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Stable Isotope Characterization of TICs/TIMs: Analytical Progress Report

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AUSPICES

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Summary

We measured twelve alkali cyanide samples that were also sent to ORNL and PNNL collaborators. While results indicate distinct $\delta^{13}C$ and $\delta^{15}N$ values that would be useful to signature studies, the alkali cyanides, especially NaCN, show chemical breakdown during storage that will influence forensic analysis. Carbon and nitrogen stable isotopic compositions of raw materials used to synthesis TETS were measured. Results indicate wide ranges in $\delta^{13}C$ and $\delta^{15}N$ values. Using these raw materials, LLNL scientists synthesized three batches of TETS following published procedures. Stable isotopic measurements of TETS synthesis products indicates nitrogen ($\varepsilon\ ^{15}N$ = -1.7 to -0.8) and carbon ($\varepsilon\ ^{13}C$ = -1.0 to -0.1) fractionation during production.

1. Background

The approach of this research project is to measure stable isotope ratios ($^{13}C/^{12}C$, $^{18}O/^{16}O$, and $^{15}N/^{14}N$) in various TICs/TIMs, and to test whether man-made toxic chemicals comprised of these light elements have individual signatures traceable to specific production facilities. We hypothesize that any observed variation in bulk stable isotopic abundance of these man-made compounds depends on isotopic composition of raw materials used to produce them, as well as the potential fractionation of stable isotopes during the manufacturing process. That is, the <u>bulk</u> stable isotope composition of a TIC/TIM reflects the integrated profile of a production facility, that batch-to-batch variability within a production facility would reflect change in raw material and/or production processing, and that there will be measurable variability in the stable isotope abundance of a given TIC/TIM produced at different facilities.

We plan to work with the following bulk compounds:

1) sodium cyanide (NaCN) and potassium cyanide (KCN)

2) brodifacoum ($C_{31}H_{23}BrO_3$).

3) ammonium metavandate (NH_4VO_3)

Stable isotope characterization would be a critical forensic tool for source attribution if it can be shown that the bulk isotopic composition of a TIC integrates raw material, process, and plant location. To further test this hypothesis, we propose to include a proof-of-principle study that looks at stable isotope fractionation during synthesis of TETS under controlled laboratory conditions. The goal of this study will be to determine, through quantitative analysis and mass balance calculation, the relative importance of raw materials and processing fractionation on the isotopic composition of synthesized TETS.

We plan to work with the following raw materials required to synthesize tetramethylenedisulfotetramine, or TETS ($C_4H_8N_4O_4S_2$):

1) sulfamide, $H_4N_2O_2S$

2) paraformaldehyde, $(CH_2O)_n$ (n = 8 - 100)

3) 1,3,5-trioxane, $C_3H_6O_3$

4) trifluoroacetic acid, $C_2HF_3O_2$

2. Materials

We discussed materials that would be used in this research project in a previous status report (Feb-2009). Complete lists of procured materials are presented in the Appendix that follows this report.

3. Analytical Methods

3a. Nitrogen and Carbon analysis method

An automated, online method that couples an elemental analyzer with an isotope ratio mass spectrometer (EA-IRMS) is used to analyze TIC/TIM samples and precursors for nitrogen and carbon isotope composition and elemental abundance. Solid samples are loaded into 3.5x5 mm tin capsules, and weighed out on a Mettler Toledo XP2U microbalance with a target weight of approximately 80 ug of carbon or nitrogen. The tin capsules are sealed and loaded onto a zero-blank Eurovector rotary autosampler. Elemental composition and isotope ratios are determined using a Eurovector EA3024 elemental analyzer coupled to a Micromass (now Elementar) IsoPrime gas inlet isotope ratio mass spectrometer. Samples dropped into the EA are combusted at 1020° C over chromium oxide in a continuous stream of helium carrier gas. The resulting gases then pass through a reduced copper reactor at 650° C. Following water removal using a magnesium perchlorate trap, the N_2 and CO_2 analyte gases are separated on a 0.7 m GC PLOT column held at 115° C. The gases enter the IRMS as separate peaks in the helium carrier stream, where the isotope ratios of $^{13}C/^{12}C$ and $^{15}N/^{14}N$ are determined based on the ratio of masses 45/44 and 30/28. The following certified standard reference materials are analyzed along with the unknown samples to standardize the results: USGS-24, USGS-25, USGS-34, USGS-40, IAEA-N1, NBS-21, and ANU-Sucrose. All samples were analyzed a minimum of two times, and the standard deviation of these runs is shown as error bars in this report. In general, the expected precision for this method is <0.2 ‰. Samples with standard deviations higher than this value will be rerun.

3b. Oxygen isotope analysis methods

Two methods will be tested for analyzing the oxygen isotope composition of TIC/TIM samples.

3b.1. Sealed tube combustion method

Samples are loaded into quartz tubes, along with 4–5 mg of finely ground spectrographic graphite. The tubes are evacuated and torch sealed. The samples are combusted in a furnace at 850° C, and the CO_2 produced during combustion is cryogenically purified on a vacuum line. Gas yields are measured with a manometer.

The CO_2 is then transferred to a sample tube for analysis on a Micromass (now Elementar) Prism III dual inlet isotope ratio mass spectrometer (DI-IRMS).

3b.2. High Vacuum Fluorination method

The High Vacuum Fluorination System (HVFS) is an offline method that liberates oxygen gas from solid samples by a reaction with ClF_3 gas at 550° C. The oxygen gas is converted to CO_2 on a heated graphite rod, and analyzed with a Micromass (now Elementar) Prism III dual inlet isotope ratio mass spectrometer (DI-IRMS).

