

Fourth FIRMS Network Conference



April 11-14, 2010
Washington, D.C.

Co-Hosted by the
Federal Bureau of Investigation



TABLE OF CONTENTS

ABBREVIATED CONFERENCE AGENDA	2
DETAILED CONFERENCE AGENDA	3
MONDAY April 12, 2010	3
Poster Session Titles	4
TUESDAY April 13, 2010	5
WEDNESDAY April 14, 2010	6
Poster Session Titles	7
ABSTRACTS.....	8
AUTHOR INDEX.....	84
CONTACT LIST.....	86

FOURTH FIRMS CONFERENCE

Abbreviated Conference Agenda

All events will take place at the Carnegie Institution Building located at
16th and P St NW, Washington DC

Sunday April 11, 2010

19:00 – 21:00 Reception and Registration with drinks

Monday April 12, 2010

07:30 – 08:00 Registration

08:00 – 17:30 Technical Program, including oral and poster presentations; Lunch on
premises

Tuesday April 13, 2010

08:00 – 17:00 Technical Program, oral presentations only; Lunch on premises

19:00 – 21:00 Conference Banquet

Wednesday April 14, 2010

08:30 – 15:30 Technical Program, including oral and poster presentations; Lunch on
premises

15:45 – 17:00 FIRMS Steering Group Meeting

Detailed Conference Agenda

Monday April 12, 2010

Time	Page #	Morning session chaired by Jurian Hoogewerff
07:30 – 08:00		Registration
08:00 – 08:15		<i>Welcoming Remarks</i> Dr. D. Christian Hassell, FBI Laboratory Director
08:15 – 08:30		<i>Introduction to the FIRMS Network</i> Jim Carter
08:30 – 09:30	9	<i>PLENARY TALK - CSI or Academic Iso-Gap? Forensic Potential of Isotopes, Investigative Needs, and Judicial Requirements</i> James Ehleringer
09:30 – 10:00		Coffee Break
Oral Session on Geographic Attribution Related to Humans		
10:00 – 10:20	10	<i>Tracking Geographical Movements: Laser Ablation Multicollector ICP-MS to Study Longitudinal Stable Isotopic Variations in Single Human Hair Strands</i> <u>Rebeca Santamaria-Fernandez</u> , Justo Giner Martinez-Sierra, Ruth Hearn
10:20 – 10:40	11	<i>The Application of Trace Element and Multi-isotope Analysis of Hair Samples for Detecting Human Travel</i> <u>Sabine Schneiders</u> , Thomas Holdermann, Nicole Scheid, Stefan Becker
10:40 – 11:00	12	<i>The Canadian Human Hair Provenance Project - Questions and (Some) Answers</i> <u>Michelle Chartrand</u> , Gilles St-Jean, Claude Dalpé, James Wojtyk
11:00 – 11:20	13	<i>An Integrated and Comprehensive Model of ^2H and ^{18}O Isotope Composition in Primates</i> <u>Shannon O'Grady</u> , C. Remien, L. Enright, L. Valenzuela, L.A. Chesson, M. Jorgensen, J. Kaplan, J. Wagner, T.E. Cerling, J.R. Ehleringer
11:20 – 11:40	14	<i>Characterizing Temporal Variations in the Isotopic Composition of Human Drinking Water</i> <u>Casey Kennedy</u> , Gabriel J. Bowen, James R. Ehleringer
11:40 – 12:00	15	<i>Spatial and Seasonal Variability of Stable Isotopic Compositions ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of Tap Waters throughout the United States</i> <u>Jurate Landwehr</u> , Tyler B. Coplen
12:00 – 12:20		Discussion of Geographic Attribution Related to Humans
12:20 – 13:20		Lunch
13:20 – 15:30	4	Posters – See next page
15:00 – 15:30		Tea Break
Oral Session on Provenance Determination Using Isotope Methodologies Chaired by Max Coleman		
15:30 – 15:50	35	<i>A Geochemical System for Verifying Honey Floral Type and Provenance</i> Kiri McComb, <u>Russell Frew</u>
15:50 – 16:10	36	<i>Beeswax Hydrogen Isotopes as Validation of Environment (B-HIVE)</i> <u>Brett J. Tipple</u> , Lesley A. Chesson, Brad Erkkila, James R. Ehleringer, Thure E. Cerling
16:10 – 16:30	37	<i>Wine and Champagne: Evidence from Lithium Isotopes</i> <u>Romain Millot</u> , Philippe Négrel
16:30 – 16:50	38	<i>Geographical Region-of-Origin Assignment of American Milk Using Stable Isotope Analysis</i> <u>Lesley A. Chesson</u> , Luciano O. Valenzuela, Shannon P. O'Grady, Thure E. Cerling, James R. Ehleringer
16:50 – 17:10	39	<i>Provenancing Plant materials from Isoscapes</i> <u>Jason B. West</u> , James R. Ehleringer, Helen M. Kreuzer, Janet M. Hurley, Thure E. Cerling
17:10 – 17:30		Discussion of using Isotope Methodology for Provenance Determination

Monday April 12, 2010 Poster Session - 13:20 – 15:30

Page #	Poster Themes	Title and Authors
16	G,H	<i>Isotopic Analysis of Modern Human Hair for Geosourcing</i> <u>Sophie Raynaud</u> , Stuart Black , Matthew Almond
17	G,H	<i>Spatial Distribution of Sulfur Isotope Ratios in Human Hair Across the USA</i> <u>Luciano O. Valenzuela</u> , Lesley A. Chesson, Shannon P. O'Grady, Thure E. Cerling, James R. Ehleringer
18	G,H	<i>Distinguishing Americans and Europeans on the Basis of Carbon and Sulfur Isotope Ratios of Hair</i> <u>Luciano O. Valenzuela</u> , Lesley A. Chesson, Shannon P. O'Grady, Gabriel Bowen, Thure E. Cerling, James R. Ehleringer
19	G,H	<i>"I Know Where You Spent Last Summer": Isotopes in Hair and Teeth to Trace the Regions-of-Origin of Unidentified Murder Victims</i> <u>James Ehleringer</u> , Thure Cerling, Lesley Chesson, Gabriel Bowen, Luciano Valenzuela, David Podlesak
20	G,H	<i>CO₂ in Breath as a Short-Term Record of Geographic Movement</i> <u>S.P. O'Grady</u> , C. Remien, L. Enright, L. Valenzuela, L.A. Chesson, D.W. Podlesak, T.E. Cerling, J.R. Ehleringer
21	G,H	<i>A National Survey of Human Body Water Variation</i> <u>S.P. O'Grady</u> , C. Remien, L. Enright, L. Valenzuela, L.A. Chesson , D.W. Podlesak, T.E. Cerling, J.R. Ehleringer
22	G,F	<i>Geographical Region-of-Origin Assignment of American Beef Using Stable Isotope Analysis</i> <u>Lesley A. Chesson</u> , Luciano O. Valenzuela, Shannon P. O'Grady, Thure E. Cerling, James R. Ehleringer
23	G,T,F	<i>Source of Strontium (Food vs. Water) in Alligator Bioapatite</i> <u>Patrick V. Wheatley</u> , Paul L. Koch
24	G	<i>Multi-Isotope Analysis to Monitor Animal Provenance: A Case Study of Migratory Birds</i> <u>Laura Font</u> , Gareth Davies, Mårten Hjertqvist, Thor Veen, Marcel Klaassen, Hubert Vonhof, Graham Pearson, Steve Willis, Geoff Nowell
25	G,F	<i>How the Alcohol and Tobacco Tax and Trade Bureau (TTB) is Using Stable Isotope Ratio Mass Spectrometry to Protect the Public and Collect the Revenue</i> <u>Amanda Smith</u>
26	G	<i>Surface Water Isotope Models for Retrospective Geolocation of People and Products</i> <u>Gabriel J. Bowen</u> , Zhongfang Liu, Casey Kennedy, James R. Ehleringer
27	G	<i>The Use of Isotope Ratio Mass Spectrometry in the Forensic Analysis of Australian Papers</i> Kylie Jones, <u>Timothy Simpson</u> , Claude Roux, Sarah Benson
28	G	<i>Biogeochemical Isotopes and Trace Elements as Geo-location Markers for Biosecurity: Can the Technology Determine the Origin of Pests?</i> P.W. Holder, K. Armstrong, T. Clough, <u>R. Frew</u> , R. Van Hale, J.A. Baker, M-A. Millet
29	G,H,T	<i>Development and Validation of Regional Spatial Prediction "Isoscape" Models for the Provenancing of Unidentified Human Remains</i> <u>Robert Posey</u> , Khudooma Al Na'imi, Tal Simmons, Henriette Ueckerman, Jurian Hoogewerff
30	G,T	<i>The Use of Strontium Isotope Ratios and Biological Profiling for Forensic Provenancing of Soils</i> Hilary Bathgate, Julian Andrews, Andrew Lovett, Jonathan Clarke, Henriette Ueckermann, <u>Jurian Hoogewerff</u>
31	G,T	<i>Strontium Isotopes in European Soils - Spatial Variation and Discrimination Potential for Forensic Applications</i> Henriette Ueckermann, <u>Jurian Hoogewerff</u> , Grishja van der Veer, Susanne Rummel, Christian Dekant, Malcolm Baxter, C Quetel, Daniel Goitom Asfaha, Marleen van Bockstaele, and the TRACE Consortium
32	G,X,D	<i>Isotope Ratio Mass Spectrometry for Tracing the Origin of Forensic Agents</i> Eric Galimov, <u>Vyacheslav Sevastyanov</u> , Olga Kuznetsova
33	M,T	<i>Discrimination of Duct Tapes using Isotope Ratio Mass Spectrometry</i> <u>Martin van Breukelen</u> , Francis Vogelpoel, Marianne Schrader, Wim Wiarda, Andrew van Es, Gerard van der Peijl
34	M	<i>Forensic Utility of Stable Isotope Ratios of PVC Tape Backings</i> Libby Stern, Andria Hobbs Mehlretter, Ashley Parish, Velvet McLasky, <u>Marianne Dietz</u> , Roman Aranda IV

G = Geographic Attribution, H = Human Tissues, M = Manufactured Materials, E = Environmental Forensics, T = Trace Elements and Heavy Isotopes, X = Explosives, F = Food and Drink, D = Narcotics and Pharmaceuticals, I = Technical Innovations

Tuesday April 13, 2010

Time	Page #	Morning session chaired by Tyler Coplen
Oral Session on Isotopes in Environmental Forensics		
08:00 – 09:00	40	<i>PLENARY TALK - The Evolution of Stable Isotope Applications in Environmental Forensics - Past, Present and Future</i> <u>R. Paul Philp</u> , Tomasz Kuder
09:00 – 09:20	41	<i>Differentiating Nuclear Processing from Multiple Sources of Anthropogenic Nitrate in a Complex Groundwater System using Dual Isotope Systematics</i> <u>Toti Larson</u> , Julianna Fessenden, Jeffrey Heikoop, Evelyn Bond, George Perkins, Mary Ann Stroud, Patrick Longmire, Michael Rearick, Michael Dale, Paul Davis
09:20 – 09:40	42	<i>Investigation of the Fate of Nitrate in the Interflow Zone of Mantled Karst</i> <u>Jozef Lajncz</u> , Phillip D. Hays, Byron Winston, Susan Ziegler
09:40 – 09:50		Discussion of Isotopes in Environmental Forensics
09:50 – 10:20		Coffee Break
Oral Session on Explosives		
10:20 – 10:40	43	<i>Application of Isotope Ratio Mass Spectrometry (IRMS) for the Forensic Analysis of Explosives</i> <u>Timothy Simpson</u> , Sarah Benson
10:40 – 11:00	44	<i>Forensic Investigation of Isotopic Linkages between Hexamine and the Peroxide Explosive HMTD</i> <u>Claire Lock</u> , Martin van Breukelen, Mattijs Koeberg
11:00 – 11:20	45	<i>Peroxide Bomb - Don't Think You're Foolin' Me</i> <u>Janet E. Barnette</u> , Mike J. Lott, John Howa, James R. Ehleringer
11:20 – 11:40	46	<i>Multi-Collector ICP-MS: A New Direction for Isotopically Characterising Explosives?</i> <u>David Widory</u> , Romain Millot
11:40 – 12:00		Discussion of Explosives
12:00 – 12:15	47	<i>Identification of Fake Archeological Artifacts Using Stable Isotope Methods: Authenticity Examination of the Inscription on the Ossuary Attributed to James, Brother of Jesus Case Study</i> <u>Avner Ayalon</u> , Miryam Bar-Matthews, Yuval Goren
12:15 – 12:20		Questions
12:20 – 12:35	48	<i>Microns-Scale Determination of Pb Isotopic Compositions for Forensic Analysis</i> <u>Jeremy Bellucci</u> , William F. McDonough, Richard Ash, Javier Iñanez
12:35 – 12:40		Questions
12:40 – 13:40		Lunch
Oral Session on Strategic Issues / Isotope Data in Legal Systems Chaired by Sean Doyle		
13:40 – 14:00	49	<i>Two New Human Hair Reference Materials for Stable Isotopes of H, C, N, O, and S</i> <u>Tyler B. Coplen</u> , Haiping Qi, James A. Jordan, Glenda Singleton
14:00 – 14:20	50	<i>Reporting of Forensic IRMS/ICPMS Results in The Netherlands</i> <u>Gerard van der Peijl</u> , Martin van Breukelen, Andrew van Es, Wim Wiarda
14:20 – 14:40	51	<i>Confirming Testosterone Abuse in Athletes using GC-C-IRMS: A Quality Assurance Perspective</i> <u>Adam Cawley</u> , Lance Brooker, Vanessa Agon, Ray Kazlauskas
14:40 – 15:00	52	<i>Bad Science: The Floyd Landis Case</i> <u>Robert D. Blackledge</u>
15:00 – 15:20	53	<i>Lessons from the Human Provenance Project</i> <u>Will O'Reilly</u> , Andy Baker
15:20 – 15:50		Tea Break
15:50 – 16:10	54	<i>The Changing Forensic Landscape and its Impact on Isotope Forensics</i> <u>Seán Doyle</u> , Niamh Nic Daéid
16:10 – 16:50		Discussion on Strategic Issues / Isotope Data in Legal Systems
16:50 – 17:00		<i>Update on ILCs</i> <u>Jim Carter</u>
Conference Banquet		
19:00 – 21:00		

