial suggestion on appropriate methodology for oxygen isotope analysis of explosives and does a preliminary assessment of isotopic variability. There are not yet any accepted methods for this problem for use by those doing forensic analyses of explosives. The accepted methods for oxygen isotope analysis of solids work poorly on high explosives, due to their high nitrogen content. This presentation explains these difficulties and recommends ways to overcome these complications.

Introduction: The natural relative abundances of isotope of light elements, like carbon, nitrogen and oxygen, vary by small, but measurable, amounts due chemical processes which fractionate the isotopes based on their mass. The forensic applications of stable isotopes are rapidly increasing, but this is still an uncommon analytical technique, and has not yet been used as evidence in any U.S. criminal case, but has been used in civil cases and cases overseas. Stable isotope abundances are measured as the ratio of the heavy, rare isotope to the light, common isotope ($^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$). However, the precision of the measurements is so low (~1 part in 10^6 variation in the raw ratio) that typically these isotope ratios are reported as a per mil deviation from of the isotope ratio of a standard material, or delta notation.

Methods: Explosive components were purified from plastic explosive samples using hexane (2x) extraction to remove plasticizers followed by acetone extraction (2x) and filtering to purify the explosive, in this case RDX. No further purification was needed on these samples as RDX was the only explosive component. Carbon and nitrogen isotope ratios were measured by a standard EA-IRMS method, with no need for dilution of the CO_2 peak due to the high N content. Instrumentation used was a Eurovector EA interfaced with a GVI Isoprime magnetic sector mass spectrometer. Oxygen isotope ratio measurements done by standard methods presented some problems. Using a Thermo TC/EA- IRMS (high temperature reduction coupled to a Delta V+ isotope ratio mass spectrometer), the conversion of the explosive-oxygen to CO appeared reasonable as quantitative yields were produced, there was good chromatographic separation of N_2 from CO on masses 28 and 29, and isotope ratio measurements were reproducible. However, the mass 30 background following the N_2 peak never returned to their nominal values, making the $\delta^{18}O$ measurements offset from their true values. The cause of this problem is the creation of NO (with a mass 30 interference) in the ion source following the N_2 peak (discussed for $\delta^{18}O$ measurements of nitrates in: Gehre and Strauch, 2003; Révész and Böhlke, 2002). Use of the Conflo III dilutor during the N_2 peak improved measured isotope ratio measurements by almost 8‰. Replacement of the standard 0.6m 5Å molecular sieve column in the TC/EA with a 1.5m column permits extension of the delay time between the N_2 and CO elution, further reducing the NO background affecting the CO oxygen isotope ratio measurements.

Preliminary Study: A suite of RDX-based plastic explosives, thought to be derived from a common production operation, was assessed for its range in C,N and O isotopic composition. Other forensic analyses found no differences in these explosive materials including FTIR, GC-ECD, and LC-MS, yet an unexpectedly wide range of isotopic compositions was observed. The $\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$ of RDX had ranges of 19.8, 17 and 10.3 ‰ respectively. The large majority of these samples showed a negative correlation between the $\delta^{15}N$ and $\delta^{18}O$ values suggesting that they had been manufactured in batches and the manufacturing process caused this anti-correlation. A few samples fell off of this curve, but had isotope ratios within the ranges of the other samples suggesting that these multivariate statistical approaches are needed for interpretation of data of this nature. Moreover other RDX- based explosives with different binder chemistry, and thus of clearly distinct origin, also fell off of the main O-N isotope trend demonstrating that stable isotope analysis of explosives is a useful approach.

Conclusions: The forensic value of stable isotope measurements of high explosives is only useful in the context of other more established forensic analyses. However, in cases where a direct comparison of material from a crime scene with that from a suspect or direct comparison of explosives from two devices, the carbon nitrogen and oxygen isotope ratios of the explosive can be useful for demonstrating that the devices were constructed with the same batches of explosives. Substantial C, N and O isotope variations of RDX provide a means to categorize explosives which are otherwise chemically identical. Special precautions must be used in oxygen isotope analysis of high nitrogen explosives due to the creation of NO in the ion source.

Inaccurate results may be obtained despite excellent yield and reproducible oxygen isotope measurements, but for inter-laboratory comparisons accurate results are crucial.

Stable Isotopes, RDX, Explosives