4. TICs/TIMs Stable Isotope Characterization

4.1 Cyanides (KCN, NaCN)

We shipped eight KCN and four NaCN samples to investigators at ORNL and PNNL (see Apppendix). Preliminary results for these alkali cyanides are shown on Figure 1. Similar to our ORNL collaborators, we observe poor precision in stable isotope measurements due to material breakdown during storage that results in carbon and nitrogen weight fractions that do not match stoichiometry (i.e., Na:C:N = 0.469:0.245: 0.286; and K:C:N = 0.600:0.184:0.215). There is significant nitrogen loss, particularly with NaCN samples, and absorption of water. These samples have been stored in glass bottles at LLNL for a long period. Chemtrack started at the lab around 1993, so any materials with "late 1993" first inventory date were probably purchased much earlier (see Appendix). ORNL is working on obtaining production dates from product and lot numbers.

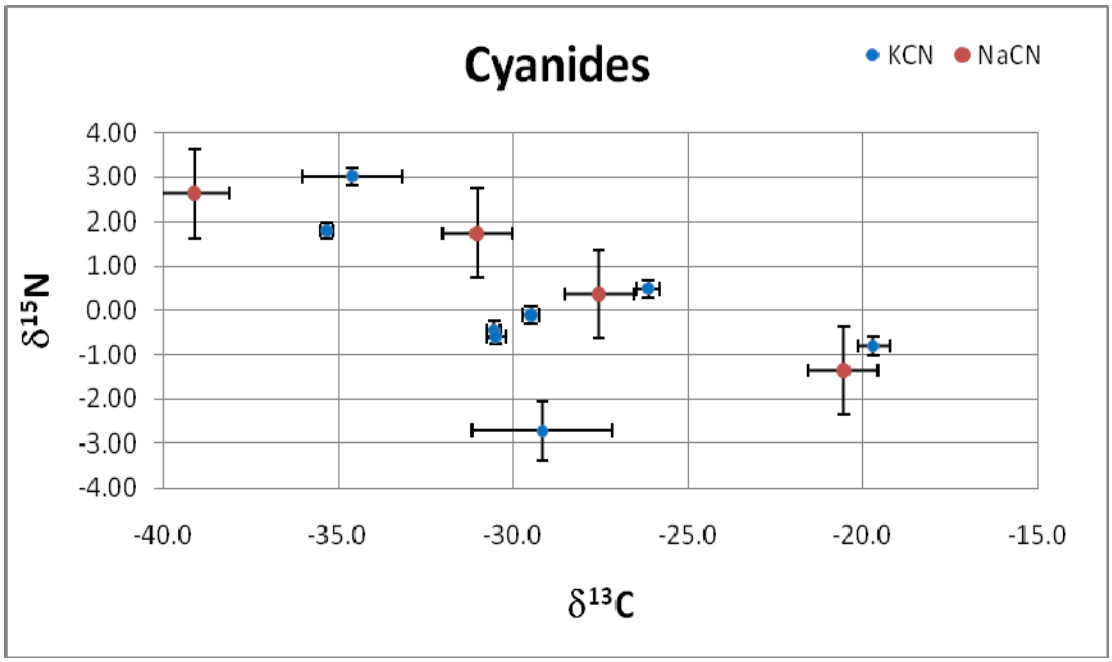


Figure 1. Carbon and nitrogen isotope delta values for LLNL cyanides.

Preliminary data show distinct C-N isotopic ratios for each cyanide, though precision is poor for some samples. To improve analytical precision, small amounts (~ 0.5 g) of the cyanides were dried at 120°C, ground into a granular powder, and then stored in an evacuated dessicator bell jar. Several weight percent (1-10%) water was removed during the drying process. Shelf stability and breakdown of alkali cyanide has implication for forensic attribution. Our ORNL collaborators analyzed the crystal composition (using XRD) of one of the NaCN samples that we shipped, which shows significant nitrogen loss. Their result suggests that NaCN in the presence of water breaks down to $NaCO_3$, liberating HCN (gas).

4.2 TETS: Raw Materials

We measured $^{13}C/^{12}C$ and $^{15}N/^{14}N$ in raw materials used for TETS synthesis (see sample list in Appendix). Figure 2 shows $\delta^{15}N$ results for eight sulfamides, with values ranging from -10 to -19 ‰. Two sulfamide samples representing different lots from Aldrich (S-2, S-3; 12.3, 12.5) have values within analytical uncertainty.