Wednesday April 14, 2010

Time	Page #	Morning session chaired by Rebeca Santamaria-Fernandez
08:00 – 08:30		Free
Oral Session on Radiogenic and Heavy Stable Isotopes		
08:30 – 08:50	55	<i>Combining Light Isotope, Trace Element and Isotope of Metals in Environmental and Forensic Investigations</i> G. Stewart Walker
08:50 – 09:10	56	<i>The Fabrication of Uranium Isotope Standards for Laser Ablation ICPMS</i> Madara Jayatilake, <u>Richard D. Ash</u> , William F. McDonough
09:10 – 09:30	57	<i>Analyses of U Isotopes in Glasses, Mud, Dust and Filter Papers</i> Brian Mumaw, Ricardo Arevalo Jr., <u>William F. McDonough</u> , Richard D. Ash
09:30 – 09:50	58	<i>Precise Determination of ⁶³Cu/⁶⁵Cu, ⁶⁶Zn/⁶⁸Zn and ⁸⁷Sr/⁸⁸Sr in Solid Materials via in situ LA-ICP-MS</i> <u>Ricardo Arevalo Jr.</u> , William F. McDonough, Richard D. Ash, Jeremy Bellucci
9:50 – 10:10		Discussion of Radiogenic and Heavy Stable Isotopes
10:10 – 10:40		Coffee Break
10:10 – 12:20	7	Posters - See next page
12:20 – 13:20		Lunch
Oral Session on Controlled Materials – Drugs, Microbes and Plants Chaired by Jim Carter		
13:20 – 13:40	79	<i>Stable Isotope Ratios of Marijuana from Brazil and Paraguay: Carbon and Nitrogen as Guides for Growth Conditions. Strontium Isotopes as References for Possible Geographic Origin</i> Jorge Jardim Zacca, <u>Nelson Fava</u> , Roberto Ventura Santos, Luis Henrique Mancini, Murilo Quintans Ribeiro Bastos, Wesley Luis Pacheco, Bárbara Alcântara Ferreira Lima
13:40 – 14:00	80	<i>Integrating Stable Isotope Ratio and Other Mass Spectral Data for Microbial Forensics</i> <u>Helen Kreuzer</u> , Kristin Jarman, Craig McKinstry, Bobbie-Jo Webb-Robertson, and Karen Wahl
14:00 – 14:20	81	<i>Comparison of P2P Seizures using GC/MS Impurity Profiling and IRMS</i> <u>Martin van Breukelen</u> , Marnix Hoitink, Anneke Poortman
14:20 – 14:40	82	<i>Comprehensive Two Dimensional Gas Chromatography-Combustion IRMS (GCxGCC-IRMS). Instrument Principles for Rapid Isotope Analysis</i> <u>J. Thomas Brenna</u> , Herbert J. Tobias, Ying Zhang
14:40 – 15:00	83	<i>Stable Isotope Ratio Methodologies for Illicit Drug Intelligence Programs</i> Michael Collins, <u>Adam Cawley</u> , Helen Salouros, Aaron Heagney, Hilton Swan, Sasha Vujic
15:00 – 15:20		Discussion on Controlled Materials – Drugs, Microbes and Plants
15:20 – 15:30		Closing Remarks
15:30 – 16:00		Tea Break
15:45– 17:00		FIRMS Steering Group Meeting

Page #	Poster Themes	Title and Authors
59	X,I	<i>An Off-Line Method to Eliminate Nitrogen-Oxide Interference for ¹⁸O Analysis of Nitro-Organics</i> Glendon B. Hunsinger, A. Hope Jahren, William M. Hagopian
60	X	<i>The Relationship Between HMX and RDX Stable Isotopes Can Reveal Production and Subsequent Mixing Information in Explosive Seizures</i> John D. Howa, Michael J. Lott, James R. Ehleringer
61	X	<i>Forensic Utility of Isotope Ratio Analysis of the Explosive Urea Nitrate and its Precursors</i> Roman Aranda IV, Libby A. Stern, Marianne E. Dietz, Meghan C. McCormick, Jason A. Barrow, Robert F. Mothershead II
62	D,G	<i>Geographical Region-of-Origin and Cultivation Assignments of Marijuana Seizures in Major Cities Across the United States</i> James R. Ehleringer, Jason West, Janet Hurley
63	D,T	<i>High Accuracy Carbon, Magnesium & Sulfur Isotope Ratio Measurements Combined with Trace Metal Profiling for the Detection of Counterfeit Tablets of an Antiviral Drug for HIV/AIDS Treatment</i> Rebeca Santamaria-Fernandez, Jean-Claude Wolff, Ruth Hearn
64	D	<i>In situ Laser Ablation ICP MS Trace Element and Isotope Fingerprinting of Powdered Pharmaceuticals</i> Richard D. Ash, William F. McDonough
65	E	<i>Nitrogen Stable Isotope of Ammonia and Nitrate Ion of Atmospheric Particulate Matter</i> Takahiro Kurahashi, Hiroto Kawashima
66	E	<i>Measurement of Stable Hydrogen Isotope Ratio of Atmospheric VOCs</i> Nami Kikuchi, Hiroto Kawashima
67	I,X	<i>Reduction of Sample Size for Oxygen Isotope Analysis in Organic Compounds</i> William M. Hagopian, A. Hope Jahren
68	I	<i>LIAISON: World's First Fully-Automated Universal Interface for Bulk ¹³C High-Precision Isotope Analysis using Cavity Ring-Down Spectroscopy</i> Nabil Saad, Bruce Richman
69	I	<i>Continuous Flow – Cavity Ring Down Spectroscopy: A Powerful Tool for Food Origin Analysis and Adulteration Detection</i> Nabil Saad, Gregor Hsiao
70	I	<i>Micro-sampling of Organic and Biological Solid Samples for Stable Isotope Measurements Using Laser Ablation Coupled to a Capillary Reactor</i> M. Elizabeth Alexander, Matt Newburn, James J. Moran, James F. Kelly, Robert Sams, Helen W. Kreuzer
71	I	<i>New Product Developments at Isoprime Ltd.</i> Robin Sutka and Scott Hughes
72	I	<i>High Precision Isotopic Reference Material Program</i> Jacqueline L. Mann, Robert D. Vocke, Jr., Therese Butler
73	T	<i>Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) to Provide Forensic Isotopic Evidence: An Overview</i> Rebeca Santamaria-Fernandez
74	T	<i>A Laser Desorption Resonance Ionization Mass Spectrometer for Geolocation and Source Attribution</i> F. Scott Anderson, Keith Nowicki
75	I,T,G	<i>Stable Isotope and Ultratrace Metal Impurity Analysis for Forensic Characterization of Cyanides</i> Helen Kreuzer, April Carman, James Moran, Orville T. Farmer, Juske Horita, Bruce Tompkins
76	T	<i>Casework IRMS/ICPMS Examples in The Netherlands</i> Gerard van der Peijl, Martin van Breukelen, Andrew van Es, Wim Wiarda
77	M	<i>Discrimination of Candle Wax Materials by Gas Chromatography (GC) and Isotope Ratio Mass Spectrometry (IRMS)</i> Gerard van der Peijl, Martin van Breukelen, Jeanet Hendrikse, Judith Dogger, Marianne Schrader, Marco van Grol
78	T	<i>Compound-Specific IRMS of n-Alkanes for Fingerprinting Stolen Diesel</i> S. Muhammad, A. Hayman, R. Van Hale, Russell Frew

G = Geographic Attribution, H = Human Tissues, M = Manufactured Materials, E = Environmental Forensics, T = Trace Elements and Heavy Isotopes, X = Explosives, F = Food and Drink, D = Narcotics and Pharmaceuticals, I = Technical Innovations

**Abstracts
(By Session Topic)**

MONDAY, APRIL 12, 2010	9
Plenary Talk by James Ehleringer	9
Oral Session on Geographic Attribution Related to Humans	10
Poster Session: 13:20 – 15:30	16
Oral Session on Provenance Determination Using Isotope Methodologies.....	35
TUESDAY, APRIL 13, 2010	40
Oral Session on Isotopes in Environmental Forensics	40
Plenary Talk by R. Paul Philp	40
Oral Session on Explosives.....	43
Oral Session on Strategic Issues / Isotope Data in Legal Systems	49
WEDNESDAY, APRIL 14, 2010	55
Oral Session on Radiogenic and Heavy Stable Isotopes.....	55
Poster Session: 9:50 – 12:00	59
Oral Session on Controlled Materials – Drugs, Microbes and Plants.....	79

Monday, April 12, 2010

PLENARY TALK

**CSI or Academic Iso-Gap?
Forensic Potential of Isotopes, Investigative Needs, and Judicial Requirements**

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^bIsoForensics Inc., 423 Wakara Way, Suite 205, Salt Lake City, UT 84108, USA

Isotope analyses of both light and heavy elements are the basis of FIRMS and these measurements have tremendous potential for contributing to law enforcement investigations, regulatory activities, and the judicial process. Isotope forensics is a new scientific application that complements other analytical measurements and should not be "over promised" at this stage of its development. Currently isotope analyses can be most useful to the judicial process in situations involving multiple sample comparisons, where one or more possibilities can be eliminated because the isotope ratio of one sample is not consistent with another. Isotope analyses should stand up well to Bayesian interpretation methods now commonly applied to evidence in courts. Isotopes offer a potential beyond other analytical measurements – that of geo-based (i.e., isoscapes) or production-based (i.e., manufacturing) interpretations. Predictive aspects of isotope analyses are emerging that hold potential for many areas on law enforcement and regulatory interests from food safety and animal origins through murder investigations. Several aspects will be discussed in this presentation as well as factors constrain interpretations of isotope abundances.

Despite the potential of isotopes as a tool for law enforcement and regulatory applications, several critical issues that must be addressed now including the needs for:

- a. Appropriate reference materials so that results can be compared among analytical laboratories;
- b. More published literature appropriate to Daubert challenges;
- c. Databases against which to compare isotope values in specimens for provenancing studies at the regional to international scales.

Oral Session on Geographic Attribution Related to Humans

Tracking Geographical Movements: Laser Ablation Multi-Collector ICP-MS to Study Longitudinal Stable Isotopic Variations in Single Human Hair Strands

Rebeca Santamaria-Fernandez^a, Justo Giner Martinez-Sierra^b, Ruth Hearn^a

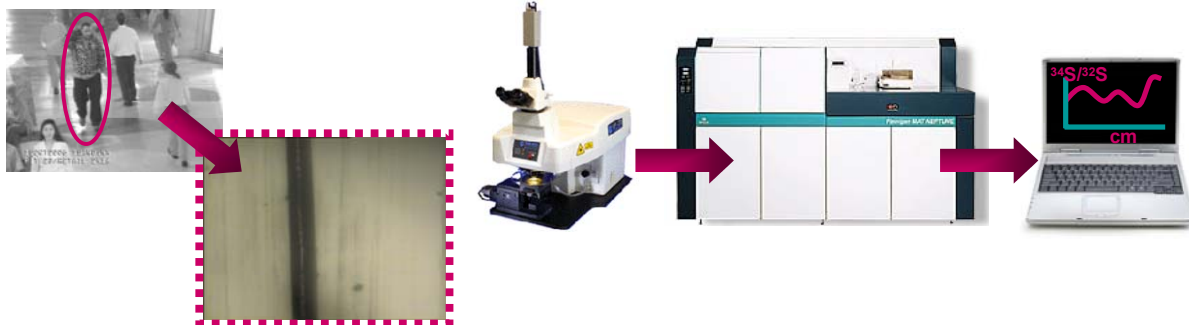
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The measurement of stable isotopic variations in human tissues has the potential to provide information regarding the geographical origin and lifestyle of individuals.

A new method for the measurement of longitudinal variations of sulfur isotope amount ratios in single hair strands using a laser ablation system coupled to a multicollector inductively coupled mass spectrometer (LA-MC-ICP-MS) has been developed. A horse hair sample, previously characterised for carbon and nitrogen isotope ratios in an inter-laboratory study, has been characterised for S isotope ratios by LA-MC-ICP-MS to be used as an in-house standard for the bracketing of human hair strands. $^{34}\text{S}/^{32}\text{S}$ isotope amount ratios have been measured and corrected for instrumental mass bias adopting the external standardization approach using NIST RM8553 and full uncertainty budgets have been calculated using the Kragten approach.

Proof of concept is shown with human scalp hair strands from eight individuals, seven UK residents and one traveller (long periods of time abroad). The results confirm the potential of the measurement of sulfur isotopic variations in hair as an indicator of geographical origin and recent movements. The study is ongoing and further samples (2-4cm hair strands) have now been collected from >100 volunteers and update of progress will be reported. The approach has vast potential to be combined with DNA fingerprinting and IRMS to become a powerful tool for human provenance that will be of immeasurable value to security, police & forensic services.



The Application of Trace Element and Multi-Isotope Analysis of Hair Samples for Detecting Human Travel

Sabine Schneiders^a, Thomas Holdermann^a, Nicole Scheid^a, Stefan Becker^a

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In 2008 the BKA started a project dealing with the investigation of human travel by collecting hair and water samples of liaison officers, going abroad for approximately 4 years. At the moment 67 BKA liaison officers are located in 40 cities in 37 countries. Their mission is to enhance the bilateral international cooperation between law enforcement agencies.

The collection of hair took place at different times. The first samples were collected before departure in Germany; the second samples shortly after the arrival in the foreign country and the last samples were collected 6 month or a year after the arrival.

Besides that hair samples of employees of the BKA were collected who travelled seldom or only for short-time periods to build a sort of reference population. Additionally we took the chance to ask for volunteers at conferences to provide hair and water samples.

All of them had to fill in a questionnaire concerning their nutritional habits, personal height and weight and usual hair treatment.

The study is planned to be finished in the end of 2012 to allow flexible changes of the project design according to the first results.

The isotope ratios $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ of the hair samples were determined using an elemental analyser (EA) - IRMS system, the $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of both hair and water samples were determined using a high temperature conversion elemental analyser (TC/EA) -IRMS system. The isotope ratios are expressed in delta notation relative to primary international standards (e.g. V-PDB, Vienna Pee Dee Belemnite).

The presentation shows preliminary results of the water samples and chronological segmental hair analyses.

