

2016

Program

ASITA 2016

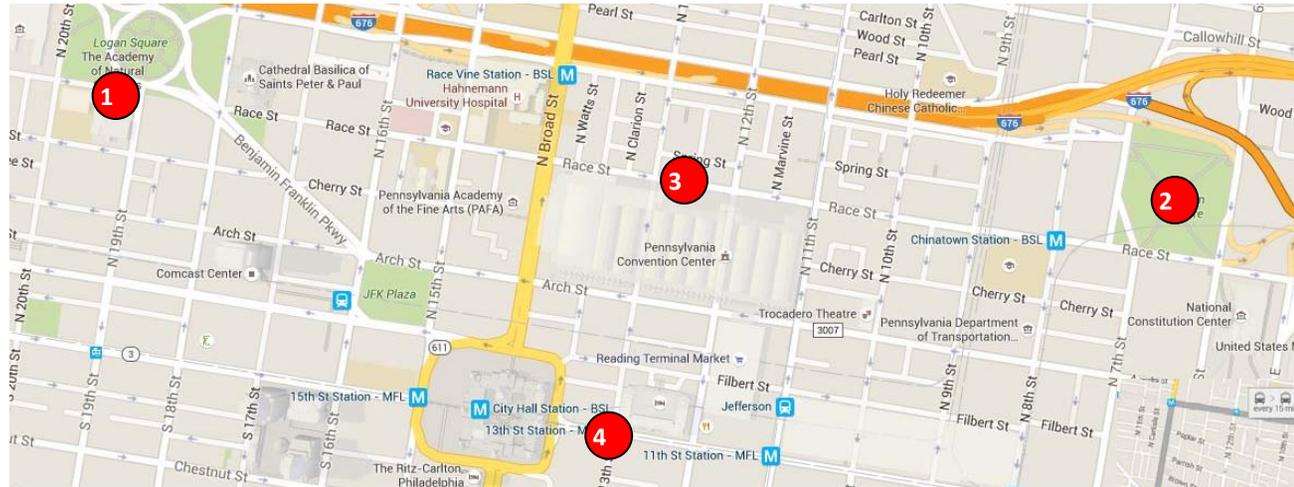
at the Academy of Natural Sciences
Philadelphia



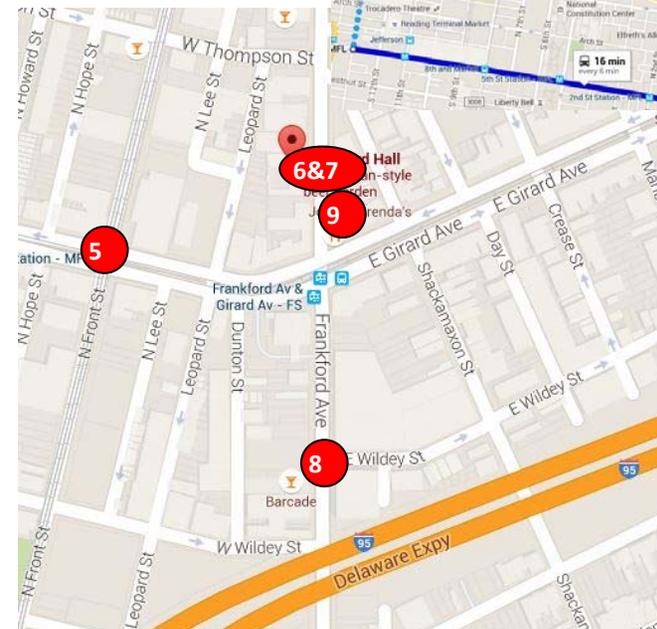
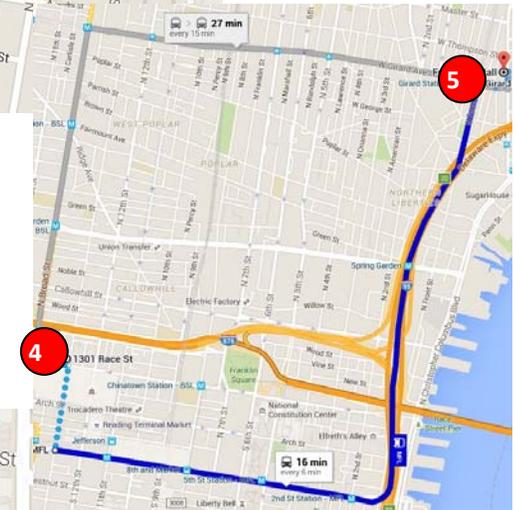
Advances in
Stable Isotope Techniques & Applications

June 19 – 21, 2016

Maps



- 1) The Museum of Natural History 1901 Benjamin Franklin Parkway
- 2) Franklin Square – Site of Saturday night Icebreaker
- 3) Hampton Inn Philadelphia Convention Center
- 4) Metro Station for Market-Frankford line – to travel to suggested “Pub Crawl/Open Dinner” area
- 5) Girard Station – Market-Frankford Line – Exit for Pub Crawl/Open Dinner area
- 6) Frankford Hall, 1210 Frankford Ave. Big German-style beer garden with communal seating & food options to soak up the brews
- 7) Fette Sau, 1208 Frankford Ave – Arguably the best BBQ in Philadelphia
- 8) Barcade, 1114 Frankford Ave- Big bar with 50 arcades from the 80’s & 90’s
- 9) Jonny Brendas 1201 N Frankford Ave – live music – crawl to last



Subway Information

Get on at 13th Street and Market (13th Street MFL)

Depart after 6 stops at Girard Station (8 minutes)

Cost \$2.25 cash or 2 tokens for \$3.60– get token at vending machine at stations (cash only)

Cost for Taxi cab is about \$14 each way.

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General Information

Locations:

Saturday Night Ice Breaker: Franklin Square
200 6th St, Philadelphia

Conference

The Academy of Natural Sciences,
1900 Benjamin Franklin Parkway, Philadelphia

Presentations: Auditorium
Breaks/Posters/Vendor Tables: Commons
Times: 8:30 AM– 5:00 PM

Contact

For any questions or issues, please contact Scott Hughes, ASITA Conference organizer at:

Cell Phone: 609-707-4395

Email: scott@eaconsumables.com

General Safety

We all desire a safe and trouble free ASITA 2016 conference. To this end, please be sure to be aware of your surroundings, and note all emergency information and exit information which is posted.

ASITA 2016 Schedule

Saturday June 18

7:00 – 9:30 PM	Ice Breaker Reception Location: Franklin Square 200 6th St, Philadelphia, PA 19102	Provided by: Elementar Americas, Inc. Including Philly Cheese Steaks, Beer, Wine and unlimited Mini Golf and Carousel rides!
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Sunday June 19 Location: The Academy of Natural Sciences

7:00 AM Sponsor Set-up – Commons room

8:30 AM Open Registration – Auditorium

9:00 AM	Short Course #1 Introduction to Stable Isotopes	Peter Stow Isomass, Ltd.
10:00 AM	Short Course #2 Elemental Analysis	Paul Middlestead GG Hatch Stable Isotope Labs University of Ottawa
11:00 AM	Break	
11:30 AM	Short Course #3 GC-IRMS: Putting the Gas in Gas Chromatography.	Paul Eby Alberta Innovates

12:30 – 1:30 AM Lunch – Commons

1:30 PM	Welcome and Announcements	Scott Hughes – Conference Organizer David Velinsky – Director of Environ. Biogeochemistry The Academy of Natural Sciences
1:40 PM	Keynote Address: High sensitivity nitrogen isotopic analysis of diverse sample types through conversion to nitrous oxide	Dr. Daniel Sigman Dusenbury Professor of Geological & Geophysical Sciences Princeton University
2:40 PM	Challenges in Preparation, Application and Maintenance of Stable Isotopic Reference Materials	Haiping Qi USGS Reston, VA
3:00 PM	Molecular Isotopic Engineering (MIE): Industrial Manufacture of Naproxen of Predetermined Stable- Isotopic Compositions for Novel Intellectual Property Coverage As Well as for Authenticity and Security Protection	John P. Jasper Nature's Fingerprint /MIT LLC, Niantic, CT