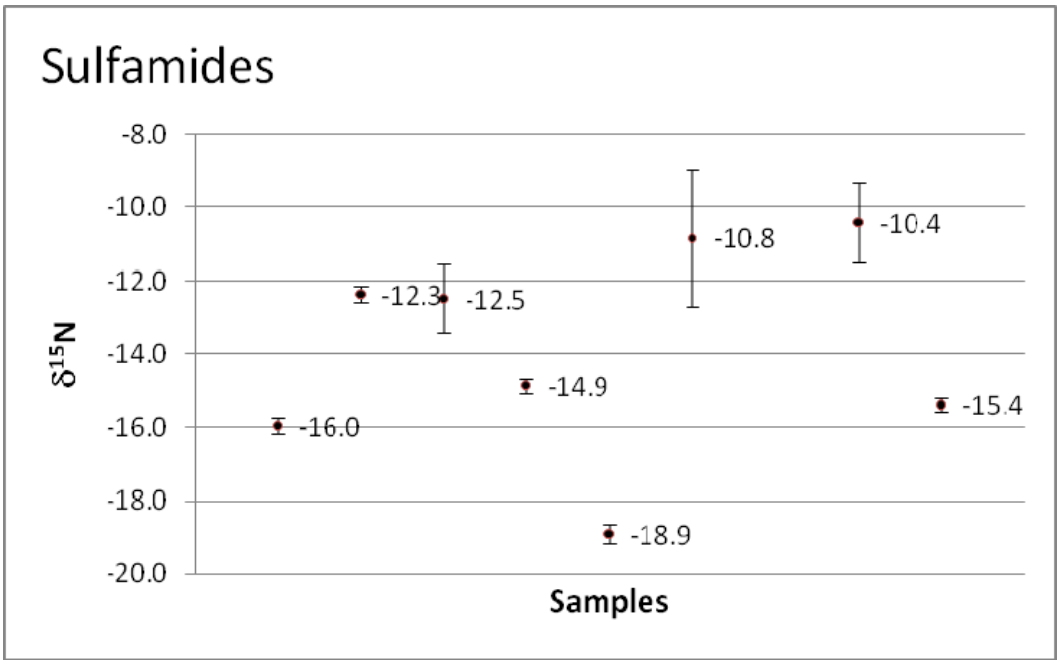


Figure 2. $\delta^{15}N$ isotope ratio values for sulfamides

Figure 3 shows $\delta^{13}C$ isotope results for fourteen paraformaldehyde samples (Appendix) with values ranging from -31 to -43 ‰. Raw materials from different lots of the same supplier (Aldrich – PF-6, PF-9, PF-10; JTBaker – PF-1, PF-14; and Sigma – Pf-3, PF-4) have distinct $\delta^{13}C$ isotope values.

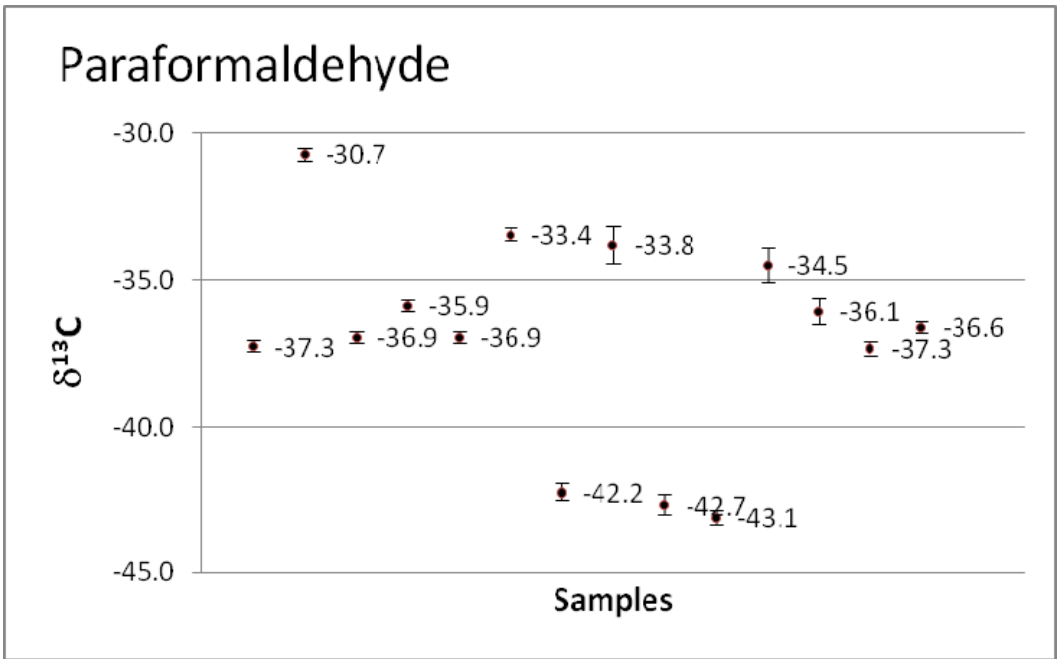


Figure 3. δ^{13}C isotope values for paraformaldehyde

Figure 4 shows δ^{13}C isotope results for five 1,3,5-trioxane samples with values ranging from -32 to -41 ‰. Each sample is from a different supplier.