The Canadian Human Hair Provenance Project – Questions and (Some) Answers

Michelle Chartrand^a, Gilles St-Jean^{a*}, Claude Dalpé^b, James Wojtyk^c

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^bForensic Science and Identification Services, Materials Profiling, Royal Canadian Mounted Police, Ottawa, ON, Canada

^cScientific Analysis and Assessments, Public Safety Canada, Ottawa, ON, Canada

In the context of isotopic analysis, the Canadian human hair provenance project has two main objectives: to build a Canadian database of isotopes and trace elements from water and hair samples, and to assess the extent of temporal effects on these samples.

To address objective 1, a cross-Canada sampling campaign has been started to collect hair and water samples. In the past two years, our group has traveled around eastern Canada (all eastern provinces including Ontario). Collected water samples are divided into three groups – groundwater, surface water and bottled water. The GIS maps show the isotopic distribution of the water sources varies with latitude. Hair is analyzed for carbon (C), nitrogen (N), hydrogen (H) and oxygen (O) isotopes. The C and N results show that in general, Canadians eat a typical diet showing a small isotopic variation. However, some cases will be presented which may explain why some people have C and N values outlying the collected sample average. In terms of H isotopes in human hair, GIS maps illustrate the distribution of this isotope in the eastern provinces of Canada. In some cases, a large variation in H was observed for the same locality. However, based on hair collected from across Canada from previous years, H isotopes in hair show a correlation to water collected from the same locality (Figure 1).

To address objective two, hair and water samples were collected at 4 month intervals from several volunteers residing in Sudbury ON, Ottawa ON and Montreal QC (to represent different seasons). For all isotopes measured, there was little variation observed over the course of the year in any individual. On-going sampling efforts will address if any variation may occur on a yearly basis.

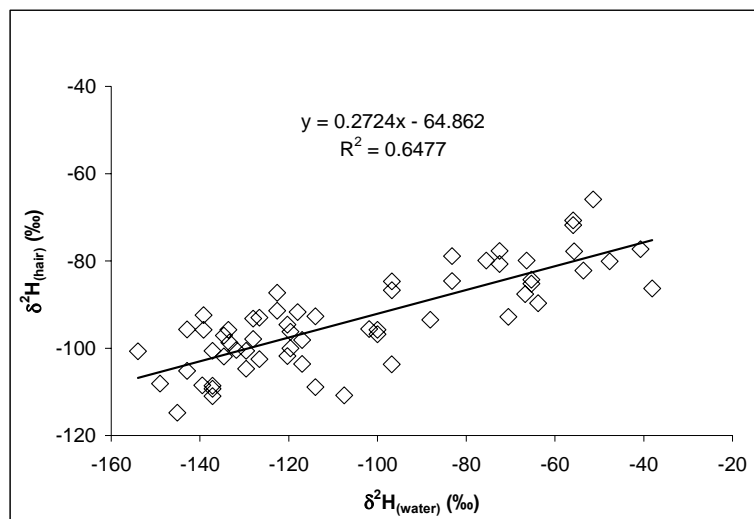


Figure 1. $\delta^2\text{H}$ of hair vs. $\delta^2\text{H}$ of water sampled from the same location across Canada.

An Integrated and Comprehensive Model of ^2H and ^{18}O Isotope Composition in Primates

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The isotopic composition of drinking water and diet influence the isotopic composition of body water. In turn, body water influences the isotopic composition of organic matter in tissues, such as hair and teeth, which are used to reconstruct movement patterns of animals and humans. While predictive models of both the isotopic composition of body water and the isotopic composition of hair exist, they are independent and have yet to be coupled. Here we present an integrated model linking the isotopic composition of body water to that of hair. We use observations from two species of non-human primates to test the coupled model. Hair and plasma samples were obtained from *Macaca fascicularis* and *Chlorocebus aethiops sabaues* via the Wake Forest University Primate Center (WFUPC). Animals were maintained on three different, yet isocaloric, diets: a soy-protein based diet, a casein-protein based diet, and a standard chow diet. We analyzed the ^2H and ^{18}O isotope ratios of hair, water cryogenically extracted from plasma, all diet types, and drinking water. Measured isotope ratio values were then used to test the comprehensive and integrated model of ^2H and ^{18}O isotope ratios in these primates.

Characterizing Temporal Variations in the Isotopic Composition of Human Drinking Water

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Geographic location of origin and the isotopic “fingerprints” associated with these locations provide a means of distinguishing between two pieces of forensic evidence that have identical chemical compositions (e.g., hair samples found at a crime scene and on the suspect’s body). Although the application of H and O isotopic ratios ($\delta^2\text{H}$, $\delta^{18}\text{O}$) in forensic investigations is relatively new, supporting data documenting the regional-scale correlation between human tissues and tap water have existed for several years. One key to forensic applications of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in environmental and biological fields is accurate prediction of the spatial and temporal distributions of H and O isotopes in human drinking water. Although more is known about the spatial variations of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in tap water, few studies have addressed the question of how temporal variations in the isotopic composition of tap water may influence or smear predictability of “iso-regions” (i.e., isotopically-determined geo-locations of human and/or biological materials).

To address this question, a 2-year survey was conducted of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in tap water from across the contiguous U.S. and Canada. Results indicate that temporal variations in the isotopic composition of tap water were related to water resource type (Figure 1a), with low variability in groundwater, low to high variability in surface water, and high variability in “managed water” (seasonal mixtures of groundwater and surface water or imported water). Surface water sites having low temporal variability ($\sim 4\%$ for $\delta^2\text{H}$, approximately two times the measurement precision of $\delta^2\text{H}$) were consistent with groundwater-dominated streams and large reservoirs with turnover times on the order of tens of years or more. In contrast, surface water sites having high temporal variability were strongly correlated with the isotope seasonality in precipitation, with approximately 10% of the isotopic variation in precipitation preserved in tap water (Figure 1a, inset). Further, 4 of the 7 surface water sites located in the Great Lakes Region (USA) exhibited temporal variations that were consistent with a sinusoidal model (e.g., Figure 1b). The isotopic composition of managed water was consistently highly seasonal (Figure 1a), due mainly to seasonal “switching” between surface water and groundwater. Overall, the results suggest that where tap water is supplied by (1) managed water or (2) small streams in highly seasonal climates, the predicted iso-region may be, in relative sense, more uncertain due to temporal variability. Characterizing and quantifying these patterns of temporal variability in the isotopic composition of tap water will support ongoing efforts to develop predictive models of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in tap water using globally-available GIS data.

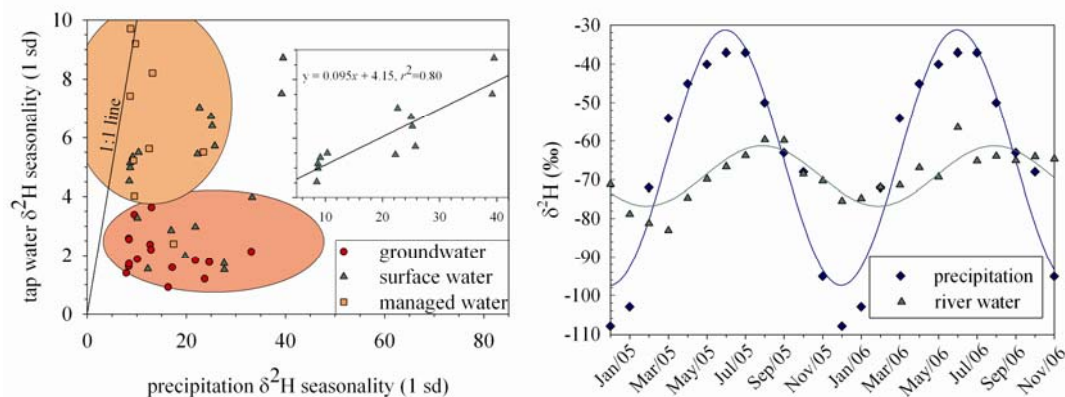


Figure 1. (a) Seasonality of $\delta^2\text{H}$ measured in tap water versus that of $\delta^2\text{H}$ in precipitation; surface water sites with significant seasonality ($>4\%$) in inset. (b) Monthly measurements of $\delta^2\text{H}$ in a small stream in Ithaca, New York and in local precipitation.

Spatial and Seasonal Variability of Stable Isotopic Compositions ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of Tap Waters Throughout the United States

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The stable isotopic compositions ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of environmental waters vary spatially and seasonally due to physical processes. These stable isotopic compositions will be reflected in the body tissues of biological organisms, specifically humans, which ingest such waters. Consequently, the use of isotopic compositions of drinking waters as tracers for determining the history of an individual's location, or at least ruling out unlikely locations, has been of increasing interest to archaeological and forensic analyses.

To determine $\delta^2\text{H}$ and $\delta^{18}\text{O}$ variations of drinking water over a national scale, we obtained tap water samples from 349 sites throughout the United States, including Puerto Rico, the Virgin Islands, and Guam. All sites were sampled concurrently, on August 15, 2007 and February 20, 2008, to observe seasonal differences. Large variability was observed both spatially at one time and at one location between seasons. The values of $\delta^2\text{H}$ over the full national data set ranged from -162‰ to $+2\text{‰}$ in August, and from -164‰ to $+2.5\text{‰}$ in February. The averaged $\delta^2\text{H}$ for both summer and winter collections over the full national data set are identical within analytical uncertainty, at -61.3‰ and -61.4‰ , respectively, but with large standard deviations of 37.2‰ and 36.9‰ , respectively. Although the at-site $\delta^2\text{H}$ seasonal differences had an average value close to zero (-0.3‰), both the standard deviation (5.3‰) and the range (between $+29.5\text{‰}$ and -26.7‰) were large. The $\delta^{18}\text{O}$ measurements were similarly behaved. Thus, for purposes of geolocation, differences in isotopic composition within biological materials can reflect the presence of either seasonal changes in tap waters at one location or tap waters from different locations. Even within a relatively small spatial area, tap water samples exhibited substantially different isotopic compositions. For example, in the hydrologic subregion around San Francisco Bay, California, a region of approximately 4,500 square miles with a population of over five million, people had access to drinking water with $\delta^2\text{H}$ values ranging from -28‰ to -99.3‰ in August, and from -27.9‰ to -75.4‰ in February.

Such possible substantial variations in isotopic compositions as noted above (at a single site over time or at neighboring sites at the same time) illustrate the need for specific at-site isotopic measurements, and not just statistical interpolations, for purposes of forensic geolocation. It is also noted that spatial patterns of isotopic compositions in U.S. human water supplies may be anticipated by those observed for U.S. river waters, which are the source of water supplies for most of the population.

Poster Session: 13:20 – 15:30

Isotopic Analysis of Modern Human Hair for Geosourcing

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Isotope Ratio Mass Spectrometry (IRMS) is a widely used technique for analysis of hair in forensic science. This technique, used initially for other scientific purposes, is increasingly used for crime scene investigations and other crime related purposes, in order to either associate a suspect to a victim, or an individual to a crime scene or to identify potential geographical localities to these individuals. However, if this tool is to be useful we need to evaluate whether the hair associated with individuals is isotopically consistent with local/regional environmental factors, and to what extent these vary. This is possible relatively easily due to the fact that approximately 100 scalp hairs are shed by an individual each day and most of this hair can be easily collected (or transferred during contact between two individuals). Furthermore, hair tissue is metabolically inactive, and as such hair growing at a steady rate of approximately 10 mm per month enables some linear sectioning to take place. Hair can therefore, be regarded as an isotopic archive recording isotopic signals relating to dietary and location changes.

Isotopic analysis using a stable isotope ratio mass spectrometer for carbon (C), oxygen (O), hydrogen (H), nitrogen (N) and sulphur (S) are most widely analysed and helpful in such studies.

The aim of this study is to determine the potential forensic application of isotopic hair analysis and to set up a database of the hair keratin isotopic compositions. For this study, appropriate sampling and cleaning procedures were set up in order to obtain high precision isotopic data. Different sampling techniques such as cutting, pulling or collecting shed hair were compared together with different cleaning pre-treatment techniques such as Hexane, chloroform/methanol and acetone washing.

In order to study the effect of the diet and the water intake (and thus the location) C, N, O and H isotopic composition of keratin is being carried on between 100 and 200 volunteers from the Reading area of the U.K. The survey includes at least 30 people from each of the 3 diet groups (omnivore, vegetarian and vegan), of equal sex. This is to test the local variability in diet and geo location as derived from O and H. In comparison to the local study a series of individuals whom were not resident from the Reading area and who have been living outside the U.K have been tested to compare the local signal.

This study confirms the effectiveness of using stable isotopes to interpret diet and location from analysis of keratin of modern humans.

Spatial Distribution of Sulfur Isotope Ratios in Human Hair Across the USA

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The use of stable isotope analysis to investigate the region-of-origin of food, or animal and human tissues is a rapidly growing field. Particularly within the USA, stable hydrogen and oxygen isotope analyses have been used because their ratios in drinking water vary across the landscape in a predictable pattern. Stable isotope analyses of carbon, nitrogen and sulfur also hold potential as geo-locating tools. These elements are incorporated from the diet and thus provide a record of dietary inputs that may also represent geo-based patterns. Here we present data on carbon ($\delta^{13}\text{C}$), nitrogen ($\delta^{15}\text{N}$) and sulfur ($\delta^{34}\text{S}$) isotope ratios of human hair collected across the USA. We detected predictable regional differences in hair $\delta^{34}\text{S}$ across the USA, with the lowest values in the northern Great Plains and increasing values towards the east, west and south. Low $\delta^{34}\text{S}$ values were also detected in central California. No spatial variation was found for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in human hair. Using Geographic Information System (GIS) we created prediction maps by interpolating the average $\delta^{34}\text{S}$ values among the sampled cities. Because no *a priori* information on the mechanisms that influence variation of $\delta^{34}\text{S}$ values across the landscape was known, we investigated consequences of various interpolation algorithms. The accuracy of the prediction maps were tested by correlating the predicted $\delta^{34}\text{S}$ values for hair samples not included in the initial generation of the maps. Here we show that stable sulfur isotope analysis may represent a new statistically significant tool to investigate the region-of-origin of human remains.

Distinguishing Americans and Europeans on the Basis of Carbon and Sulfur Isotope Ratios of Hair

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Carbon and sulfur isotope ratios in human tissues reflect the original dietary sources of those molecules. If differences in food industries and dietary habits exist between regions, these would potentially be translated into differences in the isotopic composition of human tissues, allowing for discrimination of region-of-origin. We tested this hypothesis by analyzing human hair collected in barber shops and hair salons across the USA and in fifteen European countries. Samples were analyzed for stable carbon ($\delta^{13}\text{C}$) and sulfur ($\delta^{34}\text{S}$) isotope ratios. We detected significant differences in $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ values between samples collected in the USA and those collected in Europe. That is, little overlap in the isotope ratios between Americans and Europeans was observed despite working with large sample sizes collected from many different European countries. The isotopic spacing detected in this study provides the basis for geographic distinction of Americans and Europeans on the basis of stable carbon and sulfur isotope analysis of human tissues.