3:20 PM Break – Posters/Vendor Tables

Sunday June 19

3:40 PM	An interface for purification and analysis of methyl chloride for chlorine isotope ratios (scavenger version)	Linnea Heraty University of Delaware, Newark, DE
4:20 PM	How to break quartz combustion tubes	Scott Hughes EA Consumables, Pennsauken, NJ

6:00 – 9:00 PM	Gala Banquet in Dinosaur Hall With floor presentation from Wondergy – Things are not always what they appear	Sponsors: Elemental Microanalysis – Drinks Isomass Ltd. – Dinner Sercon – Dessert
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Monday June 20

8:30 AM	Registration	
9:00 AM	Announcements	
9:20 AM	A history of the elemental analyzer as seen from the point of view of isotope geochemistry: why has it taken so long?	Chuck Douthitt ThermoFisher Scientific,
9:40 AM	Measuring trace ^{15}N of whole rock samples. $\hat{\Delta}$ Modifications to, and comparison of two EA systems	Stephen Taylor University of Calgary, Calgary, AB
10:00 AM	20 management tips – Take some and Leave some	Paul Middlestead University of Ottawa, Ottawa, ON

10:20 AM Break – Posters/Vendors

11:00 AM	The precision and isoFLOW. IRMS as a versatile foundation for novel isotopic analysis	Sam Barker Isoprime, Stockport, UK
11:20 AM	Fractionation effects when using smaller vials on a GasBench: Is it bad and can they be used?	Alison Pye Memorial University, St Johns, NF
11:40 AM	Storage of Gas Samples for IRMS Measurement	Paul Eby Alberta Innovates, Victoria, BC
12:00 Noon	U.S. Department of Energy Stable Isotope Production	Joel Grimm DOE, Germantown, MD

12:20 PM Lunch

Monday June 20

1:40 PM	Methane Fingerprinting: Isotopic Methane and Ethane-to-Methane Ratio Analysis Using a Cavity Ringdown Spectrometer	David Kim-Hak Picarro, Santa Clara, CA
2:00 PM	Sulfur isotope analyses as a tool to enhance understanding of petroleum reservoirs	Craig Barrie GeoMark Research, Houston, TX
2:20 PM	Development and calibration of new natural gas d13C and d2H reference standards	Robert Dias USGS, Denver, CO
2:40 PM	Nitrogen isotopes on Mars	Jennifer Stern NASA Goddard, Beltsville, MD

3:00 PM Break – Posters/Vendors

3:45 PM	Group Discussions Round 1	
	Combined NCS Analysis	
	N2O by bacterial denitrification	
	Incorporation of Laser Systems into Lab Settings	
4:15 PM	Group Discussions Round 2	Allows shift to a different group
	Combined NCS Analysis	
	N2O by bacterial denitrification	
	Incorporation of Laser Systems into Lab Settings	

4:45 PM Where to next year?,
Open Dinner/Pub Crawl instructions

6:00 ish PM Open Dinner/Pub Crawl
There are many nice restaurants and bars in walking distance of the hotels. These tend to be smaller and on the higher cost side. Check Google.

As an alternative, we have given directions to the “Fishtown” section of Philadelphia which has a number of larger venues with outside seating and more economical costs. The section can be reached via an 8 minute subway ride, or by cab. Directions and suggestions for this area are provided on the inside cover of the program.

Tuesday June 21

9:00 AM	A simple method for simultaneous analysis of carbon, nitrogen and sulfur isotopes in dissolved organic matter	Sara Peek USGS, Menlo Park, CA
9:20 AM	Elemental Microanalysis has standards	Paul Stevens Elemental Microanalysis, UK
9:40 AM	The state of the art for GC combustion and pyrolysis: GC-IsoLink II	Peter Stow Isomass, Calgary, AB
10:00 AM	The need for stable isotope working standards	Anja Moritz Isospark, Dorval, Québec

Tuesday June 21

10:20 AM Break – Posters/Vendors

11:00 AM	Updated Methods for Compositional and Isotopic Profiling of Vanillin, Preliminary Research	Amanda Smith Alcohol & Tobacco Tax & Trade Bureau, Washington, DC
11:20 AM	Fractionation between bioapatite carbonate and carbon dioxide in analysis of tooth enamel	Penny Higgins University of Rochester, Rochester, NY
11:40 AM	TBD	Ben Harlow Washington State University, Pullman, WA

12:00 PM Lunch

1:20 PM User Group Meetings

Elementar/Isoprime
Sercon
Thermo/Isomass
Picarro
LGR/Isospark

Tours of The Academy of Natural Sciences
Collections and Isotope Lab

Sign up sheets will be available. Tour numbers will be limited due to 15-20 people each

1:30 PM Tour #1

2:00 PM Tour #2

3:00 PM Tour #3

3:30 PM PM Guided Tour – Philly Historic District
Meet at Independence Visitor Center

\$5 per person. Sign up sheets will be available. Maximum 50 people.
Pick up map and directions at conference.

Verbal Presentation Abstracts

Sunday 1:40 PM

High sensitivity nitrogen isotopic analysis of diverse sample types through conversion to nitrous oxide

Daniel Sigman

Princeton University

Princeton, NJ

In the “denitrifier method,” nitrate (NO_3^-) is converted to nitrous oxide (N_2O) by a strain of denitrifying bacteria that lacks an active nitrous oxide reductase, and the product N_2O is then concentrated, purified, and analyzed by continuous flow isotope ratio mass spectrometry. The denitrifier method allows for highly sensitive measurement of the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ of nitrate dissolved in natural waters, and coupling of the nitrate-to- N_2O conversion with high-temperature N_2O decomposition to N_2 and O_2 brings similar sensitivity to $^{18}\text{O}/^{17}\text{O}/^{16}\text{O}$ analyses of nitrate. When combined with techniques for oxidizing reduced nitrogen forms to nitrate, the denitrifier method also allows for $^{15}\text{N}/^{14}\text{N}$ measurement of minute quantities of organic nitrogen, such as dissolved organic nitrogen and flow cytometry-sorted plankton from aquatic environments, organic nitrogen trapped within the mineral matrix of fossils, and compounds such as porphyrins isolated from ocean sediments. In this talk, both the development of the denitrifier method and its current status will be reviewed. With regard to the measurement of $^{15}\text{N}/^{14}\text{N}$, which will be the focus of the talk, the denitrifier-based approach represents something of a historical oddity. In the context of an overwhelming shift in light isotope geochemical methods from wet chemistry (e.g., the Rittenberg reaction) to high temperature reactions (e.g., Dumas combustion and pyrolysis), the denitrifier method represents a return to the former. It is possible that this direction will be expanded in the future by our increasing understanding of the chemical capabilities of enzymes and organisms. More narrowly, the new capabilities resulting from the denitrifier method are owed ultimately to the lower nitrogen blank when N_2O (rather than N_2) is the analyte for isotope ratio mass spectrometry. In this same context, further improvements in the sensitivity of $^{15}\text{N}/^{14}\text{N}$ analysis of organic nitrogen will rely on reductions in the blanks associated with the oxidative step that converts organic nitrogen to nitrate.