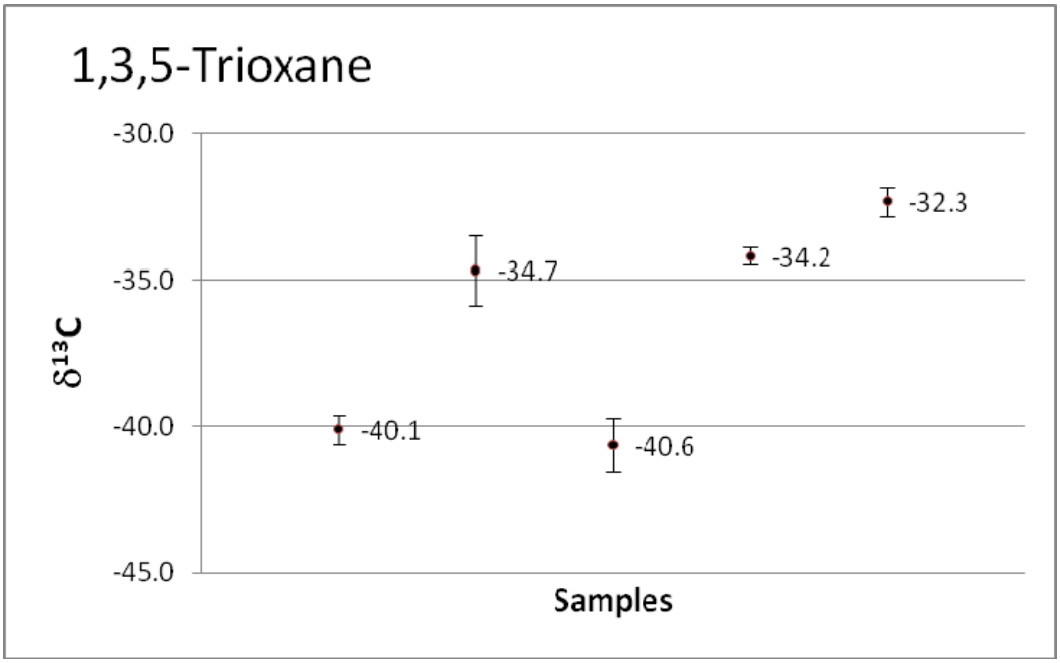


Figure 4. δ^{13}C isotope values for 1,3,5-trioxane

Trifluoroacetic acid is used as a catalyst in several TETS synthesis methods. We measured $\delta^{13}C$ of eight different sample and Figure 5 shows $\delta^{13}C$ results for TFA with values ranging from -16 to -31‰, which differ from paraformaldehyde and trioxane. TFA probably does not contribute to the C-isotopic composition of TETS product.

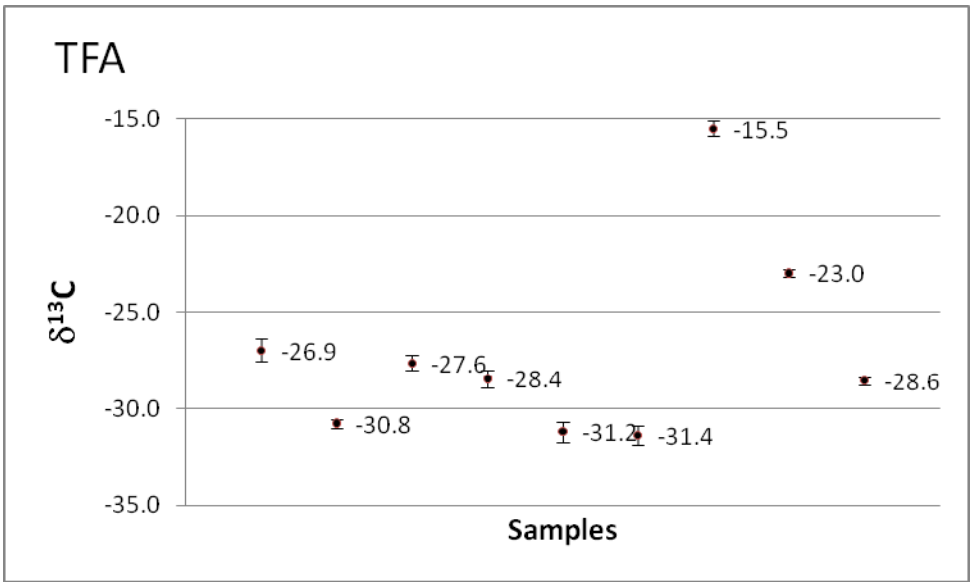
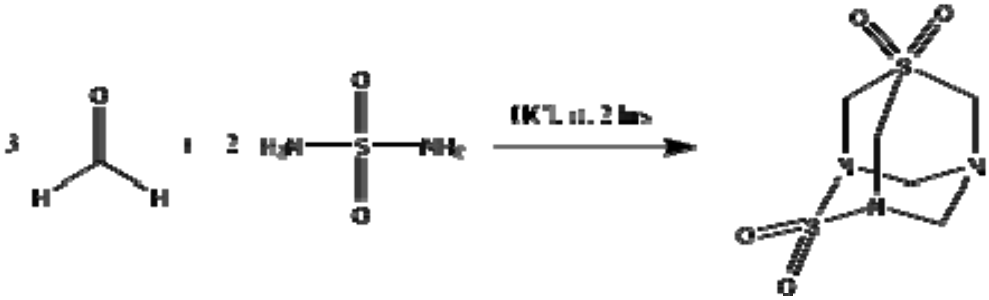


Figure 5. $\delta^{13}C$ isotope values for trifluoroacetic acid (TFA)

4.3 TETS: Synthesis – Phase I

Following stable isotopic characterization, Brad Hart and Saphon Hok, LLNL scientists, used select materials for controlled synthesis of TETS following three published procedures. We measured the C-N stable isotope composition of the products from each TETS synthesis to determine whether or not these isotopes are fractionated during production. Sections below briefly describe synthesis methodology, and data for reactants and products. Complete procedures are available and will be described in manuscripts submitted for peer-review publication.

4.3.1. Method 1



Reference: Hecht, G., and Henecka, H., 1949, Angew. Chem, 61, 365-366.

Materials: sulfamide, S-1, formaldehyde (analysis in process) and HCl (not measured).

Data: Figure 6 shows $\delta^{15}N$ versus $\delta^{13}C$ in the sulfamide reactant and TETS product (formaldehyde will be analyzed). Preliminary result suggests significant nitrogen fraction (e ^{15}N = -1.7) during Method 1 production of TETS with the $^{15}N/^{14}N$ ratio of the product lighter than the reactant.