“I Know Where You Spent Last Summer”: Isotopes in Hair and Teeth to Trace the Regions-of-Origin of Unidentified Murder Victims

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We developed and tested two models to predict the geographic regions-of-origin of humans based on the stable isotope composition of their scalp hair and teeth. The “hair” model incorporated exchangeable and non-exchangeable hydrogen and oxygen atoms in amino acids to predict the hydrogen and oxygen isotope ratio values of scalp hair. We evaluated “hair” model predictions with stable isotope analyses of human hair from 65 cities across the USA. This model, which predicts hair isotopic composition as a function of drinking water and dietary carbohydrate and protein isotope ratios, explained more than 85% of the observed variation and reproduced the observed slopes relating the isotopic composition of hair samples to that of local drinking water. The “tooth” model was simpler and was based on the relationship between tap water at a location and the oxygen isotope ratio of carbonate in five authentic tooth enamel samples; here a linear model also explained 85% of the observed variations. We constructed isoscape maps of the expected average H and O isotope ratios in human hair and O isotopes in tooth enamel carbonate across the contiguous 48 states of the USA. We then applied these models to two cases where the identity of the murder victim was unknown. In case 1, the unidentified victim was referred to as “Saltair Sally”. The hair isotope results indicated that over the last two years of her life she moved between three isotopically distinct regions, one of which was consistent with the region where her remains were recovered. Tooth analyses indicated that she likely grew up in the same region where her remains were found. In the second murder case, which has now been resolved, hair isotopes faithfully recorded the lack of movement of the individual prior to death and accurately predicted the isotopic region consistent with where Ms. Mary Alice Willey had lived over the last year of her life (San Francisco). Tooth isotope analyses indicated that she had grown up in a different region. The region predicted was consistent with the Los Angeles area where the individual is now known to have grown up.

CO₂ in Breath as a Short-term Record of Geographic Movement

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Stable isotope ratios in biological materials can yield information about movement and migratory patterns in animals, including humans. The isotopic composition of tissues such as bone, hair and teeth offer a long-term record of that movement, while analyses of breath CO₂ potentially provide a more short-term record of movement. In order to correctly interpret movement patterns relayed by breath CO₂, it is essential to know the rapid turnover rate of the ¹⁸O isotope ratio of CO₂ in breath. To simulate geographic movement across a gradient in the isotope ratios of water, we raised rats on three isotopically distinct waters and then, upon adulthood, performed a water switch. The waters used were depleted ¹⁸O, depleted ²H (DD); depleted ¹⁸O, enriched ²H (DE); and enriched ¹⁸O, enriched ²H (EE). The water switch covered both the heavy-to-light and light-to-heavy isotope transitions. We measured the isotopic composition of CO₂ in breath for four weeks following the water switch. The Cerling et al. reaction progress method adequately describes the turnover of CO₂ in breath. Based on these observations, the isotope ratio signal of the previous environment can be detected for several days if the differences in the isotope ratios of water in the two environments are sufficiently different.

A National Survey of Human Body Water Variation

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The hydrogen and oxygen isotopic composition of body water influences the isotopic composition of tissues commonly used to investigate the movement patterns of humans (i.e., hair). We developed a body water model that incorporates the isotope composition of drinking water, food, and O₂ as well as variables such as diet composition and energy expenditure to estimate the δ -values of human body water. While this model reliably estimated δ -values of body water when compared with published values, validation of the model requires considerations of normal variation within a population that might be associated with differences in diet, level of activity, and drinking habits. We measured the actual variations in body water among 10 individuals over a 5-day period in each of 8 different cities across the USA. In addition to body water measurements, participants completed a food and activity log so that the role of dietary and activity differences could be incorporated. Measured hydrogen and oxygen stable isotope ratios were compared with predicted values to account for differences in diet and energy expenditure among participants.

Geographical Region-of-Origin Assignment of American Beef Using Stable Isotope Analysis

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Animal diseases like bovine spongiform encephalopathy (BSE) and hoof-and-mouth (HMD) have highlighted the pressing need for food traceability in the modern food market. Stable isotope analysis is a promising analytical technique that may provide region-of-origin information independent of food labels since the stable isotope ratios of hydrogen and oxygen in water vary across landscapes in predictable patterns. Animals – like beef cattle – record the isotopic composition of local environmental water in their tissues and the analysis of beef meat could therefore be used to assign a geographical origin to the animal.

We collected hamburger (beef) patties from fast food restaurants in Salt Lake City, UT. Restaurants were classified as either local – those chains found only in Utah – or national. We also collected samples of beef from family-run ranches across the USA to calculate an equation for the relationship between beef $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values and local water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values. This equation was used to predict the stable isotope ratios of cow drinking water from the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of hamburgers purchased in Utah restaurants.

We found the mean hydrogen and oxygen stable isotope ratios of hamburgers from local restaurants were significantly different from those purchased in national fast food restaurants. Using the predicted cow drinking water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, we were able to calculate the average size of the food footprint (in beef transport miles) for patrons of local and national fast food restaurants in Utah. From this statewide survey, we have demonstrated the promise and potential of food tracking using stable isotope analysis.

Source of Strontium (Food vs. Water) in Alligator Bioapatite

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Strontium isotope ratios of vertebrate biological tissues potentially provide valuable information about past geographic location of the animal being analyzed. However, there is controversy in the scientific literature about the source (food vs. drinking water) of strontium in biological material. In many cases the strontium isotope ratio of an animal's drinking water may differ from that of the animal's food source. Thus, in order to locate the geographic origin of an animal, it is important to know if it is appropriate to match the animal's strontium isotope ratio to that of a regional water supply or a regional food supply.

Here we test the source of strontium in tooth bioapatite for a coastal population of American alligators in Louisiana. Alligators are obligate freshwater drinkers but often feed from estuarine or marine food chains when available. Because alligators must drink freshwater but can incorporate marine food, coastal alligator populations act as a natural experiment where strontium isotope ratios of the water source and the food source can vary from each other. We utilize carbon isotope ratios to determine the amount of marine food influence in the alligator's diet. Carbon isotope ratios are compared to strontium isotope ratios to see if increased marine food intake correlates with a strontium isotope ratio similar to that of the ocean. Initial results indicate that the source of strontium for tooth bioapatite is influenced by food source. These findings are relevant for sourcing past geographic locations of reptiles (including exotics) and are likely applicable for sourcing past geographic locations of mammals (including humans).

Multi-Isotope Analysis to Monitor Animal Provenance: A Case Study of Migratory Birds

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Stable (δD - $\delta^{18}O$ and $\delta^{13}C$ - $\delta^{15}N$) and radiogenic (Sr and Pb) isotope analyses are potential tools to track the whereabouts and movement patterns of animals¹⁻². In the case of bird migration the application of isotopes has evolved due to the low recovery rate of traditional tracking methods such as bird ringing and because radio and satellite transmitters are only suitable for large bird species. Stable isotopes are good latitudinal markers due to their relationship with precipitation and animal's diet². However, further research on the application of other isotope systems (e.g. Sr) is needed to evaluate the potential special resolution that can be obtained for migratory species. We report an initial assessment of the viability and accuracy of a non-invasive multi-isotopic approach to trace bird migration by using combined radiogenic Sr and Pb isotope ratios and δD and $\delta^{18}O$ of single bird feathers from juvenile blue/great tits and juvenile pied flycatchers. By measuring multiple isotope ratios in single feathers we obtain information about the isotopic signatures from the environment where feathers grew. We report: 1) a study at a regional European scale to evaluate the potential of combined Sr-Pb isotope ratios, δD - $\delta^{18}O$ isotopes in juvenile blue and great tit feathers, as tracers of bird origin; and 2) a study within the island of Gotland in Sweden to assess the variability of Sr and Pb isotope ratios within a small region and a preliminary look at the relationship between bio-available Sr and Pb in the environment and in juvenile pied flycatcher feathers. The study at a European scale demonstrates that by combining isotope systems it is possible to distinguish between feathers from different countries. However, Sr or Pb isotope ratios alone do not resolve the provenancing of birds in countries with a non-contrasting geology. Results from the regional study in Gotland, establishes that Sr isotope ratio variations in juvenile pied flycatcher feathers from small areas (from 4.1 to 14.8 ha) within the island vary from 0.710148 to 0.716847 and there is no simple relationship between the Sr isotope composition of the bed-rock geology and the feathers. Vegetation and Milli-Q water leachates of soils collected adjacent to the nests are good indicators of the bio-available Sr in the environment and their Sr isotope signatures correlate well with the feather Sr isotope ratios. The multi-isotope method presented here can also be applied to determine the provenance of birds and other animals for forensics investigations, such as animal trafficking. These data also imply that discriminating human provenance maybe possible in many combined geological-hydrological-atmospheric environments.

References:

¹ Hobson, K.A. & Wassenaar, L.I. (2008). Tracking animal migration with stable isotopes. Elsevier, Oxford, UK.

² Bowen, G.J., Wassenaar, L.I. & Hobson, K.A. (2005). Global application of stable hydrogen and oxygen isotopes to wildlife forensics. *Oecologia* **143**(3):337-348.

How the Alcohol and Tobacco Tax and Trade Bureau (TTB) is Using Stable Isotope Ratio Mass Spectrometry to Protect the Public and Collect the Revenue

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The mission of the Alcohol and Tobacco Tax and Trade Bureau (TTB), which is part of the Department of Treasury, is to protect the public and collect the revenue. The Scientific Services Division (SSD) supports that mission with laboratory analyses. Many different analytical techniques are employed by the Beverage Alcohol Laboratory (BAL) to determine the composition and detect adulteration of beverage alcohol products. Saké is unique in that US regulations classify it as a wine and tax it as a malt beverage; however, when any distilled spirits are added to saké, the entire finished product is taxed as a distilled spirit. The malt beverage tax rate is much lower than the distilled spirits tax rate, which could provide a monetary incentive to not claim when distilled spirits are added. Currently, BAL is using a headspace gas chromatography-IRMS method to determine the $^{13}\text{C}/^{12}\text{C}$ of ethanol in sakés, and the result is being used as an indicator of distilled spirit additions to sakés. IRMS is also being used alongside other analyses to differentiate between bourbons and other types of whiskeys, as well as to add evidence to enforcement cases.

Surface Water Isotope Models for Retrospective Geolocation of People and Products

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Hydrogen and oxygen isotope ratios of environmental waters vary widely in space and time, primarily as a result of spatiotemporal variation in the isotopic composition of precipitation. Because much of the H and O in biological tissues, geological materials, and synthetic materials can be assimilated from environmental water during synthesis, measurements of H and O isotope ratios can often be used to relate a material to its geographic origin. Such applications are of demonstrated use in investigations involving product authenticity, identification of unidentified individuals, and reconstruction of origin of evidentiary materials.

Retrospective assignment of evidence to a region of origin requires knowledge of environmental isotope ratios, which in human systems is complicated by the use of water with diverse origins (e.g., groundwater and surface water). These different water resources may have been recharged at different geographic locations or times and may have differing isotopic compositions. As a result, water source selection represents a potential source of variability in geographic water isotope patterns used for the geolocation of forensic materials.

We developed a steady-state GIS-based runoff model and applied it to predict isotope ratios of surface waters across the contiguous USA (Fig. 1). The model incorporated climatological and hydrological variables and was calibrated and validated against a network of river water isotope data. We compared the model predictions with previously published data on tap water isotope ratios from >500 USA cities and towns, and found that in many parts of the country the surface water model significantly improved estimation of tap water isotope ratios relative to previously applied precipitation-based methods. As such, the surface water model represents an important step towards the development of predictive models for water isotope distributions that will enable global application of H and O isotopes to problems of forensic geolocation.

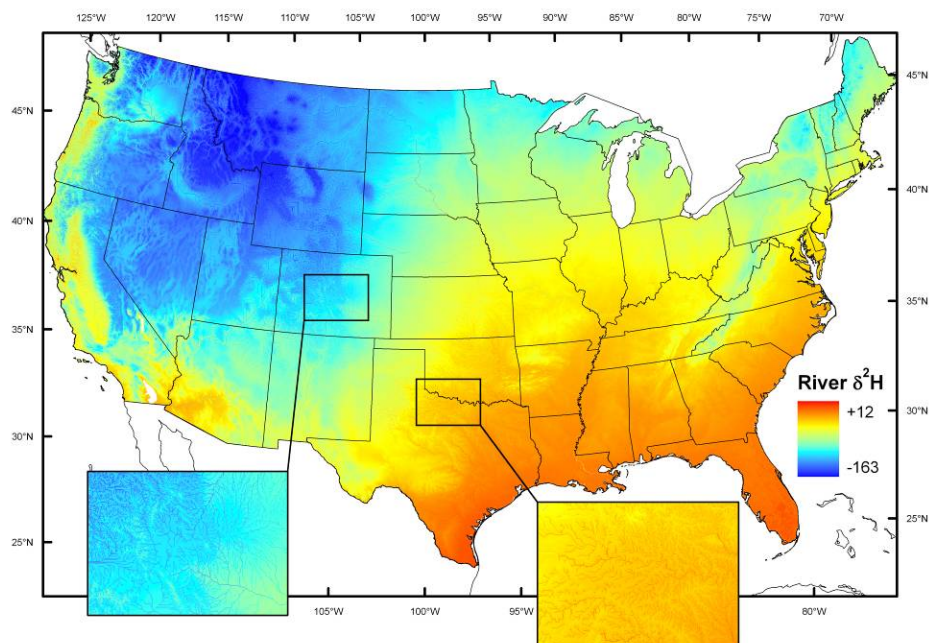


Fig. 1: Model-predicted surface water isotope distribution for the contiguous USA.

The Use of Isotope Ratio Mass Spectrometry in the Forensic Analysis of Australian Papers

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To date, the use of IRMS as a forensic technique has focused primarily on the analysis of drugs, explosives, accelerants and packaging materials. In particular, past studies have primarily considered the discrimination and geographic profiling of organic samples such as drugs and explosives using IRMS.