Sunday 2:40 PM

Challenges in Preparation, Application and Maintenance of Stable Isotopic Reference Materials

Haiping Qi

U.S. Geological Survey

Reston, VA

The technique of continuous-flow stable isotope-ratio mass spectrometry coupled with an on-line elemental analyzer (CFIRMS-EA) has advanced rapidly in the last three decades. The analysis of relative isotope ratios of hydrogen ($\delta^2\text{H}$), oxygen ($\delta^{18}\text{O}$), carbon ($\delta^{13}\text{C}$), and nitrogen ($\delta^{15}\text{N}$) by CFIRMS-EA has become routine. Accurate determinations of these delta measurements require 2-point normalization using at least two isotopic reference materials (RMs) with contrasting isotopic compositions. The development of suitable stable isotopic RMs has not kept pace with the rapid development of analytical methods. There are many challenges, not only in the preparation of high quality RMs with satisfactory isotopic homogeneity, chemical purity, and stability, but also in the appropriate application and maintenance of existing isotopic RMs. For example, recently, Gehre et al. pointed out that use of

conventional glassy carbon chips in a packed reactor can produce inaccurate $\delta^{2}\text{HVS}\text{MOW}$ SLAP results when analyzing nitrogen-bearing organic substances with a high temperature conversion technique using an elemental analyzer (TC/EA) IRMS method. The formation of hydrogen cyanide (HCN), which leads to non-quantitative conversion of a hydrogen- and nitrogen-bearing sample into molecular hydrogen (H_2). As a result, the $\delta^{2}\text{HVS}\text{MOW}$ SLAP values of USGS42 and USGS43 human hair RMs, previously determined by TC/EA with a glassy carbon reactor, were biased by 5.7 mUr or ‰ toward more negative values. For accurate determinations of the $\delta^{2}\text{HVS}\text{MOW}$ -SLAP values, a chromium packed reactor on TC/EA is required. These examples illustrate the importance of continued testing and evaluation of new methods by research community.

Sunday 3:00 PM

Molecular Isotopic Engineering (MIE): Industrial Manufacture of Naproxen of Predetermined Stable-Isotopic Compositions for Novel Intellectual Property Coverage As Well as for Authenticity and Security Protection

J. P. Jasper	Nature's Fingerprint/MIT LLC	Niantic CT
P. Farina	Canaan Partners	Westport, CT
P. Mezes	Nature's Fingerprint/MIT LLC	Old Lyme, CT
A. Pearson	Harvard University	Cambridge, MA

Molecular Isotope Technologies LLC has developed four patented or patent-pending generations of stable-isotopic methods and technologies:

- (i) product characterization (for both small molecules and biologics),
- (ii) process characterization (notably, process patent protection),
- (iii) in-process (continuous) analysis, and now
- (iv) molecular isotopic engineering.

Early work in cooperation with the US FDA on the product characterization of naproxen revealed manufacturer-level isotopic provenance of this small analgesic molecule (Wokovich et al., 2005) which was referred to as "The Manufacturer's Fingerprint." This isotopic provenance represented the convergence of the effects of the stable-isotopic compositions of starting materials and isotopic effects of the synthetic process. Rather than merely accepting the random effects of variable sourcing and synthetic process on the stable-isotopic compositions of products, we take a proactive approach to purposefully determine the stable-isotopic composition of bio/pharmaceutical products. The main rationale for MIE is to predetermine the isotopic ranges of products for reasons of product identification and of product security, and also for intellectual property considerations. As an example of MIE, we analyzed the products of the isotopic-synthetic reactions for the last two steps of naproxen synthesis:

2-Bromo-6-methoxynaphthalene + Bromopropionate \diamond \pm Naproxen \diamond (S)-Naproxen

Pre-selection of the stable-isotopic compositions of the starting material, 2-Bromo-6-methoxynaphthalene (viz., $\delta^{13}\text{C} = -29.88 \pm 0.04\text{‰}$, $-28.73 \pm 0.03\text{‰}$, $-24.01 \pm 0.04\text{‰}$ vs VPDB) respectively yielded the product of discrete stable-isotopic ranges ($-29.75 \pm 0.08\text{‰}$, $-29.18 \pm 0.08\text{‰}$, and $-25.19 \pm$

0.04‰ vs VPDB). Our directed isotopic synthesis is just one example of MIE to predetermine the discrete isotopic ranges of bio/pharmaceutical products. In principle, the MIE approach should be readily adapted to existing bio/pharmaceutical manufacturing units.

Sunday 3:40 PM

An interface for purification and analysis of methyl chloride for chlorine isotope ratios (scavenger version)

Linnea Heraty

University of Delaware

Newark, DE

Sunday 4:20 PM

How to break quartz combustion tubes

Scott Hughes

EA Consumables, Inc.

Pennsauken, NJ

Ian Smith

Elemental Microanalysis Ltd

Okehampton, UK

Paul Stevens

Elemental Microanalysis Ltd

Okehampton, UK

Jon Davies

Elemental Microanalysis Ltd

Okehampton, UK

It is fair to say that everybody running an elemental analyzer using quartz combustion tubes have experienced breakage at one time or another. Whenever this subject comes up on Isogeochem, there are always dozens of experiential responses.

This talk will look at the properties of quartz with respect to elemental analysis, and the things that lead to breakage, and some hints on how to avoid or at least delay, the crumbling of the combustion tube.

Monday 9:20 AM

A history of the elemental analyzer as seen from the point of view of isotope geochemistry: why has it taken so long?

Chuck Douhitt

ThermoFisher Scientific

Monday 9:40 AM

Measuring trace ^{15}N of whole rock samples. A Modifications to, and comparison of two EA systems

Stephen Taylor

University of Calgary

Calgary, AB

Whole rock (powdered) samples containing Nitrogen <0.10 (wt%) are frequently submitted to our lab for $\delta^{15}\text{N}$ analysis by EA-IRMS. This type of sample poses a particular problem for EA-IRMS analysis due to the large (total) mass of sample which must be combusted in the EA in order to generate N_2 signals large enough to be within the dynamic linear range of the IRMS. Various strategies/concepts on how best to prepare and measure this type of sample will be reviewed. Specifically, the results of modifications to two different EA instruments to optimize their respective "Trace N" modes will be

shown.

Monday 10:00 AM

20 management tips – Take some and Leave some

Paul Middlestead

University of Ottawa

Ottawa, ON

Monday 11:00 AM

The precisION and isoFLOW. IRMS as a versatile foundation for novel isotopic analysis

Sam Barker

Isoprime, Ltd.

Stockport, UK

Rob Panetta

Isoprime, Ltd.

Stockport, UK

Isoprime now introduce the precisION stable isotope ratio mass spectrometer with the highly versatile IONOS software. This innovative combination delivers useful instrument flexibility to pursue isotope science across the broadest spectrum of research. The ability to acquire up to 10 ion beams simultaneously at a resolution of 110 with large dynamic range 100V amplifiers permits samples to be analysed at the highest level of performance. The instrument and software presents a straightforward user interface whilst offering complete control of every hardware parameter. Automation of tasks, flexibility with interfacing and ease of analytical data output are enabled with the inclusion of the centrION interface and IONOS software.

Central to precisION is the ability for the user to generate and incorporate customized inlet systems. The NICM (novel inlet control module) can incorporate and automatically control a large range of devices providing access to valves, mass flow controllers, motors, gauges and sensors.

The isoFLOW preparation system is the new generation gas analyzing devised to maximize these advantages for gas analysis. The introduction of solid-state cooling technology enables sub-zero temperatures without cryogenics or refrigerants, eliminates all moving parts, and increases analytical longevity due to no boiling losses of coolant. This new technology makes it possible for the system to be deployed as both a focusing device and as a gas separation device. Initial data of synthetic gas mixtures (CO₂/CH₄/N₂O in air), and real-world applications including long-term room air, solid carbonates and a comparison between carbonated waters of different origins show excellent agreement with previous technologies.

Monday 11:20 AM

Fractionation effects when using smaller vials on a GasBench: Is it bad and can they be used?

Alison Pye

Memorial University

St. Johns, NL

The usual method of analysing carbonate samples on the GasBench makes use of 12 ml Exetainer® vials. However, some materials, such as forams and otoliths, can only be sampled in very small amounts. With these samples, peak amplitudes of CO₂ are too small for accurate analysis using the regular vials. Other

samples may be impure, such as tooth enamel or drill core samples. With these samples, larger amounts can be added to the vials and may produce enough CO₂, but they also require larger amounts of acid, additional digestion time, and often result in “dirty” CO₂. This “dirty” CO₂ inevitably leads to moisture getting into the sampling capillary and clogging the line, resulting in missing peaks and often, higher standard deviations of the aliquots from each vial.

In theory, the main obstacle to good analysis of smaller and impure samples is obtaining sufficient peak amplitudes. Smaller vials should produce larger peaks from smaller amounts initially, however, peak size would likely decrease more rapidly with subsequent injections. What affect this may have on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is of concern.