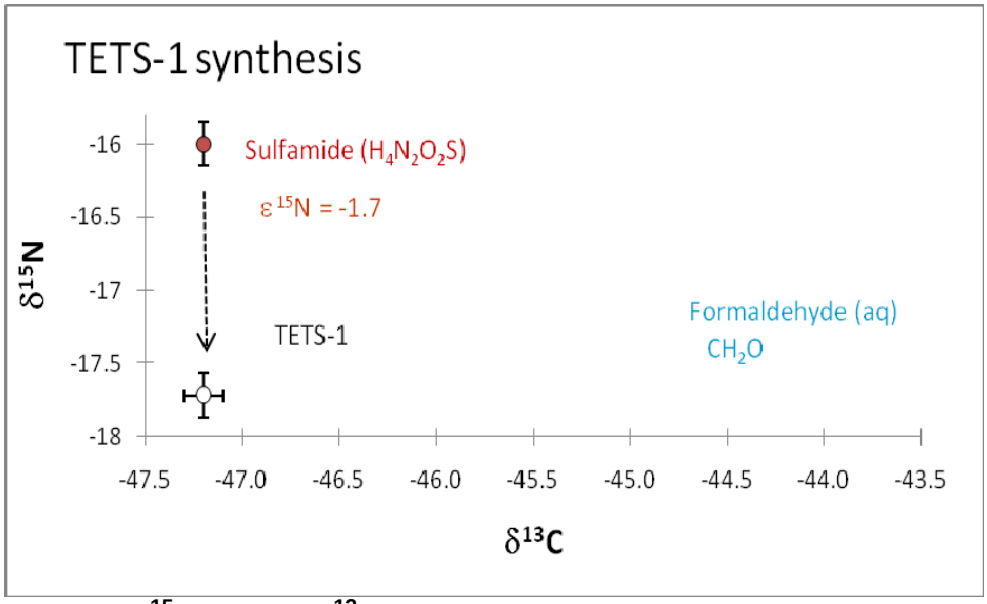
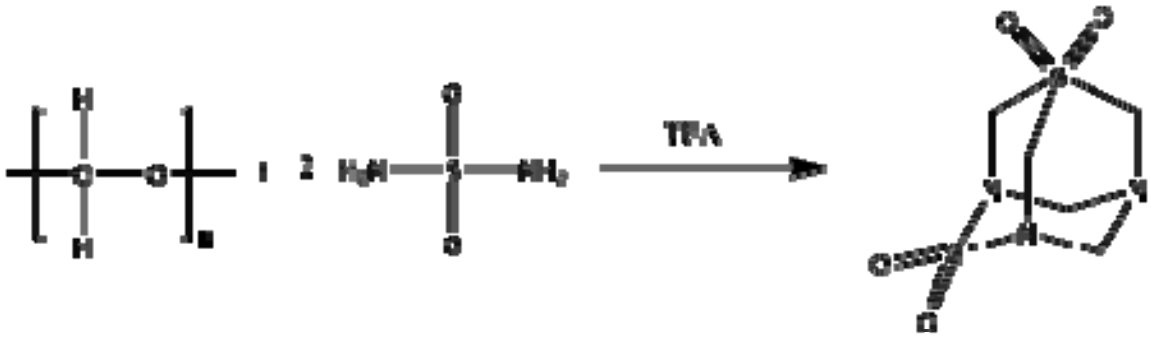


Figure 6. $\delta^{15}N$ versus $\delta^{13}C$ in sulfamide reactant and TETS product

4.3.2. Method 2



Reference: Kang, Jung-Bu, et al., 1971, Intl. J. Sulfur Chem., A, vol. 1, no 4, 261-268.

Materials: sulfamide, S-1, paraformaldehyde, PF-14, and trifluoroacetic acid (TFA-2).

Data: Figure 7 shows $\delta^{15}N$ versus $\delta^{13}C$ in the reactants, sulfamide and paraformaldehyde, and the TETS product. Preliminary result suggests measurable nitrogen ($\varepsilon\ ^{15}N$ = -0.8) and carbon ($\varepsilon\ ^{13}C$ = -1.0) fractionation during Method 2 production of TETS, with the $^{15}N/^{14}N$ and $^{13}C/^{12}C$ ratios of the product lighter than the reactants. The fractionation effect is larger than analytical uncertainty. The $\delta^{13}C$ value for the trifluoroacetic acid is -30.8 +/- 0.2 ‰, suggesting the catalyst does not contribute to the composition of the product.

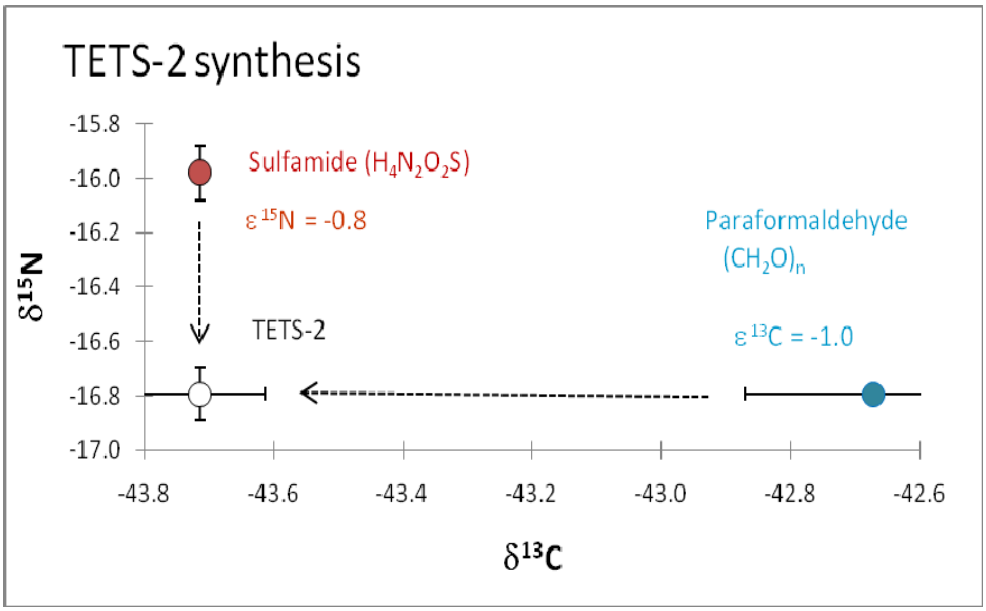
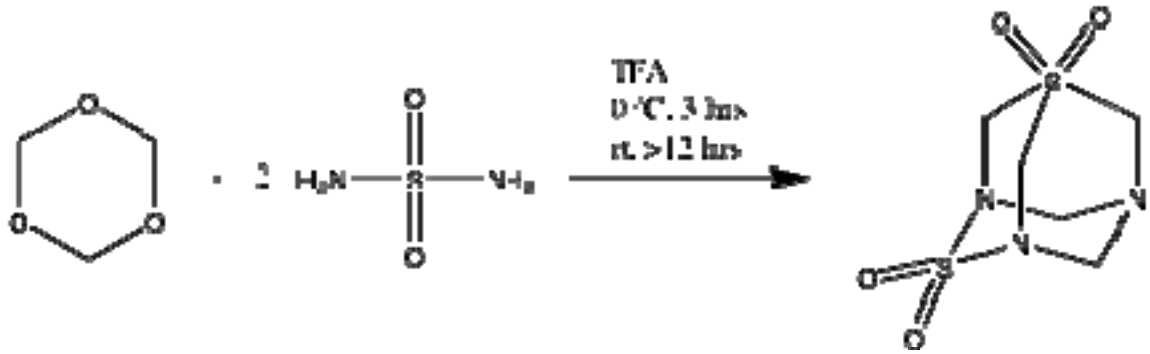