The present work will build upon this knowledge and will be studying the potential applications of IRMS to forensic paper examination. A recent paper by A. van Es, J. de Koeijer and G. van der Peijl (Science and Justice, 49 (2009), pgs 120-126) demonstrated the potential application of IRMS to papers, with 21 out of 25 European samples being able to be discriminated. In addition to discriminating paper samples, the potential for geographical profiling of paper samples is significant given the difference in origin of materials, water, additives and production processes between paper mills. This would allow forensic practitioners to expand the scope of their work to include the provision of crucial investigative leads.

The main aims of this project will be:

- Development of a method for analysis of carbon, nitrogen, oxygen and hydrogen stable isotopes in papers that are commercially available in Australia.
- Study of the background of Australian papers with respect to the expected homogeneity of papers (within sheets, within reams, within brands, between reams and between brands) to give context to the results obtained during comparison work.
- Examination of the results with respect to the geographical region and originating paper mill over time to collate information with respect to the variations in results due to seasonal or production changes.
- Examination of the effects of issues likely to be encountered during casework e.g. heavily handled papers, printed papers, sun or water damaged papers.

In addition, the collection of background information with respect to Australian papers will allow for the creation of reporting guidelines using Bayesian Statistics.

This poster presentation will present the aim of the project and preliminary results to date.

Biogeochemical Isotopes and Trace Elements as Geo-location Markers for Biosecurity: Can the Technology Determine the Origin of Pests?

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Background. Benefits of accurate point of origin discrimination in biosecurity include achieving appropriate operational responses in exotic pest eradication and post-border incursion campaigns, and identifying risk pathways. Stable isotope and trace element analyses are used to trace the origin of a wide range of materials. In an earlier attempt to determine the origin of important biosecurity pests, analyses of ²H and ¹³C were employed. However, the results were tenuous as the accuracy of the method in biosecurity applications is unknown, as the samples sizes are small and from an unknown and unpredictable place, time and host. Despite the potential of isotope tracing, the application of mass-spectrometry methods in insect geo-location has been limited to date and our understanding in this field is rudimentary.

Research aims. The internationally distributed *Helicoverpa armigera* [Lepidoptera: Noctuidae] is being used to examine the processes fundamental to the location-to-plant-to-insect elemental profile imprinting in phytophagous insects, including the turn over of elements in adult insects, the influence of polyphagy and local variation in precipitation ²H. This improved understanding is being applied to assess the validity of using stable isotope ratios and trace element profiles to differentiate insects of New Zealand natal origin from insects of exotic origin.

Results. The presence of readable stable and radiogenic isotope and trace element signatures in plants and individual insects has been confirmed. An integrated method of TC-IRMS, ICP-MS and MC-ICP-MS analyses of natural abundance ²H, ⁸⁷Sr/⁸⁶Sr, ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb isotope ratios and trace element profiles from single insect specimens has been developed. No single geo-location marker has been found in a comparison of international moths, although the latitudinal cline of $\delta^2\text{H}$ on a continental scale is confirmed. In contrast, a preliminary multi-element, multivariate analysis indicates that geo-location discrimination between the study regions is possible.

Conclusion. The promising preliminary geo-location demonstrated here provides solid leads for further investigation. Any geo-location system developed is likely to be applicable to other disciplines, including forensics, ecological studies and pest management.

Development and Validation of Regional Spatial Prediction “Isoscape” Models for the Provenancing of Unidentified Human Remains

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The development of spatial isotope maps, “Isoscapes”, is an area of increasing interest among the scientific community as highlighted in the recent Journal of Geochemical Exploration Special edition, JGE(2009). Applications of Isoscape models range from the prediction of bird migration pattern to wildlife forensics and forensic human identification. A number of studies have utilized stable or radiogenic isotopes as predictors for the geographical origin of human tissue but at present, other than for hair (Ehleringer et al (2008)), there are no validated prediction models for this purpose.

The need for additional research into forensic human identification has been highlighted over the past decade in the aftermaths of catastrophes such as the terrorist attacks on the World Trade Centre (2001) and Hurricane Katrina (2005) that led to the loss of thousands of lives, many of whom still remain unidentified. We postulate that by combining spatial data from multiple analytical techniques it may be possible to significantly increase the probability of successful provenancing of human remains. In our research we aim to combine existing geological, isotopic and ancestry information to form the foundations of a spatial predictive model and validate the results using specific tissue targets, e.g. bones and teeth.

Attendees to this poster presentation will be introduced to our preliminary development of Isoscape models for the provenancing of human remains in our ongoing case studies in Northern Spain and the Middle East.

Our research in Spain focuses on well documented Spanish Civil War graves in the Pallars Sobira region in northern Catalunya. Although excavation of the Catalan graves of interest is expected in early 2010 we performed an initial reconnaissance survey of the area in 2008 during which 103 surface water samples were collected. Collaboration with local researchers and researchers from the Autonomous University of Barcelona yielded information about the victims in the Catalan graves including origin at birth, migration and location of death. The water samples were analysed for oxygen and strontium isotope ratio and trace element concentrations as proxies for regional differences in the human diet. The data has been interpreted and used to produce spatial chemical maps “Isoscapes” of the area which will be presented in this poster presentation.

Our interest in the Middle East arose as one of the authors collected (KAN) a unique set of teeth from a number of Middle Eastern countries. The results of this sample set provides a unique opportunity to validate regional oxygen and strontium Isoscapes with a human target tissue and provides a basis for further study.

References:

Ehleringer, J.R. et al. (2008) Hydrogen and oxygen isotope ratios in human hair are related to geography. Proc Natl Acad Sci USA 105:2788–2793.

The Use of Strontium Isotope Ratios and Biological Profiling for Forensic Provenancing of Soils

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Locard's principle that "every contact leaves a trace" suggests that everywhere we travel will be recorded by the geological materials retained on our shoes. In this way, the movements of a criminal or an instrument used to commit a crime can also be traced through the analysis of any soil residues found upon on them.

Geological samples, including soils, are frequently analysed by forensic laboratories, usually on a case by case basis, by comparing a suspect sample to an especially collected control. Unlike other materials that can be analysed and compared to a central database, soils as yet cannot be 'matched' to an area unless the area in question has already been identified. There is a need for a method of soil profiling that would allow an unknown sample to be tested and assigned a quantitative likelihood that it originated from a given region. Spatial models can then be created to house data relating to multiple variables and be used to map soils across geographical areas.

Generally, the more variables available with which to compare any two items, the greater the certainty a forensic analyst can have when asserting their similarity and the same applies to geological materials. This poster aims to show results of ongoing research at the Centre for Forensic Provenancing, England, involving the analysis of soil samples collected from across the county of Norfolk. A number of chemical and biological profiling methods have been used to build up a unique signature for soils from different locations. ⁸⁷Sr/⁸⁶Sr ratios have been measured using MC-ICP-MS. The ⁸⁷Sr/⁸⁶Sr ratios are significantly different at each of the sample locations across Norfolk; although there is some variation in the multiple samples collected at each location this variation is shown to be smaller than the regional variation. This variation is related to the underlying geology and soil parent material of the area and gives the possibility of the prediction of the origin of a soil sample based upon the ⁸⁷Sr/⁸⁶Sr ratio.

In order to increase the certainty with which we can predict the origin of a soil sample, vegetation maps have been produced for Norfolk showing all of the plant species recorded in the area since 1975. The poster highlights how the presence, or not, of specific plant species, or even the presence of a suite of species can be used alongside the chemical data to enhance the prediction of the origin of soil samples. Additional biological components highlighted in the poster are plant DNA using MALDI-TOF-MS and pollen analysis; each additional independent dataset allowing for an increasingly unique signature of each soil sample to be built up.

The data has been collated and modelled using geographical information system (GIS) software to map the sample area. This technique allows for the visualisation of geographical relationships. The use of different layers for each dataset allows one to determine the most effective parameters for the discrimination of soils and this multidisciplinary approach allows a greater degree of certainty when identifying the origin of the soil samples.

Strontium Isotopes in European Soils – Spatial Variation and Discrimination Potential for Forensic Applications

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^fwww.trace.eu.org

In many archaeological, forensic and food authentication studies, Sr isotope ratios are applied to relate products/objects to a geological point/area of origin. Often the local Sr isotope composition is simply inferred from the geological age and type of lithology of the bedrock as expressed on maps. The general assumption is that Sr isotope ratios in topsoil will reflect for the most part the Sr isotope ratio of the underlying geology, except in areas where overlying soil was transported in. However it is known that various natural processes, for example deposition of atmospheric dust, could introduce mixing/dilution effects to the Sr budget.

One of the aims of the EU funded project TRACE on food traceability was to establish the extent to which chemical signatures are transferred from bedrock to soil and subsequently incorporated in food. The locations of 26 test sites were chosen to represent different geological and climatic environments, so that it would be possible to measure how the geological signature is transferred through environmental and biological processes. Besides whole soil digests, ammonium nitrate extracts were prepared from the soil samples, as this fraction probably best represents the bio-available fraction of the soil which will be available for incorporation into organic material. Additional sub soil samples were also digested to compare the soil mother material composition with the topsoil extractions.

The relationship between bulk soil samples and ammonium nitrate extracts of the soil samples was investigated, and subsequently both were also compared to predicted values based on underlying geology. Although Sr isotope ratios in bulk soil digests and soil extracts do correlate, the more extreme ratios are observed in the bulk soils and the values from the extracts are more concentrated around the average value of the sites, e.g. show much less variance.

One possible reason for the discrepancy is that external environmental contribution through dust deposition and other factors affecting soil composition are much more significant than previously assumed. This would imply that the contribution from the local bulk bedrock itself to bio-available Sr is probably limited. Another mechanism to explain the observations is selective weathering of minerals with a low Rb/Sr and Sr isotoperation, and thus contributing more to the soil Sr budget, than resistant high Sr ratio, Rb-rich minerals. Addition of fertilizer to agricultural soils could also contribute to altered isotopic ratios. Our main conclusion is that it is not advisable to blindly compare measured Sr isotope ratios in biological materials to expected values based simply on underlying geology as inferred from geological maps. Clearly further detailed study is required to assess all possible influencing factors on each of the test sites and other sites in general.

Isotope Ratio Mass Spectrometry for Tracing the Origin of Forensic Agents

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Analysis of natural stable isotope compositions of biomolecules is a useful tool applicable to environmental sourcing studies, food analysis and forensic research. As a rule, stable isotope ratios in plant materials are dependent on both environmental and metabolic factors operating while the organism is growing. The processes of biological fractionation of isotope have been studied in details [1].

We have developed the procedures and studied the carbon and nitrogen isotope ratios of drugs, explosives and ethanol. For isotope analysis of these objects we used the HP 6890 gas chromatograph and EA 1110 (CE Instruments) elemental analyzer, interfaced on-line to a Delta Plus (Thermo Finnigan) isotope ratio mass spectrometer, respectively method EA-IRMS and GC-C-IRMS.

We have analyzed 25 samples of drugs (cocaine, heroine, morphine). The EA 1110 elemental analyzer was used for combustion of individual samples (0.5-1.5 mg). The concentration of drugs in methanol was 2 mg/ml for carbon isotope analysis, 18-20 mg/ml for nitrogen tests. Individual compounds of this solution were separated by GC and successively converted into the simple gases. The volumes of 1 μ l were injected into GC using CTC A200S autosampler. Each sample was analyzed in triplicate. All drug compounds were identified by HP 5973 mass-selective detector. We have founded the presence of acetylcodeine, monoacetylmorphine and codeine in heroin, lidocaine in cocaine. We had reached a success in detecting some impurities by GC-C-IRMS which were not found, unfortunately, in HP 5973 spectra and, hence, were not identified. Comparing the carbon isotope ratios of heroin samples and the literature data, we came to conclusion that carbon isotope ratios of heroin samples from Colombia, Korea and Afghanistan were different from that estimated for heroin produced in Niger, Thailand, Pakistan, but not being different, however, from heroin originated in Turkey. Presence of common impurities in drugs gives an opportunity to improve reliability of geo-location

Method EA-IRMS was used for analyzing samples of TNT (trinitrotoluene). The results of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ confirmed that IRMS analysis is powerful enough to allow the distinctions of TNT from different producers. It was found that carbon isotope ratios vary in a narrow range from -29.86 ‰ to -29.51 ‰, while nitrogen isotope ratios vary in a wider range from -8.41 ‰ to +4.54 ‰.

Method GC-C-IRMS was used for measuring carbon isotope ratios of ethanol produced from different raw materials. First we have made a database of carbon isotope ratios of ethanol, than we applied this database for the detection of adulteration in spirits of alcohol drinks.

Referenses:

1. Galimov E.M. *The biological fractionation of isotopes*, Academic Press, N-Y, 1985, p.262.

Discrimination of Duct Tapes Using Isotope Ratio Mass Spectrometry

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The Netherlands Forensic Institute uses IRMS in combination with (LA-)ICPMS to investigate potential relations between different materials in forensic casework investigations. In this poster we present a study on the isotope variation of grey duct tape in the Netherlands and will focus mostly on IRMS results.

Duct tape is nowadays commonly used in Dutch households and it is also often found at crime scenes if tape is encountered. If a visually similar tape is retrieved during *e.g.* a search at a suspect's house, a request is almost always made to compare the tape materials.

Duct tape consists of three different layers: 1) a backing film, 2) a network of cotton or polyester fibers and 3) an adhesive layer. If tapes are not discriminated using visual comparison (colour, thickness, width) and FT-IR, other techniques are used such as LA-ICPMS and IRMS to investigate chemical and isotope characteristics.

With LA-ICPMS trace element signals are measured for both the backing film and the adhesive layer. Cotton or polyester fibers of the intermediate network were not further investigated up till now because of the cumbersome and time consuming sample preparation to completely separate the adhesive from the fiber network.

With IRMS $\delta^2\text{H}$ and $\delta^{13}\text{C}$ (and $\delta^{18}\text{O}$ where appropriate) analyses are performed on the backing film and glue layer after the two are separated using petroleum ether. Petroleum ether will mobilize the adhesive so it can be physically separated from the backing and the fiber network, after which the solvent is evaporated under vacuum. Both LA-ICPMS and IRMS techniques are complementary to each other as different chemical characteristics of the duct-tape are measured.

Stable isotope and trace elemental composition results for different rolls of duct tape collected from various stores in the Netherlands are presented.

For validation purposes grey duct tape rolls were obtained from the Dutch producer Supertape. The influence of previous treatment with dactyloscopic reagents methyl violet and cyano acrylate as well as sample preparation were investigated. Both intra- and inter batch variation was determined for samples from three production batches.