To test the viability of using smaller vials, reference materials were weighed into regular 12 ml vials at the usual size (~0.2 mg) and at ~0.1 mg into 4.5 ml Exetainer® vials and analysed in the same run. A comparison of the accuracy and precision of the analyses showed differences between the two vial sizes. Analyses from the 4.5 and 12 ml vials did not have quite the same calibration factor. As expected, peak sizes from the smaller vials decreased more rapidly with subsequent injections. The degree of fractionation of aliquots from the smaller vials also appeared to be higher, resulting in higher standard deviations, which was much more pronounced with $\delta^{18}\text{O}$. Not wishing to discard the potential for using the small vials, I attempted to quantify the size (peak area) to isotope ratio trend to see if a correction could be applied. The results of these tests are presented.

Monday 11:40 AM

Storage of Gas Samples for IRMS Measurement

Paul Eby

Alberta Innovates

Victoria, BC

Various gas sampling containers and septa types were tested for their effectiveness at storing natural gas samples for stable isotope measurement. Results are presented.

Monday 12:00 Noon

Department of Energy Isotope Program

Joel Grimm

Department of Energy

Germantown, MD

The Department of Energy’s Isotope Program produces and distributes radioactive and stable isotopes in short supply. The program also supports R&D efforts associated with developing new and more cost-effective and efficient production and processing techniques, and on producing isotopes needed for research purposes. Isotopes are commodities of strategic importance for the Nation and are essential in fields such as energy exploration, medical diagnosis and therapy, manufacturing quality control, national security, advanced computing and telecommunications, and basic research. These applications touch the lives of almost every citizen. The goal of the program is to make key isotopes more readily available to meet U.S. needs. The program is relatively small with a FY 2016 federal appropriation of \$21 million and FY 2015 isotope sales of approximately \$41 million. The Isotope Program is running low on some enriched stable isotopes produced with Calutrons during the Cold War. In response, DOE is funding a new generation of stable isotope enrichment infrastructure that will use electromagnetic separators

combined with gas centrifuge technology. Grants are also being funded to develop new stable isotope enrichment methods.

Monday 1:40 PM

Methane Fingerprinting: Isotopic Methane and Ethane-to-Methane Ratio Analysis Using a Cavity Ringdown Spectrometer

David Kim-Hak

Picarro, Inc..

Santa Clara, CA

Natural gas analysis and methane specifically have become increasingly important by virtue of methane's 28-36x greenhouse warming potential compared to CO₂ and accounting for 10% of total greenhouse gas emissions in the US alone. Additionally, large uncontrolled leaks, such as the recent one from southern California, originating from uncapped wells, storage facilities and coal mines have increased the total global contribution of methane emissions even further. Determining the specific fingerprint of methane sources, by quantifying $\delta^{13}\text{C}$ values and C₂:C₁ ratios, provides us with means to understand processes yielding methane and allows for sources of methane to be mapped and classified through these processes; i.e. biogenic or thermogenic, oil vs. gas vs. coal gas-related.

In this study we present a fully developed Cavity Ring-Down Spectrometer (CRDS) that precisely measures ¹²CH₄ concentration and its ¹³C H₄ isotope concentration, yielding $\delta^{13}\text{C}$ measurements, C₂H₆ concentration, along with CO₂ and H₂O. This provides realtime continuous measurements without an upfront separation requirement or multiple analyses to derive the origin of the gas samples. The highly sensitive analyzer allows for measurements of scarce molecules down to sub-ppb 1- σ precision in 5 minutes of measurement; with CH₄

Monday 2:00 PM

Sulfur isotope analyses as a tool to enhance understanding of petroleum reservoirs

Craig Barrie

Geomark Research

Houston, TX

John Zumberge

GeoMark Research

Houston, TX

Roger Summons

MIT

Cambridge, MA

Michael Engel

University of Oklahoma

Norman, OK

Kyle W.R. Taylor

Isoprime Ltd

Stockport, UK

Sulfur isotope analysis of petroleum has been poorly explored as a tool for 'oil-oil' and 'oil-source' correlation, and guidelines for interpretation are considered vague, at best. The existing literature on the interrogation of $\delta^{34}\text{S}$ signatures in petroleum is sparse, compared to analogous work which characterizes the $\delta^{13}\text{C}$ compositions of such materials. The majority of studies suggest that bulk organic $\delta^{34}\text{S}$ signatures in petroleum fall midway between coeval seawater sulfate and coetaneous sulfide in pyrite. However, to date there have been no comprehensive, systematic studies evaluating petroleum samples to examine what controls this reported relationship. Factors such as extent of microbial sulfate reduction (MSR) in the sediments and water column, activity of photosynthetic bacteria and non-photosynthetic sulfur oxidizers and thermochemical sulfate reduction (TSR) have all been proposed as

possible mechanisms.

This study aims to improve understanding of the incorporation mechanisms of sulfur into petroleum, and how the isotopic composition of that sulfur relates to age, origin and thermal history. Initial samples investigated are all from sulfur rich (>1 %) basins (i.e. Los Angeles, Ventura, South Florida, etc) and reflect a range of $\delta^{34}\text{S}$ values from -19 to +20‰. Within individual basins the range in sulfur isotopic composition varies from apparent homogeneity (< 0.5‰) to differences of up to 15‰ between individual oils. $\delta^{13}\text{C}$ & $\delta^{34}\text{S}$ isotope cross plots of these data show distinct data clustering and any overlap likely signifies some relationship between sulfur signature and the geologic ages of the oils studied. Overlaying our initial $\delta^{34}\text{S}$ results from oils of known age with the isotopic trend of seawater sulfate through time shows that a simple process of MSR cannot explain all of the signatures preserved.

Monday 2:20 PM

Development and calibration of new natural gas $\delta^{13}\text{C}$ and $\delta^2\text{H}$ reference standards

Robert F. Dias

USGS

Denver, CO

In 2007, the National Institute of Standards and Technology (NIST) published a report certifying the stable carbon isotope values of three natural gas standards. These reference materials included a coal-associated gas (RM 8559), an oil-associated gas (RM 8560), and a biogenic gas (RM8561) (Wise and Watters, 2007). Prior to 2007, these gases were known as NGS1, NGS2 and NGS3, respectively, based upon recommended carbon and hydrogen isotope values reported by the International Atomic Energy Agency (IAEA) (G. Hut, 1985). They were distributed by the Chevron Oil Field Research Company and for more than thirty years, these materials were used as natural gas isotopic standards by industry, academia and governmental agencies.

Recently the supply of these isotopic gas standards was exhausted and NIST discontinued their distribution. The residual gas, cylinders, and manifold assembly were subsequently transferred to an academic research institution, then to a private company. Although a round-robin interlaboratory study of select natural gases from China was recently conducted (Dai et al., 2012) in a presumed effort to replace the NGS gases, this was not a true calibration and the new gases were not made available for general use as reference standards.

In response, the Energy Resources Program of the U.S. Geological Survey (USGS) initiated a project to develop a new suite of natural gas standards to replace the exhausted supply of NGS gases. This project is a collaborative effort by researchers from academic, governmental, and industrial organizations from around the world. USGS personnel took the lead to administer and coordinate the work related to the development of new standards.

All analytical work related to this project is complete, carbon and hydrogen isotope values have been assigned, and the gases are ready for distribution. This presentation summarizes the USGS effort to produce three new natural gas isotope standards.