Figure 7. $\delta^{15}N$ versus $\delta^{13}C$ in sulfamide and paraformaldehyde reactants and TETS product.

4.3.3. Method 3



Reference: Esser, Thomas, et.al., 1991, Chem Res. Toxicol., 4, 162-167

Materials: sulfamide, S-1, 1,3,5-troxane, T-5, and trifluoroacetic acid, TFA-2.

Data: Figure 8 shows $\delta^{15}N$ versus $\delta^{13}C$ in the reactants, sulfamide and 1,3,5-trioxane, and the TETS product. This preliminary result suggests significant nitrogen (ε ^{15}N = -1.7) and minor carbon (ε ^{13}C = -0.1) fractionation during Method 3 production of TETS, with the $^{15}N/^{14}N$ and $^{13}C/^{12}C$ ratios of the product lighter than the reactants. The nitrogen fractionation effect is comparable to Method 1, while the carbon fractionation effect for method 3 is within $\delta^{13}C$ analytical uncertainty. The $\delta^{13}C$ value for trifluoroacetic acid is -30.8 +/- 0.2 ‰, which again suggests the catalyst does not contribute to the composition of the product.

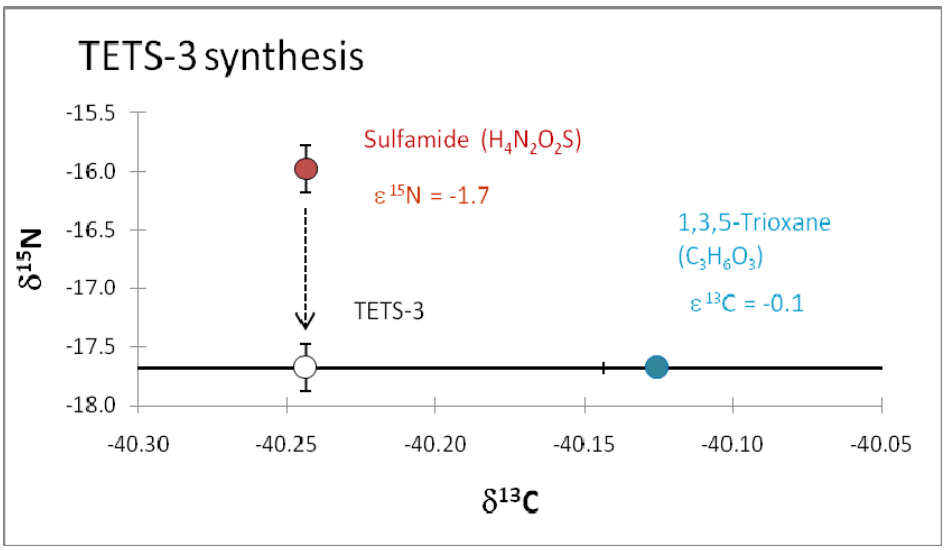


Figure 8. $\delta^{15}N$ versus $\delta^{13}C$ in sulfamide and trioxane reactants and TETS product.

4.4 TETS: Synthesis – Phase II

After analyzing data and procedures, we decided to implement the following changes for a second round of TETS synthesis.

1. Substitute argon for nitrogen for the reaction inert gas. Though nitrogen gas, which is supplied by the building liquid nitrogen tank ($\delta^{15}N$ ~ 0), is probably not a factor, using argon as the inert gas is a simple way to avoid any unintended complication.
2. Filtration: Preserve solution from the filtration process that separates supernatant (TFA or HCl) from solid TETS (precipitant).
3. Products
   a. supernatant - first filtration (TFA or HCl), ~10-30mL

b. TETS crude
c. TETS purified

We plan to generate a second round of TETS synthesis products using the following reactants and methods. This work will be finished before the end of June 2009.