Forensic Utility of the Stable Isotope Ratios of PVC Tape Backings

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Forensic interest in adhesive tapes with polyvinyl chloride (PVC) backings (electrical tape) derives from their use in a variety of illicit activities. Due to the range of physical characteristics and chemical compositions of these tapes, traditional microscopic and chemical analysis of the tape backings and adhesives can offer a high degree of discrimination between tapes from different manufacturers and products. However, due to variations in starting materials and recycling reactants during manufacture, different PVC tapes have distinct carbon isotope ratios which may permit further differentiation between tape samples that would be otherwise physically and chemically indistinguishable.

To evaluate whether carbon isotope ratios may be able to increase discrimination of electrical tapes, particularly with regards to different tapes of the same product, we assessed the PVC-backings of 87 rolls of black electrical tape (>20 brands, >60 products) for their $\delta^{13}\text{C}$ values. Because the plasticizers in PVC tapes can have different carbon isotope values than the backings, the plasticizers were removed, along with the tape adhesives, to ensure the isotopic analysis of the tape backings alone. There was negligible carbon isotopic variation within single rolls of tape. The $\delta^{13}\text{C}$ values of the 87 PVC tape backings ranged between -23.5 and -41.3 (‰, V-PDB). For each sample within the population of tapes, carbon isotopes alone were enough to exclude a majority of the tapes as a potential match, with an average exclusion power of 93.7%, using a window of +/- 0.3‰. Analyses of pre- and post-blast tape sample pairs to test the fidelity of carbon isotope values during an explosion will also be presented.

Oral Session on Provenance Determination Using Isotope Methodologies

A Geochemical System for Verifying Honey Floral Type and Provenance

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New Zealand beekeepers have enjoyed premium prices for their honey for many years as few pest to content with and so the honey is high quality and free of antibiotics. Additionally, New Zealand Manuka honey commands a premium price due to its perceived medicinal qualities. Prices upward of \$30 per kg are obtained c.f. <\$5 per kg for most honeys so there is a strong incentive to pass off of other honey types in its place. Even within genuine Manuka honeys there is a large range in values as it is only Manuka from certain regions in New Zealand that present the high levels of beneficial activity. The honey industry and consumers require a rapid and robust system to authenticate claims of both floral type and geographic origin.

Oritain Global Ltd and University of Otago have undertaken a study to map the geochemical composition of New Zealand honey. Honey samples have been collected from the Airborne Honey library. Results from the first 50 samples show that the trace element and light isotope composition can be used to distinguish floral type and provenance. Here we present a demonstration of the system of authentication of floral type and provenance based on the light isotope and trace element composition of the honey. In this case a sample of honey purporting to be New Zealand Manuka was obtained from the U.S. and the floral and geographic origin were tested.

Beeswax Hydrogen Isotopes as Validation of Environment (B-HIVE)

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Recent public awareness of the food industry's safety shortcomings has raised concern about the lack of traceability and authenticity assurance of food products. Meteoric waters hydrogen isotope composition varies predictably across landscapes. An organic material's hydrogen isotope composition ($\delta^2\text{H}$) is related to the $^2\text{H}/^1\text{H}$ ratio of local meteoric water and record the spatial variations in meteoric waters that are characteristic to specific geographic areas. Thus, the $\delta^2\text{H}$ value of organic materials potentially can be use to geo-locate an organic material's region-of-origin. While carbon isotope ratios have long been applied to detect adulteration in honey and honeybee-products, the stable isotope analysis of hydrogen has yet to be explored in depth. To test the applicability of hydrogen isotope ratios for geo-location of honeybee-products, we studied 43 samples of chunk honey produced by *Apis mellifera*, the European honeybee, purchased from producers at known locations within the United States, Australia, and New Zealand. We find liquid honey hydrogen isotope ratios reflect a combination of original and post-production isotopic signals, limiting its applicability as a geo-location indicator. The $\delta^2\text{H}$ values of beeswax and its individual molecular components, on the other hand, are related to predicted precipitation $\delta^2\text{H}$ values for the commercial producers' locations. These data suggest beeswax and beeswax hydrocarbon $^2\text{H}/^1\text{H}$ ratios can be use to elucidate the product's source region precipitation $\delta^2\text{H}$ value. Furthermore, these data indicate multiple components of individual food/animal product can be used either in combination or individually; both yield consistent geographic information about product's region of production.

Wine and Champagne: Evidence from Lithium Isotopes

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Lithium is a chemical element with two isotopes of mass 6 and 7, with natural abundances of 7.5% and 92.5%, respectively. In order to better understand lithium isotope fractionation during geo-biological processing, we report here the first results for lithium isotopic compositions of red wines, white wines and champagnes.

Trace element concentrations in wines and champagne depend in part on geographical origin. Therefore a primary objective of the sampling strategy was to consider the large spectrum of geological bedrock types in France in order to test the efficiency of Li isotopes as a useful tool for wine and champagne characterization. Further, the overall objective of the present work was to establish the extent of Li isotope fractionation and discuss the possible mechanisms of Li isotopes variation resulting from vinification of red wine, white wine and champagne in France. The innovative aspect of this study is the application of lithium isotopes to trace the processes involved during vinification.

Lithium isotopic compositions were measured using a Neptune Multi-Collector ICP-MS at BRGM. ${}^7\text{Li}/{}^6\text{Li}$ ratios were normalized to the L-SVEC standard solution (SRM 8545) following the standard-sample bracketing method. Typical in-run precision on the determination of $\delta^7\text{Li}$ is approximately 0.2‰ (2 standard deviation). Before mass analysis, solution samples for analysis were prepared with chemical separation/purification by ion chromatography in order to produce a pure mono-elemental solution (using a cation exchange resin and HCl acid media 0.2N).

Lithium concentrations in our sample set of wines and champagnes (n=27) ranged by a factor of 10 between 1.7 and 17.6 $\mu\text{g/L}$, while $\delta^7\text{Li}$ values ranged between -1.4 and +53.9‰. These results indicate that Li isotope fractionation associated with the vinification processes is important since $\delta^7\text{Li}$ values are not correlated with the bedrock type or geographical origin, but are dependant on the wine type (red, white or champagne).

These results will be discussed in light of B isotopic data currently being obtained for the same wine and champagne samples. In addition, data for Sr and Pb isotopes, known to be good tracers of the origin of the soil where the grapes have grown, will be incorporated to provide a “multi-tracer” assessment of the vinification process. This multi-isotopic characterization could be also applied in the framework of controlling fraud for the wines and champagnes.

Geographical Region-of-Origin Assignment of American Milk Using Stable Isotope Analysis

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There is increasing demand for reliable information on the region-of-origin of foodstuffs as recent outbreaks of food borne illness have generated concern regarding the traceability of food. Stable isotope analysis may be a useful food-sourcing tool because the stable isotope ratios of hydrogen and oxygen in water vary across landscapes in predictable patterns. Animals and plants incorporate the isotopic signal of local water and the stable isotope analysis of an animal- or plant-derived food product could therefore be used to investigate the product's geographical origin. In this survey, we purchased milk from USA supermarkets and fast food restaurants and analyzed the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of water extracted from milk. We also collected paired samples of milk and cow drinking water from dairies across the USA. We hypothesized that milk water stable isotope ratios record information on the geographic location of dairy cows. We further hypothesized that it would be possible to predict the original region-of-origin for a milk sample if we understood the relationship between cow drinking water and milk water.

Measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for supermarket and restaurant samples spanned large isotope ranges. Restaurant samples clustered into three distinct groups, indicative of the regional distribution pattern for restaurant milk. We found the hydrogen and oxygen stable isotope ratios of paired cow drinking water and milk samples were significantly related. Using the equation that described the relationship between cow drinking water and milk water, we calculated predicted cow drinking water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for samples in the three restaurant sample groups. From this survey, we have demonstrated the feasibility of geographical origin assignment using the stable isotope analysis of milk.

Provenancing Plant Materials from Isoscapes

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The geographic provenance of materials is of importance to many forensic, regulatory, and intelligence interests, including illegal drugs, sourcing of fabrics, and sourcing food or beverages. There is growing recognition that the ability to explicitly model the spatio-temporal variability of stable isotopes (isoscapes) in plants and plant products is of significant utility for these endeavors. Isoscapes-based approaches relevant to these questions are now being pursued in several areas by a number of different groups. Here we present an overview of advances in understanding that have led to useful insights related to the relevant scales, utility of different isotope ratios, and mechanisms that may be underlying observed variability. In addition, we outline areas in need of further development as more specific questions are tackled and the potential for more detail is discovered. Three topics of forensic interest are used to illustrate the utility and current challenges of isoscapes: the drug trade (marijuana), tools for tracking poisons used in crimes (ricin), and fraud detection in the wine industry. The latter is also relevant to broader questions related to food provenance. We have developed isoscapes in each of these target areas and highlight insights related primarily to the geospatial use of hydrogen and oxygen isotope ratios, as well as the potential for combining information from other sources.

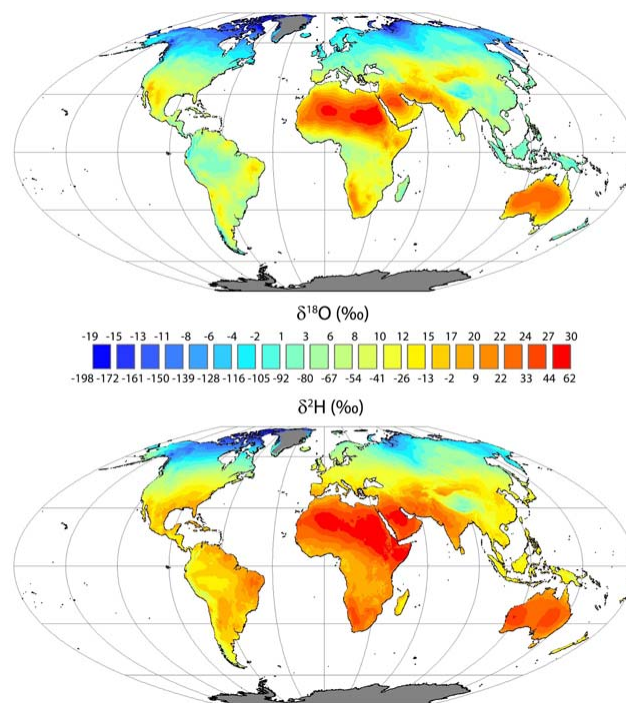


Figure 1. Global average leaf water oxygen and hydrogen isoscapes – a foundation for process-level plant isoscapes modeling at the global scale.

Tuesday, April 13, 2010

Oral Session on Isotopes in Environmental Forensics

PLENARY TALK

The Evolution of Stable Isotope Applications in Environmental Forensics-Past, Present and Future

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Since the commercial availability of the combined gas chromatograph-isotope ratio mass spectrometer (GCIRMS) system there has been an exponential increase in the number of environmental forensic applications that have utilized stable isotopes as a fingerprinting tool. Environmental forensics is primarily concerned with determining the nature and source of organic, or inorganic, compounds that have been spilled, either accidentally or intentionally, in the environment. Such spills are many and varied and range from complex mixtures such as crude oils or refined hydrocarbon products to single components such as MTBE or PCE. There are many analytical tools that have been used for many years to identify these products such as gas chromatography (GC) and gas chromatography-mass spectrometry (GCMS). Apart from identifying the nature of the spilled product these techniques are also used to undertake correlations between the spilled product and suspected source(s). In many cases the stable isotope fingerprint will be used as a supporting correlation tool. One area where isotopes have become exceedingly important is with groundwater contaminants and for a number of good reasons. First for example with a single contaminant, GC and GCMS are of little use for correlation purposes since there is no means of discrimination between different sources. However there is the possibility that compounds derived from different sources or suppliers may be discriminated isotopically and the use of a multi-isotope approach will greatly improve the chances of success in this area. The second major application is studying the onset and extent of natural attenuation of groundwater contaminants. Companies are increasingly looking to the regulators for permission to leave contaminants in place and allow them to degrade naturally. In order to do that they have to convince the regulators that degradation is already underway. Concentrations are not sufficient to do this since they may change as a result of dilution and dispersion. Isotopic enrichment coupled with decreasing concentration becomes compelling evidence for natural attenuation.

In this presentation it is proposed to review how environmental forensics has evolved since the introduction of the GCIRMS systems. It will include a brief review of the highlights of the development of the GCIRMS systems and the results from this early work. Much of the work in the 1990s was concerned with the determination of C isotope compositions of crude oils and refined products and at the end of that decade papers started to appear on applications to ground water contaminants such as MTBE and the chlorinated solvents. With the introduction of the necessary interface to determine HD isotopes it was not long before papers started to appear on HD compositions of similar compounds ultimately leading to ²D isotope determinations increasing confidence in correlations and providing more mechanistic evidence for degradation of groundwater contaminants. The past three or four years have seen methods evolving that permit determination on stable Cl and N isotopes, greatly expanding the range of potential applications.

Recently that has been much greater emphasis on improving the capabilities for quantitative assessment of chlorinated solvents mass destruction from natural attenuation processes, using a combined compound-specific isotope analysis (CSIA) and numerical reactive transport modeling approach. Progress in this area and future developments and applications such as vapor intrusion investigations will be discussed.