Monday 2:40 PM		
Nitrogen isotopes on Mars		
Jennifer Stern	NASA Goddard	Beltsville, MD
Heather Franz	NASA Goddard Space Flight Center	Greenbelt, MD
Caroline Freissinet	NASA Goddard Space Flight Center	Greenbelt, MD
Charles Malespin	NASA Goddard Space Flight Center	Greenbelt, MD
Amy McAdam	NASA Goddard Space Flight Center	Greenbelt, MD
Samuel Teinturier	NASA Goddard Space Flight Center	Greenbelt, MD
Paul Mahaffy	NASA Goddard Space Flight Center	Greenbelt, MD
<p>Fixed nitrogen was detected in the form of nitrate in ancient rocks on Mars by the Curiosity Rover. The isotopic composition of nitrogen in these rocks could reveal the state of the martian atmosphere at the time of deposition. The modern martian atmosphere is enriched in ^{15}N (and other heavy isotopes) due to massive loss of atmosphere to space ($\delta^{15}\text{N} = 572$ per mil), while primordial nitrogen is recorded in Mars meteorites ($\delta^{15}\text{N} = 4$ per mil). The exact timing of the loss of martian atmosphere, which is thought to have been catastrophic, is unknown. The extent to which nitrate-N has a modern, enriched $\delta^{15}\text{N}$ vs. primordial $\delta^{15}\text{N}$ may tell us about the timing of the loss of martian atmosphere, and by extension, the loss of a major resource in supporting and sustaining life on the Red Planet.</p> <p>The Sample Analysis at Mars (SAM) Instrument Suite on the Curiosity Rover consists of six gas chromatography columns, a quadrupole mass spectrometer, and a tunable laser spectrometer for high precision CO_2 and H_2O isotope measurements. This instrument was not designed to make high precision ^{15}N measurements of solid samples. Here we describe method development to achieve this measurement using the SAM testbed at NASA Goddard Space Flight Center, and present results from preliminary analyses.</p>		

Tuesday 9:00 AM		
A simple method for simultaneous analysis of carbon, nitrogen and sulfur isotopes in dissolved organic matter		
Sarah Peek	USGS	Menlo Park, CA
Tirumalesh Keesari	Bhabha Atomic Research Center	
Steve Silva	USGS	Menlo Park, CA
Megan Young	USGS	Menlo Park, CA
<p>A method for extraction of dissolved organic matter (DOM) from natural waters is adapted to allow simultaneous analysis of the carbon, nitrogen, and sulfur isotopic composition ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$) of the extracted DOM. DOM is concentrated by solid phase extraction, using a commercially-available</p>		

pre-packed column (Agilent Bond Elute PPL). Eluted DOM is reduced in volume in a glass vial, then dried directly in a tin capsule suitable for combustion on an elemental analyzer coupled to a mass spectrometer. Sufficient material can be obtained from a small volume of water: for example, 1 L of sample water containing at least 2 mg / L DOC. With sufficient material, method blanks are found to be small compared to analytical error. There is little difference in extraction yield between fresh and saline waters. Inorganic salts are rinsed from the extraction column prior to elution to avoid interferences. For the San Francisco Bay estuary, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$ track the values found for analysis of particulate organic matter (POM), suggesting a common source.

Tuesday 9:20 AM

Elemental Microanalysis has standards

Paul Stevens	Elemental Microanalysis	Okehampton, UK
Jon Davies	Elemental Microanalysis	Okehampton, UK

Elemental Microanalysis has been manufacturing consumables used in elemental analyzers for 40 years. In the last decade, we have added analytical standards to the product range, and now offer over 200 different types.

This presentation will focus on the isotopic standards we offer, and give a glimpse into how they are collected, processed and standardized.

Tuesday 9:40 AM

The state of the art for GC combustion and pyrolysis: GC-IsoLink II

Peter Stow	Isomass	Calgary, AB
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Tuesday 10:00 AM

The need for stable isotope working standards

Anja Moritz	ISOSPARK CANADA INC.	Montreal, QC
Jean-François Hélie	Geotop, UQAM	Montreal, QC

The use of stable isotopes has gained importance in various fields over the past few years. These fields can vary greatly in applications, matrix and isotopic composition of samples and hence require appropriate reference material. Because international stable isotope reference materials are costly and only available in limited quantities, laboratories require “working standards” for routine stable isotope analyses. As for international isotope standards, these working standards should be chemically stable over a long period of time and isotopically homogeneous. To meet the demands of customers, ISOSPARK CANADA INC. has started developing these standards in collaboration with GEOTOP, UQAM. Preliminary data will be presented and challenges in the preparation, analysis and storage of these standards will be discussed.

Tuesday 11:00 AM		
Updated Methods for Compositional and Isotopic Profiling of Vanillin, Preliminary Research		
Amanda Smith	Alcohol and Tobacco Tax and Trade Bureau (TTB)	Beltsville, MD
<p>Vanilla bean yields and prices have been fluctuating, making the use of natural vanillin less desirable from both an economic and a supply chain standpoint. In contrast, synthetically produced vanillin is relatively inexpensive and produced in high supply. As a result, the economic incentives to substitute natural vanillin with a low cost synthetic vanillin may lead to product adulteration and mislabeling. For alcohol beverage products, natural or artificial vanillin alone could mean the difference between natural or imitation appearing on the label. The Alcohol and Tobacco Tax and Trade Bureau (TTB) is responsible for approving all labels that appear on alcohol beverages.</p> <p>The purpose of compositional and isotopic profiling of vanillin is to determine whether the source is natural or artificial. Compositional and isotopic profiling of vanillin is not new; however, historical methods involved lengthy extractions, hazardous reactions, or modified equipment. This presentation will demonstrate the use of Ultra High Performance Liquid Chromatography (UHPLC) and GC-Isolink IRMS (d13C and d18O) to improve the process of vanillin authentication.</p>		

Tuesday 11:20 AM		
Bioapatite and matrix matching: Why using carbonate standards for analysis of tooth enamel is bad.		
Penny Higgins	University of Rochester	Rochester, NY
<p>Analysis of isotopes of carbon and oxygen in substituted carbonate in tooth enamel (bioapatite) is widely used to make inferences about past climates, habitats, and dietary habits of fossil and modern vertebrates. As no international standard exists for isotopes in bioapatite (or any apatite mineral for that matter), most scientists use carbonate standards instead, especially NBS-19, the benchmark for the V-PDB isotopic scale. Nearly all laboratories normalized bioapatite data using carbonate minerals, all of which are calibrated back to the V-PDB scale using NBS-19.</p> <p>It is widely known that the magnitude fractionation from carbonate (the solid) to carbon dioxide (the gas to be measured) is temperature dependent. Laboratory analyses of carbonates (and bioapatites) are completed at temperatures ranging from 25°C to 90°C. When unknowns are themselves carbonates, it is a relatively safe assumption that temperature-related fractionation affects all samples, standards and unknowns, equally. Where bioapatites are measured, this may be a poor assumption.</p> <p>While scientists have gone to great lengths to show how different treatments of bioapatite prior to analysis may affect resultant isotopic values, few concern themselves – at least not openly – about the problem of using standard reference materials of a different matrix. Here, I show that the consequences of incorrect matrix matching appear to outweigh the differences due to pretreatment protocols for bioapatites.</p>		

Tuesday 11:40 AM		
Modifications for nitrate and total N analysis from aqueous samples		
Ben Harlow	Washington State University	Pullman, WA
<p>Nitrate stable isotope analysis is becoming commonplace in many isotope labs. Here, we report on modifications for measurement of ^{15}N, ^{18}O and ^{17}O from NO_3^-, as well as total N from aqueous samples. Total N from samples was measured using persulfate oxidation in conjunction with the denitrifier technique.</p> <p>The existing 96 position gasbench II tray can be easily modified to accommodate shorter, wider crimp seal vials. We added a second valco valve, controlled by existing pneumatics, to allow for quick switching between N_2O analysis and N_2O thermal decomposition. An additional GC column and Supelco type "F" hydrocarbon trap fit in a modified GC oven to allow for easy reconditioning. A script was developed to introduce heating to the initial slush trap and plumbing was revised to backflush the front end when not trapping the sample.</p> <p>For total N analysis, we observed best results with original growth medium and no additional phosphate buffer. Reproducibility of the total N method has been 0.5 per mil or less. Once oxidized samples are stable over long periods of time.</p>		