1. TETS-1b: repeat Method 1, using Ar inert gas, sulfamide S-1, formaldehyde, and HCl.
2. TETS-2b: repeat Method 2, using Ar inert gas, sulfamide S-1, para-formaldehyde PF-14, and trifluoroacetic acid TFA-2.
3. TETS-3b: repeat Method 3, using Ar inert gas, sulfamide S-1, trioxane T-5, and TFA-2.
4. TETS 3c: Method 3, using Ar inert gas, S-4, T-5, TFA-2
5. TETS-3d: Method 3, using Ar inert gas, S-5, T-5, TFA-2
6. TETS-3e: Method 3, using Ar inert gas, S-6, T-5, TFA-2

4.5 Brodifacoum ($C_{31}H_{23}BrO_3$) and Ammonium Metavanadate (NH_4VO_3)

We plan to measure $^{13}C/^{12}C$ and $^{18}O/^{16}O$ in brodifacoum, and $^{15}N/^{14}N$ and $^{18}O/^{16}O$ in ammonium metavanadate samples (see Appendix). Oxygen isotope measurements described in the method section above are experimental

5. Research Plan

Stable isotope measurements for the following materials will be performed during June-August 2009:

a. brodifcaoum – four samples
b. ammonium metavanadate – eighteen samples
c. cyanides – twelve samples
d. TETS synthesis – six syntheses, total thirty sub-samples

Data synthesis and preparation of manuscripts for peer review publication will start in August and conclude by the end of the performance period (7Nov2009).

APPENDIX – Samples

1. Cyanides

Investigators at ORNL and PNL have SI projects focused on cyanides, which started months before this project. We talked to Bruce Tomkins and Juske Horita (ORNL) and Helen Kreuzer (PNNL) about potential collaboration, and plan to work together developing, exchanging, and analyzing standard reference material, in addition to exchanging samples. We recognize that these labs will be principal investigators for cyanide analysis and plan to support them by providing stable isotope measurements for cyanide samples that have been distributed from LLNL.

We shipped the following samples to both ORNL and PNNL.

ID	Product Name	Manufacturer	Product #	Lot #	Original Quantity	Bar Code (LLNL)	First Inv Date
KCN-1	Potassium Cyanide	Allied	2107	R204	1lb	CT00047403	Nov-93
KCN-2	Potassium Cyanide, 94-96%	Baker & Adamson	2108	J121	1lb	CT00010388	Sep-93
KCN-3	Potassium Cyanide, 97%	Baker Analyzed Reagent	3080-1	32143	1lb	CT00017520	Oct-93
KCN-4	Potassium Cyanide	Aldrich Chemical Co.	207810-500G	00813TA	500g	CT00714492	Mar-04
KCN-5	Potassium Cyanide, 97%	Aldrich Chemical Co.	n/a	05423AR	500g	CT00594172	Jun-97
KCN-6	Potassium Cyanide, 99.2%	Baker Analyzed Reagent	3080-1	628350	500g	CT00156574	Dec-93
KCN-7	Potassium Cyanide	Baker Analyzed Reagent	3080-1	524724	500g	CT00093401	Dec-93
KCN-8	Potassium Cyanide, 96.3%	Baker Analyzed Reagent	3080-1	524724	500g	CT00154878	Dec-93
NaCN-1	Sodium Cyanide, 95-98%	Allied Chemical Co	2236	H165	1lb	CT00047376	Nov-93
NaCN-2	Sodium Cyanide, 95-98%	Allied Chemical Co	2236	J262	1lb	CT00047375	Nov-93
NaCN-3	Sodium Cyanide	Mallinckrodt Chem Works	7616 (13588)	YEM	1lb	CT00018319	May-99
NaCN-4	Sodium Cyanide, 98.5%	JT Baker	3662-01	A12338	500g	CT00112189	Dec-93

2. Brodifacoum

We have sub-samples of four brodifacoum samples that Armando Alcaraz purchased from Sigma-Aldrich. All samples have identical product and lot numbers. We plan to analyze stable isotopes of these four samples, and offered splits to Herman Chou at PNNL for NMR study.

3. Ammonium Metavanadate

We plan to obtain/procure the following materials for stable isotope analysis, and will work with suppliers to identify manufacturing plants.

Ammonium Metavanadate

ID	Bar Code	CAS No.	Product Name	Supplier	Product #	Lot #	Qty
AMV-1	CT00933672	7803-55-6	NH4VO3, 99.995%	Alfa Aesar, Puratronic	10902-06 TJ-02-02	22049	5g
AMV-2	CT00933671	7803-55-6	NH4VO3, 99%	Alfa Aesar	36213-18 TI-04-03	122T052	50g
AMV-3	CT00933670	7803-55-6	NH4VO3, 99%	Alfa Aesar	11091-30 TG-09-04	K05T015	250g
AMV-4	n/a	7803-55-6	NH4VO3, 99.995%	Alfa Aesar, Puratronic	10902-14 TJ-02-02	23844	25g
AMV-5	CT00933948	7803-55-6	NH4VO3, 99%	JT Baker	JT0715-4	E30602	125g
AMV-6	*CT00527934*	7803-55-6	NH4VO3, 99.6%	Baker Analyzed Reagent	1-0715	417053	4g (500g)
AMV-7	CT00933949	7803-55-6	NH4VO3, 99.995%	Strem	02-0700	127004S1	5g
AMV-8	CT00933950	7803-55-6	NH4VO3, 99%	Strem	93-2301	A1351098	100g
AMV-9	CT00933652	7803-55-6	NH4VO3, 99.5%	Acros Organics	AC194912500	A0240349	250g
AMV-10	CT00933947	7803-55-6	NH4VO3, 99%	Pfaltz & Bauer	A30321	114007-4	100g
AMV-11	CT00933655	7803-55-6	NH4VO3, 99.999%	Aldrich	573884-5G	04106DE	5g
AMV-12	CT00933654	7803-55-6	NH4VO3, 99.99%	Sigma-Aldrich	204846-10G	11703JE	10g
AMV-13	CT00933659	7803-55-6	NH4VO3, 99%	Sigma-Aldrich	398128-50G	10214CJ	50g
AMV-14	CT00933656	7803-55-6	NH4VO3, 99%	Sigma-Aldrich	205559-50G	06713ME	50g
AMV-15	CT00933653	7803-55-6	NH4VO3, 99%	Fluka Chemical Corp	10028-5G	1351672	5g
AMV-16	CT00933657	7803-55-6	NH4VO3, 99.5%	Sigma-Aldrich	33153-100G	52300	100g
AMV-17	CT00933658	7803-55-6	NH4VO3, 99%	Fluka Chemical Corp	10030-100G	1316739	100g
AMV-18	*CT00553605*	7803-55-6	NH4VO3	SPEX Industries		1831G	5g (50g)