Differentiating Nuclear Processing from Multiple Sources of Anthropogenic Nitrate in a Complex Groundwater System Using Dual Isotope Systematics

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Los Alamos National Laboratory (LANL), New Mexico, USA has released multiple sources of anthropogenic nitrate into the groundwater system. The goal of this project is to identify evidence of nuclear processing using dual isotope systematics of nitrate. This requires identifying signatures of nuclear processing, developing a methodology to differentiate these signatures from background nitrate and other sources of anthropogenic nitrate, and quantifying the effects of uncertainty associated with the methodology. Three well defined sources of anthropogenic nitrate have mixed with natural background nitrate across alluvial and perched intermediate-depth aquifers beneath LANL. Results indicate that groundwater nitrate can be described based on $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values by four end-member sources of nitrate that include (1) natural background nitrate, (2) sewage effluent, (3) neutralized nitric acid, and (4) ^{15}N -depleted neutralized nitric acid. This four-component mixing system can be solved for molar-mixing ratios of the three anthropogenic nitrate sources by subtracting out the effect of background nitrate and then calculating, using linear algebra relations of nitrate concentrations and nitrate isotope ratios, the molar fraction of the three anthropogenic end-members present in each groundwater sample. The effect of uncertainty in background nitrate stable isotope ratios and concentration is quantified by latin hypercube sampling (500 trials) of isotope and concentration probability density functions. The calculated molar mixing ratios are used to determine the spatial and temporal variability of nitrate sources in the alluvial and vadose zones of Mortandad Canyon. Temporal trends indicate that neutralized nitric acid is the earliest source of anthropogenic nitrate in this watershed. Alluvial groundwater sampled at various wells preserve a time series of decreasing nitrate concentration that is concomitant with decreasing contributions of ^{15}N -depleted nitric acid. Nearby wells that sample intermediate-depth groundwater aquifers have increasing nitrate concentrations with respect to time that is concomitant with an increasing component of a mixture of ^{15}N -depleted nitric acid and sewage. Interestingly, the alluvial wells in Mortandad canyon preserve an isotopic signature that is consistent with the mixture of ^{15}N -depleted nitric acid and sewage, yet no sewage effluent has been down this canyon. The isotopic composition of the alluvial wells is consistent with preliminary stable isotope data of effluent from the radiological liquid waste treatment facility that neutralizes nitric acid effluent from a plutonium processing facility. These data are interpreted as indicating that the nitrate dual isotope technique may be used to differentiate nitrate related to nuclear processing from other sources of anthropogenic nitrate. The probabilistic approach to quantify uncertainty related to variations in natural background nitrate allows for a confidence analysis.

Investigation of the Fate of Nitrate in the Interflow Zone of Mantled Karst

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Anthropogenic nitrate (NO_3^-) contamination of groundwater is a common problem in vulnerable terrains dominated by karst topography, and elucidation of in-situ NO_3^- dynamics is critical to the design of sustainable practices in these terrains. A field-scale study was conducted at a manure-amended mantled karst site in the Ozark Highlands to determine multiple potential sources and processes affecting NO_3^- along the flowpaths of the subsurface interflow zone, a zone situated between the soil and focused-flow (bedrock) zones, where increased residence time and water-matrix contact may favor NO_3^- bioremediation processes such as denitrification. Groundwater samples were collected along the hydrologic gradient and analyzed for NO_3^- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, reactive (NO_3^-) and conservative (Cl^-) species concentration, and dissolved organic carbon concentration and bioavailability. Nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ indicated a mixed soil organic matter/manure origin of NO_3^- . Mass balance calculations indicated that although mixing was the primary process removing NO_3^- along the interflow zone flowpaths, up to 37 percent of NO_3^- moving through the interflow zone may have been microbially processed. The magnitude of this processing varied spatially and temporally. Dissolved organic carbon bioavailability in the interflow zone was elevated relative to the focused-flow zone, providing a needed substrate for NO_3^- processing in this zone. Overall, the observations suggest that the interflow zone may be important for NO_3^- attenuation in karst.

Oral Session on Explosives

Application of Isotope Ratio Mass Spectrometry (IRMS) for the Forensic Analysis of Explosives

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An evaluation was undertaken to determine if isotope ratio mass spectrometry (IRMS) could assist in the investigation of complex forensic cases by providing a level of discrimination not achievable utilising traditional forensic techniques. The focus of the research was on ammonium nitrate (AN), a common oxidiser used in improvised explosive mixtures. A secondary objective was to adapt the methods and protocols developed for AN for the analysis of other threat explosives, namely triacetone triperoxide (TATP) and pentaerythritol tetranitrate (PETN).

The potential of IRMS was demonstrated through the successful development and validation of a method for the measurement of bulk nitrogen isotope ratios in AN samples. Limited discrimination was achieved between the AN samples from three different Australian manufacturers utilising nitrogen alone.

A comparison of nitrogen isotope ratios from intact AN prill samples with those from post-blast AN prill residues highlighted that the nitrogen isotopic composition of the prills is not maintained.

Combining oxygen and hydrogen stable isotope ratios permitted the differentiation of AN prills from three different Australian manufacturers. Groups corresponding to source were also identified in overseas AN prill samples analysed.

The IRMS procedures developed were successfully applied to the analysis of both TATP and PETN. Preliminary results from a limited sample set demonstrated that TATP sources may be discriminated utilizing carbon and hydrogen isotopes alone, and in combination with oxygen isotopes. Preliminary results for PETN samples demonstrated that different sources can be discriminated based on carbon and nitrogen isotope ratios.

An inter-laboratory comparison for carbon and nitrogen bulk stable isotope ratios across seven Australian and New Zealand IRMS laboratories was conducted and this provided an initial snapshot of the potential for traceability. A Microsoft Access 2.0 database was developed for the IRMS data and the successful operation of this database demonstrated.

This research highlights the significant value of IRMS in complex forensic investigations, particularly with respect to explosives analysis. Further research is justified to continue the path towards broader forensic casework application of the technique.

Forensic Investigation of Isotopic Linkages Between Hexamine and the Peroxide Explosive HMTD

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The Forensic Explosives Laboratory (FEL) and the Netherlands Forensic Institute (NFI) have investigated isotopic linkages between precursor materials used to produce the peroxide explosive hexamethylene triperoxide diamine (HMTD).

Initial studies examining hexamine as a precursor to the military explosive RDX [1] revealed relationships between isotope values of precursor and product materials which may be exploited in forensic investigations. This led to further studies considering similar relationships for the peroxide explosive HMTD. HMTD is manufactured by the reaction of hexamine with hydrogen peroxide under acidic conditions and has been encountered in forensic casework as an improvised or “home-made” explosive. In this study HMTD was synthesised both in the laboratory and in field studies. The isotope delta values of the precursor and product materials were compared to determine whether or not relationships could be established in order to provide a useful connection for forensic investigations.

The initial phase of the investigation, undertaken by FEL, used chemical grade reagents and followed the same synthesis protocol throughout. The results demonstrated consistent isotope shifts for carbon, nitrogen and oxygen and good reproducibility for multiple syntheses using the same precursor material. To test the isotopic relationships under more realistic conditions a number of recommendations were made such as the implementation of a blind trial and use of improvised sources of precursor materials, as may be encountered in casework scenarios.

The second phase of experiments was conducted by the NFI to mimic forensic circumstances for “home-made” explosives. A unique opportunity for such an experiment was an outside training course for policemen to make HMTD under primitive circumstances using kitchen tools instead of laboratory equipment. As the participants had no or little laboratory experience and the course itself took place in a shelter the experiment mimicked more realistic forensic circumstances for making improvised explosives. Even under these circumstances an offset was found in the carbon and nitrogen isotope values of hexamine and HMTD comparable to the FEL laboratory results. However where improvised sources of hexamine were used, greater variability was observed in the results, as might be expected from the incorporation of impurities in the synthesised HMTD.

In conclusion, the isotopic relationship between HMTD and its precursor hexamine is clearly shown under laboratory conditions. Synthesis performed under “field” conditions showed similar isotopic relationships, although the strength of the isotopic relationship decreased with the amount of impurities in the materials. Nevertheless stable isotope data of precursor and explosive product might give additional information useful for intelligence purposes for example to establish a link between them.

References:

[1] C. Lock, W. Meier-Augenstein (2008). Investigation of isotopic linkage between precursor and product in the synthesis of a high explosive. *Forensic Science International*, 179 (2) pp. 157-162.

Peroxide Bomb - Don't Think You're Foolin' Me

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Triacetone triperoxide (TATP) is an organic peroxide explosive that is easily manufactured using several unregulated substrate materials including acetone and hydrogen peroxide (H₂O₂). The use of TATP in improvised explosive devices has occurred and is predicted to rise as military-grade explosives become less accessible. It is of forensic interest to link substrates or explosive materials to a synthesized product or clandestine laboratory. Here we measured stable carbon ($\delta^{13}\text{C}$), hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) isotope ratio values of TATP and the substrates, acetone and hydrogen peroxide, used to synthesize this explosive. In synthesis reactions, we expected a relationship between the isotope composition of substrates and product. To test this, we analyzed 14 TATP specimens; 96 acetone specimens; and 97 H₂O₂ specimens. Substrate specimens were obtained through personal contacts or by purchase at grocery, salon and hardware stores, from scientific catalogs or direct from the manufacturer.

We observed significant variations in the $\delta^{13}\text{C}$, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of TATP specimens. In synthesis reactions when acetone was the limiting reagent, the $\delta^{13}\text{C}_{\text{TATP}}$ value was indistinguishable from $\delta^{13}\text{C}_{\text{acetone}}$ value, as expected. We measured large manufacture-based ranges in the $\delta^{13}\text{C}$, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in acetone and in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of H₂O₂.

The source of oxygen in H₂O₂ is directly linked manufacturing processes, but the signal is obscured by the addition of dilution water during distribution. We developed a method to measure the $\delta^{18}\text{O}$ isotope value of hydrogen peroxide, distinct from dilution water, and observed a large range in ^{18}O values for H₂O₂.

The dilution water in H₂O₂ fits the meteoric water line and may be provide geographical-based information about the source of the water using isoscape-based approaches.

These results show that stable isotope ratio analyses of $\delta^{13}\text{C}$, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope ratio values are a useful forensic tool to source and relate both TATP and its acetone and hydrogen peroxide substrates. As the fractionation of TATP with evaporation is modest, stable isotope analyses should be a useful tool in TATP-related investigations.

Multi-Collector ICP-MS: A New Direction for Isotopically Characterising Explosives?

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Current instrumental techniques routinely employed for the analysis of explosives include: FT-IR, XRF, SEM/EDX, HPLC, etc..... Although the substances present can easily be identified using these techniques, it is generally not possible to distinguish one source of the same substance from another. To alleviate this difficulty, the use of stable isotopes seems really promising. Recent studies, using the stable isotopes of carbon ($\delta^{13}\text{C}$), nitrogen ($\delta^{15}\text{N}$), oxygen ($\delta^{18}\text{O}$) or hydrogen (δD), appraised the possibility of fingerprinting different families of explosives (usually before blast), and demonstrated that it could ultimately be a powerful tool.

Recently, multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has experienced a big increase in technique and application. It has been shown that rapid and precise measurements of various isotope systematics (i.e.: Li, B, Mg, Si, Cr, Fe, Hg, Pb, U ...) could be achieved by MC-ICP-MS. To date, this approach combines advantages that no other technique can match in terms of accuracy, reproducibility, sensitivity and analysis throughput. Here, we will present the isotope characterisation of 30 distinct PETN, TNT and ANFO samples. The multi-isotope approach used here includes lead (e.g. $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$) and lithium ($\delta^7\text{Li}$) isotopes.

In parallel to the isotope compositions, elemental concentrations of lead (Pb), strontium (Sr), lithium (Li), chromium (Cr), cadmium (Cd) and zinc (Zn) were measured. Except for cadmium, all samples yield concentrations sufficient for isotope analysis. The study of the sole concentrations already shows that discrimination is possible, but the combination of concentrations with corresponding isotope compositions highlights the great added of the isotope approach. The isotope-isotope approach (e.g. $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $\delta^7\text{Li}$) clearly differentiates the different families of explosives (PETN, TNT and ANFO), and hints at a possible correlation between these isotope compositions and the manufacturing origin of the explosives.

Strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) and chromium ($\delta^{53}\text{Cr}$) isotope systematics will also be discussed.

Identification of Fake Archeological Artifacts Using Stable Isotope Methods: Authenticity Examination of the Inscription on the Ossuary Attributed to James, Brother of Jesus Case Study

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The study focuses on the examination of the authenticity of the patina that coats archeological artifacts. The patina is the outermost layer which is formed on the surface of various artifacts as a result of weathering processes. Patina found on artifacts from the Judean Mountains, Israel, is composed mainly of CaCO_3 . The oxygen isotopic composition ($^{18}\text{O}/^{16}\text{O}$ ratio, expressed as $\delta^{18}\text{O}$ value) of the carbonate patina depends on the temperature, and on the isotopic composition of the water from which the patina was deposited. This study demonstrates that the $\delta^{18}\text{O}$ value of the patina can be used as a good indicator for identifying the authenticity of a patina, and whether it was formed under natural conditions.

A First Century CE ossuary belonging to a private collector, bearing engraved Aramaic inscription ‘‘Ya’akov bar Yosef achui de Yeshua’’ (James son of Joseph his brother of Jesus), has been attributed to James, Jesus’ brother, first head of the Jerusalem church. The ossuary was reportedly found around Jerusalem. Previous examination suggested that the ossuary and the inscription were genuine, and recently there is a debate concerning its authenticity.

Our research focuses on the $\delta^{18}\text{O}$ values of the patina that covers the inscription (‘‘letters patina’’). We compared the $\delta^{18}\text{O}$ values of the patina coating the inscription of the ossuary attributed to James, with the surface patina from the same ossuary developed outside the inscription, and with patinas from legally excavated ossuaries from Jerusalem, and with carbonates formed under natural conditions in the Judean Mountains in soils (pedogenic carbonate) and within closed caves (carbonate speleothems). $\delta^{18}\text{O}$ values of these carbonates range between -4‰ and -6‰ PDB.

In contrast, the $\delta^{18}\text{O}$ values of the letters patina of the James Ossuary differ significantly from the other patinas and range between -7.5‰ and -10.5‰. These values are by far too low. Our studies of pedogenic carbonate and speleothems that were formed during the last 2000-3000 years show that such a patina could not have formed under natural conditions. This fact, and the fact that the ‘‘letters patina’’ have different isotopic composition from all patina developed on ossuaries from legal excavations dated to 2000-3000 years ago suggest that this patina was not formed naturally. The low $\delta^{18}\text{O}$ values, most probably reflect that the patina was artificially formed from powdered chalk immersed in hot soda-water. These observations clearly call into question the authenticity of the inscription on ‘‘James Ossuary’’.

Micron-Scale Determination of Pb Isotopic Compositions for Forensic Analysis

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Lead isotopic measurements are an important tool in the field of criminal forensics. Lead has four isotopes, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb; ²⁰⁴Pb is non-radiogenic while the other isotopes are products of the decay of ²³⁸U, ²³⁵U, and ²³²Th, respectively. Variation in the Pb isotopic compositions of materials is a function of its U, Th concentrations, and initial Pb isotopic heterogeneities. Therefore, slight chemical variations in source materials allow for resolvable differences in Pb isotopic compositions. Combined with other physical, chemical, and isotopic data, Pb isotopic compositions can “fingerprint” a wide variety of forensic materials, including, but not limited to: metals, oxides, ballistic samples, ceramics, and organic materials (e.g., human tissue).