Poster Abstracts

POSTER		
Determining $\delta^2\text{H}$ in bone collagen – development of reference materials and methodological challenges		
Christine A.M. France	Smithsonian Museum Conservation Institute	Suitland, MD
Haiping Qi	United States Geological Survey	Reston, VA
<p>Hydrogen stable isotope values in bone collagen have the potential to add new insight into geographic provenance and ecological studies. The influence of latitudinal variations in $\delta^2\text{H}$ values of incorporated drinking water and trophic level fractionations are not currently well-understood in bone collagen.</p> <p>In order to study these relationships, appropriate reference materials for linear correction of $\delta^2\text{H}$ values are required. In keeping with the principles of identical treatment, these reference materials must be a similar organic polymer (i.e. bone collagen), with the same fraction of exchangeable hydrogen atoms as the samples of interest. This project developed six new bone collagen references from mammal bones in high-, mid-, and low-latitudes to provide a natural $\delta^2\text{H}$ range of standard values to which samples can be linearly corrected.</p> <p>The reference collagens were characterized using the dual-water equilibration technique and analyzed by Cr packed reactors, during which several methodological challenges came to light. It was observed that collagen's propensity to hydrolyze and absorb water greatly affects equilibration with reference waters and local atmospheric water vapor. Certain drying and storage methods were more effective than others at mitigating this issue. This poster presents the six new reference materials developed and offers procedural recommendations for equilibrating bone collagen samples and measuring their $\delta^2\text{H}$ values.</p>		

POSTER		
Patterns in stable isotope ratios of particulate material from the eastern US continental shelf		
Richard McKinney	US EPA	Narragansett, RI
Betty Kreakie	US EPA	Narragansett, RI
Autumn Oczkowski	US EPA	Narragansett, RI
Jerry Prezioso	NOAA / NMFS	Narragansett, RI
<p>Stable isotope measurements of nitrogen and carbon ($\delta^{15}\text{N}$, $\delta^{13}\text{C}$) in estuarine, nearshore, and open-ocean ecosystems are often used to characterize human influences, elucidate food web dynamics, or better understand nitrogen cycling. Reliable information about the spatial distribution of base-level stable isotope values is critical to interpreting values in these ecosystems. While base-level isotope data are generally readily available for estuaries, nearshore coastal waters, and the open ocean, waters of the continental shelf have been less studied. To address this and as a first step towards developing a surrogate for base-level isotopic signature in this region we collected surface and bottom samples from the United States' eastern continental shelf in the Western Atlantic Ocean, from the Gulf of Maine to</p>		

Cape Hatteras, periodically between 2010 and 2013. During the study particulate matter $\delta^{15}\text{N}$ values ranged from 0.80 to 17.37 ‰, and $\delta^{13}\text{C}$ values from -26.37 to -15.58 ‰. Spatial autocorrelation analysis and random forest modeling revealed no significant spatial trends in the data, although we did see trends towards lower values for both nitrogen and carbon at the seaward edge of the shelf. Conversely, higher $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values were observed on the landward edge of the shelf, in particular in the southern portion of the sampling area. Across all sites, the magnitude of the difference between the $\delta^{15}\text{N}$ of bottom and surface PM significantly increased with water depth ($r^2 = 0.41$, $df = 35$, $p < 0.001$), while $\delta^{13}\text{C}$ values did not change. We found a significant positive correlation between $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values for surface PM in each of the three marine ecoregions that make up the study area. Stable isotope dynamics on the shelf can inform both nearshore and open ocean research efforts, providing an important link along the marine continuum.

POSTER

Calibration Standards for IRMS Applications

M. Matthew	Air Liquide America, Specialty Gases	Plumsteadville, PA
T. Jacksier	Air Liquide, Delaware Research & Technology Center	Newark, DE
S. Miller	Air Liquide America, Specialty Gases	Plumsteadville, PA

Stable isotope analyses in Geochemistry, Environmental, Health, and Food applications are steadily increasing. The key to accurate measurements is the use of Reference Materials with low Uncertainty. The preparation of high quality calibration mixtures requires the use of cylinders and accessories prepped to exacting specifications. Material compatibility between the gas components and packaging materials insures stability of the blend. Trace moisture and oxygen contained within the cylinder are detrimental to stability in mixtures and pure gases. Calibration gases can be prepared gravimetrically, volumetrically, or by dynamic blending.

Gravimetric techniques have the advantage of high mass discrimination and the use of weights which are directly traceable to National Metrology Institutes. Volumetric methods rely on the accurate addition of components by volume, or pressure. Dynamic blending employs continuous blending using on-line analyses. Individual source materials must be characterized to take impurity constituents (both molecular and isotopic) into account in the final calculations. Errors and uncertainties can arise from three primary sources (1) analyzer calibration (2) analyzer repeatability (precision) and (3) uncertainties in concentration of Reference Materials used for calibration. 1

To decrease the total Uncertainty, each parameter must be minimized. The calibration of the instruments with the highest accuracy Standards then, is key. This presentation will examine mixture preparation processes (for both molecular and isotopic concentrations). Source materials need to be precisely characterized. Analysis of individual cylinders within batches demonstrates the ability to dynamically fill multiple cylinders, containing identical compositions without isotopic fractionation. The capability to adjust isotope ratios to more closely bracket sample types is also presented.

1. Bell, S., 1999. A Beginners Guide to Uncertainty of Measurement, NPL, UK

POSTER		
Nitrogen and oxygen isotope composition of manufactured ammonium nitrate and its isolated ammonium and nitrate ions		
Brittany L. Grimm	Visiting Scientist Program, Counterterrorism and Forensic Science Research Unit, FBI Laboratory Division	Quantico, VA
Libby A. Stern	Counterterrorism and Forensic Science Research Unit, FBI Laboratory Division	Quantico, VA
Alex J. Lowe	Visiting Scientist Program, Counterterrorism and Forensic Science Research Unit, FBI Laboratory Division	Quantico, VA
<p>Ammonium nitrate (AN, NH_4NO_3) based fertilizers are inexpensive and easily obtained, characteristics which often lead to their use in bombs and homemade explosive devices. AN is made from ammonia and nitric acid, which are produced using atmospheric N_2 and O_2 under high temperatures and pressures. Therefore, isotopic values of AN often reflect those of the atmosphere ($\delta^{15}\text{N}_{\text{Air}} \equiv 0\text{‰}$, $\delta^{18}\text{O}_{\text{VSMOW}} \approx +23.5\text{‰}$). Any isotopic fractionation that occurs during manufacturing can be used as a discriminatory tool between samples, particularly in the context of forensic comparisons. 26 AN samples were analyzed for their bulk $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values after water filtration, producing a range of $\delta^{15}\text{N}$ from -4.57 to +4.35‰ and $\delta^{18}\text{O}$ from +20.93 to +25.23‰. As expected, the average $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotopic compositions were close to atmospheric signatures at +0.16 and +22.73‰, respectively.</p> <p>To characterize the $\delta^{15}\text{N}$ of the ionic components of AN, the NO_3^- ion was isolated using the following method. An aqueous KOH solution (~13.2 mg/mL) was added to ~30 mg of a filtered and dried AN sample to achieve 1.25 molar excess KOH. In this highly basic solution, NH_4^+ volatilizes as NH_3 (g) and KNO_3 crystallizes upon drying, after which the precipitate is rinsed 3 times with methanol to remove any residual KOH. The measured $\delta^{15}\text{N}$ of the KNO_3 represents the nitrate in the AN, while the $\delta^{15}\text{N}_{\text{NH}_4}$ is calculated via mass balance ($\delta^{15}\text{N}_{\text{Bulk AN}} = \frac{1}{2} (\delta^{15}\text{N}_{\text{NO}_3}) + \frac{1}{2} (\delta^{15}\text{N}_{\text{NH}_4})$). $\delta^{15}\text{N}_{\text{NO}_3}$ exhibited a larger $\delta^{15}\text{N}$ range (-4.72 to +5.95‰) compared to the bulk AN measurements, with an average of +1.58‰. The $\delta^{15}\text{N}_{\text{NH}_4}$ average, -1.26‰, was lower than that of $\delta^{15}\text{N}_{\text{NO}_3}$, with a range of -4.69 to +2.74‰. The difference between $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{15}\text{N}_{\text{NH}_4}$ in each sample is not constant, varying between -0.36‰ to +6.35‰. This indicates that $\delta^{15}\text{N}$ values from the two component ions of AN can provide additional discriminating information than $\delta^{15}\text{N}_{\text{Bulk}}$ alone.</p>		