4. TETS bulk and synthesis

We procured the following raw materials for TETS synthesis. Our approach will be to first characterize stable isotope compositions of these raw materials, submit select chemicals to fellow LLNL researchers (Brad Hart and Saphon Hok) for controlled TETS synthesis using three published procedures, and then analyze SI composition of the products to determine whether or not isotopes are fractionated during production.

Sulfamide

ID	Bar Code	Product Name	Manufacturer	Product #	Lot#	Qty
S1	CT00862596	Sulfamide, >99%	Fluka Chemical Corp	86033	1313608	10g
S2	CT00862597	Sulfamide, 99%	Aldrich	211370-5G	08413LE	5g
S3	CT00862598	Sulfamide, 99%	Aldrich	211370-5G	06815TE	5g
S4	n/a	Sulfamide, 99%	Alfa Aesar	A18680	10111369	10g
S5-1 S5-2	n/a	Sulfamide, 99%	Acros Organics	199020050 199020050	A0212692 A0212692	5g 5g
S6	n/a	Sulfamide, 97%	Maybridge	SB01649EA	194207	10g
S7		Sulfamide, 99%	MP Biomedicals			10g
S8	n/a	Sulfamide, 99%	Pfaltz & Bauer	S11000	12616	5g
S9	*CT00144559*	Sulfamide, 99%	Fluka Chemical Corp		880033	~2g (50g)
S10		Sulfamide, 99%	Ryan Scientific			10g

1,3,5-Trioxane

ID	Bar Code	Product Name	Manufacturer	Product #	Lot#	Qty
T1	CT00875059	1,3,5-Trioxane, 98%	Alfa Aesar	A15639	10108956	500g
T2	CT00862998	1,3,5-Trioxane	TCI America	T0505	OGL01	500g
T3	*CT00080846*	1,3,5-Trioxane, 99%	Aldrich		022LJ	~2g (500g)
T4	*CT00229710*	1,3,5-Trioxane, 99%	Fluka Chemical Corp		280638 389	~3g (1kg)
T5	CT00862616	1,3,5-Trioxane, 99+%	Fluka Chemical Corp	T81108	1370684	500g

Paraformaldehyde

ID	Bar Code	Product Name	Manufacturer	Product #	Lot#	Qty
PF1	*CT00467542*	Paraformaldehyde, 95%	J T Baker		A22610	~3g (500g)
PF2	*CT00848886*	Paraformaldehyde, 91%	EMD Chemicals		70215	1.6g (1kg)
PF3	*CT00527934*	Paraformaldehyde, 95%	Sigma		042K1591	4g (500g)
PF4	*CT00788531*	Paraformaldehyde, 95%	Sigma		107K0758	~4g (sub)
PF5	CT00862599	Paraformaldehyde, >95%	Fluka Chemical Corp	76240	72070	250g
PF6	*CT00224805*	Paraformaldehyde, 95%	Aldrich	15,812.7	06723CX	500g
PF7	CT00875075	Paraformaldehyde, 95%	EMD Chemicals	PX0055-3	48079849	500g
PF8	CT00862997	Paraformaldehyde, 95%	TCI America	P0018	QTV5G	25g
PF9	*CT00153147*	Paraformaldehyde, 95%	Aldrich		41247	~2g (500g)
PF10	*CT00113604*	Paraformaldehyde, 95%	Aldrich		1912EJ	~2g (3kg)
PF11	*CT00117692*	Paraformaldehyde	Chem Service Inc		232?	~2g (10g)
PF12	CT00875058	Paraformaldehyde, 97%	Alfa Aesar	A11313	10139833	100g
PF13	n/a	Paraformaldehyde, 95%	MP Biomedicals	150146	5721H	500g
PF14	CT00933762	Paraformaldehyde, 95%	J T Baker	S898-04	G06593	125g

Trifluoroacetic acid

TFA1	CT00862600	Trifluoroacetic acid, 98%	Sigma-Aldrich	T6508-100ML	10812LH	100mL
TFA2	CT00875060	Trifluoroacetic acid, 99.5%	Alfa Aesar	44630	K21T043	500mL
TFA3	CT00875092	Trifluoroacetic acid, HPLC	EMD Chemicals	TX1276-6	48239839	250mL
TFA4	CT00862996	Trifluoroacetic acid	J T Baker	W729-05	G25605	100mL
TFA5	*CT00711399*	Trifluoroacetic acid	Spectrum Chemical		TH1448	~ 5mL(jug)
TFA6	*CT00840360*	Trifluoroacetic acid	Spectrum Chemical		XM0015	~ 1mL(jug)
TFA7	*CT00544098*	Trifluoroacetic acid	Aldrich		28901	~ 1mL(pint)
TFA8	*CT00821870*	Trifluoroacetic acid	Sigma Aldrich		07816CH	~ 1mL(pint)
TFA9	*n/a*	Trifluoroacetic acid, 99.5%	Alfa Aesar		K05N27	~ 1mL