POSTER		
Reaction Mechanism and Source Apportionment of Aerosol		
Hiroto Kawashima	Akita prefectural University	Yurihonjo city, Akita prefecture, Japan
<p>Suspended particulate matter (SPM), defined to particle size as 100 % cut-off aerodynamic diameter at 10 μm, has adverse effects on human health. It could not be decreased reduce from 1990 s and maintain approximately 30 $\mu\text{g}/\text{m}^3$. One reason of difficult to decrease SPM, the mechanism of SPM formation and behavior in atmosphere is much more complicated, and it is very difficult to comprehend the relationship between source and receptor of SPM.</p>		

In these years, stable isotope ratio of small sample volume can be analyzed high precision by isotope ratio mass spectrometry. Recently some fields are using stable isotope ratio. Moreover, stable isotope ratio of very small sample volume can be analyzed more precision by bacteria method. For environmental field, it is expected such as powerful tool for source identification and understanding mechanism. But the existed researches intended for stable nitrogen isotope ($\delta^{15}\text{N}$) of particulate matter and gas samples, NH_3 , NO_2 and NO_x have been limited. We try to analysis $\delta^{15}\text{N}$ -ammonium ($\delta^{15}\text{N-NH}_4^+$) and nitrate ($\delta^{15}\text{N-NO}_3^-$) of SPM and $\delta^{15}\text{N}$ -ammonia ($\delta^{15}\text{N-NH}_3$), nitrogen dioxide ($\delta^{15}\text{N-NO}_2$), nitrogen oxides ($\delta^{15}\text{N-NO}_x$), to estimate source of NH_4^+ and NO_3^- of SPM.

In this method, the results of the accuracy and the precision were $0.03 \pm 0.04 \text{ ‰}$ ($\delta^{15}\text{N-NH}_4^+$) and $-0.15 \pm 0.14 \text{ ‰}$ ($\delta^{15}\text{N-NO}_3^-$), respectively. In addition, Bactria method is very reasonable results in comparison with other researcher. Average $\delta^{15}\text{N-NH}_4^+$ and $\delta^{15}\text{N-NO}_3^-$ of SPM in Akita prefecture, Japan were 15.9 ‰ (1.3 ‰ to 38.5 ‰) and -0.7 ‰ (-4.6 ‰ to 4.8 ‰), respectively. $\delta^{15}\text{N-NO}_3^-$ increased in winter markedly and decreasing in summer. In generally, the dominant origin of NO_3^- of SPM is produced from NO_x emitted by combustion of some fuel and NO by agriculture source. The reason of the winter high trend in this study might be combustion process such as coal combustion source. Moreover, the baseline might be made by vehicle sources.

POSTER

Seasonal Variation in Primary Production in the Thames River, Southeastern Connecticut, as Measured by ^{13}C CO_2 Uptake

Sam C. Wainright

U.S. Coast Guard Academy

New London, CT

A year-long study examined seasonal changes in phytoplankton biomass and primary production in the Thames River, a salt wedge estuary that empties into Long Island Sound in southeastern CT. Discrete filtered samples were collected above and below the 1-3 m deep pycnocline at a 5-meter deep station.

Primary production, as measured by ^{13}C CO_2 uptake in bottle incubations, averaged $67 \text{ mgC m}^{-3} \text{ h}^{-1}$ in surface water [range 0.1 (Jan 2012) to $800 \text{ mgC m}^{-3} \text{ h}^{-1}$ (Aug 2011)], and $3 \text{ mgC m}^{-3} \text{ h}^{-1}$ [range 0.04 (Jan 2012) to $17 \text{ mgC m}^{-3} \text{ h}^{-1}$ (Aug 2011)] in the lower layer. Usually, deep water incubated near the surface had a higher primary production rate than surface water incubated at the surface; apparently the phytoplankton in the lower layer were released from light-limitation in these incubations. Surface chlorophyll concentrations, primarily from diatoms, averaged approx. 2 mg m^{-3} , with maxima (up to 10 mg m^{-3}) during summer (Jun to Aug) and minima during October through March (as low as 0.3 mg m^{-3}). The lower water layer had a similar annual average but a smaller range (0.7 - 3.3 mg m^{-3}) and a winter/spring bloom (Jan-Apr) that was not seen in surface water. During most of the winter, chlorophyll concentrations were higher in the lower layer.

During the study period there were over a dozen heavy wind or heavy rain events, including Hurricane Irene in August and a freak Nor'easter snow storm in October 2011. Hurricane Irene was associated with a large decline in phytoplankton biomass and primary production. With significant storms as frequent as the rate of sampling, it is difficult to separate a "storm effect" from a background seasonal pattern. The study reveals that phytoplankton, especially those in the lower layer, are light-limited in this estuary, and that the effects of significant storm events are superimposed on significant seasonal variation.

POSTER		
A Comparison of IRMS and CRDS for the Detection of Economic Adulteration of Lemon Juice and Honey		
Madhavi Mantha	US FDA	Cincinnati, OH
John Urban	US FDA	Cincinnati, OH
Kevin Kubachka, Ph.D	US FDA	Cincinnati, OH
<p>In the last several years, economically motivated adulteration (EMA) of foods has received increased attention. Two popular targets of EMA are lemon juice and honey; lemon juice can be adulterated with exogenous citric acid and/or low cost sweeteners while honey is commonly adulterated with low cost sweeteners. Historically, the most common adulterant of honey has been corn syrup, which is comprised of C 4 plant sugars. The FDA currently utilizes AOAC method 998.12 to analyze bulk honey samples with an elemental analyzer-isotope ratio mass spectrometry (EA-IRMS) system and compares the $\delta^{13}C$ value to that of its respective protein isolate.</p> <p>In a recent US FDA study, 75 samples of lemon juice offered for import into the US were collected for analysis using EA-IRMS as well as other techniques to detect adulteration of the lemon juice. These lemon juice samples were labeled to be 100% lemon juice from concentrate. Samples were analyzed for the presence of added citrate/citric acid using methodology adapted from a published method by Doner and coworkers.¹ A $\delta^{13}C$ value for the calcium citrate of greater than (less negative than) -23‰ was indicative of adulteration. Approximately 25% of the samples were determined to contain exogenous citric acid, and were therefore adulterated or suspect.</p> <p>For both of these types of adulteration analyses, the FDA is evaluating the use of Cavity Ring Down Spectroscopy (CRDS) to establish its suitability. CRDS offers a cheaper, robust, and simplified analysis technique that could potentially be transferred to other regulatory labs for routine use. When using both the IRMS and CDRS techniques to examine the $\delta^{13}C$ values of these materials, the results found so far for calcium citrate, bulk honey and protein isolates are quite comparable.</p> <p>1) Doner, L., "Carbon Isotope Ratios in Natural and Synthetic Citric Acid as Indicators of Lemon Juice Adulteration." J. Agric. Food Chem., 22 (1985) 770-772.</p>		

POSTER		
Splitting hairs: dietary ecology of Alaskan brown bears and the utility of sectional vs. whole hair sampling for use in stable isotope dietary mixing models.		
Matthew Rogers	NOAA Alaska Fisheries Science Center	Juneau, Alaska
<p>Stable isotope analysis of animal tissues is a widely used for studying dietary ecology. Long-lived, sequentially-grown tissues (e.g. hair, claw, and baleen) are particularly valuable for diet inference studies since they are grown over the course of months or even years. A long growth period also introduces some potential problems and pitfalls into the use of tissue stable isotope data in dietary estimation and mixing models. In the case that a consumer's diet proportions change through time, an</p>		

ecologically relevant section of the sample may be used to infer diet.

If, on the other hand, the whole sample is analyzed and the data is fed into a mixing model, then the changes in diet proportion through time may be obscured and the potential exists for erroneous model output. Additionally, sectional analysis of sequentially-grown tissue may provide more information about trophic niche breadth than analysis of the whole tissue.

Our questions are:

- 1) What are the brown bears of three Alaskan biomes eating and how does it shift seasonally?
- 2) Does the use of whole hair and sectioned hair isotopic data (^{13}C & ^{15}N) for each individual produce equal dietary estimates when used in a Bayesian isotopic mixing model?
- And 3) Does sectional analysis provide a better estimate of trophic niche breadth than whole hair analysis?

We found a high degree of omnivory in the bears sampled. We found a larger degree of salmon utilization in our northernmost population (Gates of the Arctic National Park) than we had anticipated. We also determined that whole hair sample analysis produced comparable estimates of diet to sectional hair analysis. Sectional analysis provided greater insight into seasonal changes in diet and trophic niche breadth. All of the findings, taken together, help to inform stable isotopic studies of bear diet globally and the dietary ecology of Alaskan brown bears.

POSTER

Detection of Economically Motivated Adulteration in Honey and Lemon Juice Using LC-IRMS Analysis Methods

Kevin Kubachka	US FDA, Forensic Chemistry Center	Cincinnati, OH
Madhavi Mantha	US FDA, Forensic Chemistry Center	Cincinnati, OH
Virginia Johnson	US FDA, Forensic Chemistry Center	Cincinnati, OH
Alexandra Guthart	US FDA, Forensic Chemistry Center	Cincinnati, OH
M. Kathryn Vetter	US FDA, Forensic Chemistry Center	Cincinnati, OH

Over the last several years, economically motivated adulteration (EMA) of foods has received increased attention from media outlets as well as interest from regulatory agencies. Two popular targets of EMA are honey and lemon juice. Honey is commonly adulterated with low cost sweeteners while lemon juice has been adulterated with exogenous citric acid and/or low cost sweeteners. Because of distinct $\delta^{13}C$ differences between these authentic products and common adulterants, isotope ratio mass spectrometry (IRMS) is the analysis of choice. Detection of each adulterant provides its own unique challenges. As the methods of adulteration and the sweeteners used become more sophisticated, we have begun to explore alternative methods.

In an effort to achieve C-4 plant sugar adulteration detection limits below ~7% (AOAC 998.12) or detect less common adulterants such as, rice syrup, beet sugar, etc., liquid chromatography (LC) with IRMS was

explored because this technique has the capability to examine $\delta^{13}\text{C}$ of individual components. Various commercially available honey samples have been analyzed to compare to literature reports in pursuit of a method applicable to routine honey examination. LC-IRMS was also applied to lemon juice samples to examine the $\delta^{13}\text{C}$ of ascorbic acid, malic acid, citric acid, and/or sugars. This method uses little to no sample preparation resulting in a relatively short analysis time. Additionally, the potential of using one of the components, malic acid, as an internal standard to possibly decrease the level of detectable adulteration was explored.

POSTER

Enriched Stable Isotope Target Preparation at the Oak Ridge National Laboratory

Mike Zach	Oak Ridge National Laboratory	Oak Ridge, TN
Eva Hickman	Oak Ridge National Laboratory	Oak Ridge, TN
Clint Ausmus	Oak Ridge National Laboratory	Oak Ridge, TN
Brian Egle	Oak Ridge National Laboratory	Oak Ridge, TN

Since the 1960s, the U.S. Department of Energy (DOE) Isotope Program, through the Isotope Development Group at the Oak Ridge National Laboratory, has been developing and supplying enriched stable isotope targets for nuclear, medical, academic, and industrial research around the world.

This group also maintains and distributes the DOE inventory of enriched stable isotopes. Chemical and pyrochemical techniques are used to prepare enriched stable isotopes from this inventory in the desired chemical and physical form. Metallurgical, ceramic, or vacuum processing methods are then used to prepare the isotopes in a wide range of physical forms—from thin films, foils, and coatings to large fabricated shapes—to meet the needs of experimenters.

Significant characterization capabilities are also available to assist in the preparation and evaluation of these custom materials. This work is part of the DOE Isotope Program, Office of Nuclear Physics within the DOE Office of Science. A goal of this program is to enable research and development. This presentation will focus on the custom preparation of enriched stable isotope targets and other research materials.

POSTER

Stable Isotope Applications in Aragonitic Giant Clam Shells

Michelle Gannon	Drexel University	Philadelphia, PA
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Aragonitic shells of giant clams, sub-family Tridacninae, are considered excellent bioarchives of the surrounding waters because they secrete daily growth increments and their dense shells are resistant to diagenesis.

Tridacnids are unique because they host a symbiotic relationship with photosynthetic algae

(Symbiodinium), from which they receive a significant amount of carbon. This study combines the isotopic analysis of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of organic material within the shell and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of inorganic shell carbonate, from both the internal and external layers. Inorganic $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measured from two *Tridacna gigas* individuals from Papua New Guinea and the Great Barrier Reef, allows for the exploration of differences in metabolic pathways between the shell layers.

The external shell layer is enriched in ^{13}C compared with the internal layer in each of these specimens, although there are some inter-specimen differences likely influenced by their locality. $\delta^{18}\text{O}$ does not significantly differ between shell layers and therefore clarifies that there are no vital effects to account for in comparison of growth records between the internal and external layer. However, it is likely that there is a partitioning of nutrient uptake between shell layers, influenced by the presence and activity of the photosynthetic algae.

To further explore this hypothesis, the isotopic composition of the organic matter from the shell matrix is measured through a sequence of ontogenies for two *Tridacna derasa* individuals from Palau. $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ are often utilized to assess the trophic level in biotic organisms. Enrichment of ^{15}N and ^{13}C suggests that the layer is receiving its organic material from filter feeding phytoplankton while depletion supports that the organics are from the photosynthetic algae living within the tissues of the giant clam. Stable isotope analyses of *Tridacna* shells allow for assessment of environmental interactions as well as metabolic pathways within the individual.

POSTER

Measuring the $\delta^{13}\text{C}$ of Dissolved Organic Carbon in Canada's Eastern Coastal Waters

Andrew Barber	Concordia University	Montréal, Quebec, Canada
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Yves Gélinas	Concordia University	Montréal, Quebec, Canada
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The application of carbon stable isotope analysis on dissolved organic carbon ($\delta^{13}\text{C}$ -DOC) from natural seawater samples has been limited owing to the difficulty of such analysis, with order of magnitude differences in interfering ions and analyte concentrations.

High temperature catalytic oxidation allows for the separation of interferences from the organic carbon by precipitation on quartz chips upstream from the oxidation catalyst. Unlike wet chemical oxidation, where salts inhibit the oxidation of organic matter to CO_2 via side reactions between the salt anions and the persulfate oxidizing agent, high temperature combustion ensures complete organic matter oxidation in a stream of O_2 .

Using a programmable chemical trap to switch carrier gasses, the OI 1030C combustion unit can be coupled to and IRMS, allowing for the analysis of low DOC content waters with relatively high throughput. The analytical limitations and large water volumes traditionally required for these types of analysis, have prevented any large-scale $\delta^{13}\text{C}$ -DOC studies.

Here we present DOC concentrations and $\delta^{13}\text{C}$ -DOC signatures for surface and bottom waters obtained in along Canada's East Coast. Included in the study are samples from the Esquiman channel (between

Newfoundland and Labrador), Lake Melville, the Saglek and Nachvak Fjords, the Hudson Strait and finally covering the salinity gradient across the Gulf of the St. Lawrence and St. Lawrence Estuary. Measured $\delta^{13}\text{C}$ -DOC signatures ranged from predominantly marine signatures of $-21.3 \pm 0.6 \text{‰}$ (vs. VPDB) off the coast of Newfoundland to predominantly terrestrial signatures of $\approx -25.8 \pm 0.1 \text{‰}$ in Lake Melville. Overall, proper blank subtraction using the isotope mass balance equation and 4 replicate injections are crucial for the collection of meaningful $\delta^{13}\text{C}$ -DOC signatures on natural abundance, seawater samples.

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