At the University of Maryland, College Park, we have developed a rapid, accurate, and precise method to determine the Pb isotopic compositions of micron-scale areas employing laser ablation multi-collector ICP-MS (LA-MC-ICP-MS). Precision for LA-MC-ICP-MS is a function of Poisson’s counting statistics, consequently the larger the spot size or higher the concentration of Pb, the better precision. For materials with high concentrations of Pb (>100 µg/g), ratios ²⁰⁸Pb, ²⁰⁷Pb, or ²⁰⁶Pb/²⁰⁴Pb are measured using parallel ion beams across Faraday cups. For materials with low concentrations of Pb (<100 µg/g), high-abundance isotopes (²⁰⁸Pb, ²⁰⁷Pb, ²⁰⁶Pb) are measured via parallel ion beams across Faraday cups, while the low abundance isotopes ²⁰⁴Pb, ²⁰²Hg, and ²⁰⁰Hg are measured as ion beams across parallel ion counters. The isobaric interference of ²⁰⁴Hg on ²⁰⁴Pb is stripped from the ²⁰⁴Pb peak using the natural abundances of the Hg isotopes and the measured ²⁰²Hg current. Fractionation and sample detector gain corrections are accomplished using standard-sample bracketing and the exponential fractionation law. The standard reference materials (SRMs) used are well-characterized, homogenous glasses. This technique can be applied to samples having Pb concentrations from ≥2 µg/g to those containing wt% Pb, with external precisions (2σ) ranging from ±1% - 0.1%, respectively, while consuming only femtograms amounts of Pb.

As a case study, we will present Pb isotopic data for majolica glazes of Colonial period ceramic shards from Spain, Mexico, Guatemala, and Panama. The ceramics contained wt. % concentrations of Pb and therefore, we were able to measure the Pb isotopic compositions (²⁰⁸Pb/²⁰⁴Pb) with <±0.1 % (2σ) external precision. With this precision we were able to create a diagnostic field of Pb isotopic compositions for glazes from each source region, allowing for future determination of provenance for shards with uncertain origin.

Oral Session on Strategic Issues / Isotope Data in Legal Systems

Two New Human Hair Reference Materials for Stable Isotopes of H, C, N, O, and S

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Interest in the measurement of stable hydrogen and oxygen isotopic composition of human hair is growing in biology, anthropology, and other sciences. Isotope laboratories globally need stable isotopic reference materials appropriate for the materials they analyze in order that measurement of the same homogeneous sample by any laboratory worldwide can yield the same isotopic composition within analytical uncertainty. Because there are no internationally distributed stable hydrogen and oxygen isotopic reference materials of human hair, the U.S. Geological Survey (USGS) has prepared two such materials, USGS42 and USGS43. These reference materials are isotopically homogeneous and are suitable for measurements of the isotopes of hydrogen, carbon, nitrogen, oxygen, and sulfur in human and mammal hair. Preliminary isotopic compositions of the non-exchangeable fractions of these materials are listed below.

Scale	USGS42 (Tibetan Hair)	Mass Fraction	USGS43 (Indian Hair)	Mass Fraction
$\delta^2\text{H}_{\text{VSMOW-SLAP}}$	-87 ‰	6.1 %	-49 ‰	6.1 %
$\delta^{13}\text{C}_{\text{NBS19-LSVEC}}$	-21.22 ‰	45.7 %	-21.40 ‰	43.44 %
$\delta^{15}\text{N}_{\text{AIR}}$	7.91 ‰	15.28 %	8.37 ‰	14.51 %
$\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$	10 ‰	22 %	14 ‰	22 %
$\delta^{34}\text{S}_{\text{VCDT}}$	7.39 ‰	4.52 %	10.03 ‰	4.52 %

Reporting of Forensic IRMS/ICPMS Results in The Netherlands

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IRMS and (LA-)ICPMS are used together as part of forensic casework investigations within the NFI since 2003. Various applications were developed that demonstrate the strong discriminating power of this technique combination. LA-ICPMS and IRMS are part of the NFI in-house instrumentation since 2002 and 2008, respectively.

Materials for which IRMS was used are various tape types, adhesives, paper, safe wall filling materials (combination of potassium alum and saw dust), jeans, motor oils, polyester trousers, polypropylene rope, polymethyl methacrylate objects, candles, jerrycans, remnants of burnt jerrycans. Some applications will be discussed in the presentation.

For serious crimes such as murders, results are used for different purposes in different phases of a large scale police investigation (indicative investigations) and the judicial process. Four phases can be distinguished. In the first two phases results are used to assist the police with forensic intelligence. In the last two phases results are used to assist the court with forensic evidence.

Police investigation

Phase 1: many scenarios are possible and IRMS/ICPMS can assist in eliminating some of these scenarios. In this phase it is especially of interest if samples can be discriminated.

Phase 2: later in the police investigation possible scenarios will be weighed relative to each other. At this stage it is not only relevant to be able to discriminate samples but also to at least estimate the value of a match.

Court investigation

Phase 3: apart from the prosecution hypothesis at least one alternative (defense) hypothesis is required to state the evidence logically correct. To evaluate the value of a match, knowledge on the background variation of the material is also required. If this background variation was investigated previously, a report for the court can be formulated directly after the investigation.

Phase 4: if the background variation of the material has not been investigated previously, it may be required to formulate sequential reports for the court; the first specifies the match and the limitations because of lacking knowledge on background variation. Depending on the importance of the evidence for the court, in the fourth phase the background variation is then determined and the match interpreted in the light of this information.

The advantage of these different phases is that (preliminary) results can be reported relatively fast to assist the police during their investigation, whereas in-depth reports for court will be provided later, if necessary. During the entire process transparency of the investigating expert is extremely important to provide information to the other parties on the value as well as on the limitations of the results.

The above process is illustrated with examples in the presentation.

Confirming Testosterone Abuse in Athletes Using GC-C-IRMS: A Quality Assurance Perspective

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The application of Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry (GC-C-IRMS) to doping control can provide an effective means to detect synthetic testosterone administrations in athletes.¹ To support this capability laboratories accredited by the World Anti-Doping Agency (WADA) require robust analytical methods with a high degree of sensitivity and specificity.² The demands of sensitivity with respect to urine samples (≥ 10 mL) needed to accurately and precisely measure $\delta^{13}\text{C}$ values of target steroid metabolites results in additional quality controls to demonstrate specificity. The development and validation of a confirmatory method to support adverse analytical findings is presented that involves a multi-step solid-phase, liquid-liquid, high performance liquid chromatographic (HPLC) isolation and derivatization procedure followed by full scan gas chromatography-mass spectrometry (GC-MS) identification prior to GC-C-IRMS analysis.

Knowledge of endogenous steroid biosynthesis and metabolism was the starting point for this GC-C-IRMS strategy. Testosterone is naturally metabolized to the inactive C₅-reduced metabolites – androsterone and etiocholanolone – that are subsequently excreted in urine as their glucuronide conjugates. Unfortunately many other steroids are also metabolized to these compounds, resulting in endogenous dilution (i.e. ^{13}C enrichment), even with synthetic testosterone administration. To overcome this potential disadvantage the optimized method allows the selective isolation and analysis of analogous 5 α - and 5 β -diol metabolites as their diacetate derivatives. The $\delta^{13}\text{C}$ value of pregnanediol, an endogenous reference compound produced by a separate biosynthetic pathway from the androgens, is measured as its diacetate derivative to provide a difference ($\Delta\delta^{13}\text{C}$) value capable of identifying doping violations ($>3.0\text{‰}$).

A number quality control measures have been incorporated into the method to support adverse analytical findings in the medico-legal arena of anti-doping. It is anticipated that these methodologies could be adapted to more diverse forensic toxicological studies using GC-C-IRMS analysis.

1. Full scan GC-MS analysis of each collected fraction from the HPLC isolation process.
 - a. To ensure that the correct elution program was achieved with no unintended fractionation.
 - b. To confirm steroid identity with respect to WADA ion comparison criteria.
 - b. To confirm peak purity by manual deconvolution.
2. Relative retention matching of target steroids analyzed by GC-C-IRMS and GC-MS.
3. Traceable correction for the acetylation reaction that combines the contributions of kinetic isotope effects and the derivative mass balance.
4. The use of steroid reference materials with certified $\delta^{13}\text{C}$ values allows sequence specific calibration of the GC-C-IRMS instrument an estimate of potential bias for each analysis performed.
5. The “fit-for-purpose” objective of ISO 17025 is demonstrated by the analysis of positive and negative urine controls with each set of samples that provides a verification of the method performance and measurement uncertainty estimate ($\pm 0.5\text{‰}$) using a CUSUM approach.

¹ Cawley A.T., *et al. Steroids*, **74** (2009) 379.

² Cawley A.T. and Flenker U. *J. Mass Spectrom.*, **43** (2008) 854.

Bad Science: The Floyd Landis Case

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Floyd Landis, a professional bicycle racer who grew up around Lancaster, Pennsylvania, won the 2006 Tour de France. However, not many days after the race's conclusion it was leaked to the press that the Laboratoire National de Dépistage du Dopage (LNDD) had found a urine sample obtained from Floyd after stage 17 to be positive for a form of synthetic testosterone. If this finding were to be upheld, Landis would be stripped of his title and also banned from participation in the sport for two years. Landis denied any sports doping and his strategy in fighting these charges was to try to generate public support and to make all of the documentation of the LNDD tests available to the public. GC/MS was used by LNDD for preliminary sample screening, and capillary column gas chromatography combustion stable isotope ratio mass spectrometry (GC-C-IRMS) was used for final confirmation. GC-C-IRMS is a relatively new analytical method that has many potential applications in forensic science. The purpose of this presentation will be to highlight potential sources of error in GC-C-IRMS that must be recognized and avoided. The Floyd Landis sports doping case will be used as an illustrative background.

Lessons from the Human Provenance Project

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The Human Provenance Project is a joint UKBA /SOCA proof of concept pilot project. It is aimed at tackling organised immigration crime including abuse of the UK's asylum system, particularly nationality swapping. The pilot project involves the use of a combination of forensic techniques, such as isotopic analysis of hair and nails together and ancestral DNA analysis, and will be combined with language analysis and enhanced interviewing techniques to examine whether it can indicate a person's possible origins and recent movements.

The live testing under this proof of concept pilot project started initially during September 09 but due to feedback received from external and internal stakeholders, including the wider scientific community and press, it was suspended. The initial plan was to use the results from these tests to help identify cases where further investigation into declarations of nationality may have been appropriate. The intention being to help the decision maker reach an informed decision as to the veracity of the person's claim regarding country of origin, and open up avenues enabling the return of those who have no legal right to remain in the UK.

However, following an internal review it was agreed that the testing would recommence for three months, that all of the results would be excluded from the decision making process in live cases and that the test results would be anonymised and used to determine the validity of the proposed process. Testing is voluntary and individuals are required to give their consent in writing. At the conclusion of this pilot the results will be reviewed including the underpinning science and the wider ethical and equality implications of the work considered.

As well as discussing the results of the validation study this presentation will outline the difficulties encountered in taking this forward and various conflicting issues experienced in attempting to apply science in law enforcement.

The Changing Forensic Landscape and its Impact on Isotope Forensics

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The recent publication of the US National Academy of Sciences¹ report which *inter alia* was critical of the practice and delivery of forensic science in the USA has gained some attention and, at the very least, has resulted in a reassessment of forensic practice in a number of jurisdictions. In addition, the adoption of what is sometimes known as Case Assessment and Interpretation (CAI)^{2 3}, which in essence is a likelihood ratio approach to the evaluation of forensic information, continues to gain ground to the extent that some forensic laboratories have adopted it as a standard.

A critique of the NAS report will be presented together with the response of the forensic science community. The current position regarding the evaluation of forensic information will be presented and possible futures explored. The potential impact on isotope forensics will be discussed and an assessment made of how the field may have to adapt. A strategy for isotope forensics will be proposed.

¹ Strengthening forensic science in the United States: a path forward

² Cook,R. et al Sci & Justice 1998; 38:151-156

³ Jackson,G. et al Sci & Justice 2006; 46:33-44

Wednesday, April 14, 2010

Oral Session on Radiogenic and Heavy Stable Isotopes

Combining Light Isotope, Trace Element and Isotope of Metals in Environmental and Forensic Investigations

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There has been a growing use of light stable isotopes (C, N, H, O and S) in environmental and forensic investigations and a growing awareness of the strength of coupling light isotope data with multi-elemental fingerprinting. The combination of information from more than one isotope or more than one element can provide corroborating evidence to theories. Subsequently, a number of studies have shown the power of combining Isotope Ratio Mass Spectrometry (IRMS) and Inductively Coupled Plasma Mass Spectrometry (ICPMS) techniques. The advent of High Resolution Multi Collector Inductively Coupled Plasma Mass Spectrometry (HR-MC-ICPMS) has added a third dimension with the ability to investigate the isotopic ratios of elements from Lithium through Zinc to Uranium.

For all investigations a hierarchy of techniques can be devised. [1] Whereas, it may be argued that for many investigations the simpler and the cheaper the techniques used the better, there may be a case for using a complex and more expensive technique if it can provide unequivocal answers in a faster response time. As an example nine samples of glass from different provenance were individually loaded and ablated, with replication, using a Neptune (Thermo-Finnigan) LA-HR-MC-ICPMS yielding lead isotope ratios which provided discrimination in under 50 minutes.

It will be argued, with examples from the authors work, that using a very expensive, very complex hammer to crack a walnut may be cost effective if that technique can provide very unequivocal discrimination very quickly. In this way LA-HR-MC-ICPMS could be a valuable additional technique.

[1] Walker GS "Analysis of Soils in a Forensic Context: Comparison of Some Current and Future Options" Chapter 25, pg 397-410 in *Criminal and Environmental Forensics*, Ritz K, Dawson L and Miller D (Edit) Springer 2009 [ISBN 978-1-4020-9203-9]

The Fabrication of Uranium Isotope Standards for Laser Ablation ICPMS

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Laser ablation inductively coupled mass spectrometry (LA-ICPMS) has been used for the rapid, accurate and precise measurement of trace element abundances in solid materials. It has been widely used in the analysis of geological materials as well as in the fields of material science, biology and environmental monitoring. Plasma mass spectrometry is also widely used for the determination of isotope ratios. However there have been relatively few applications of laser ablation to the *in situ* measurement of isotope ratios. One of the issues that has bedeviled the application of laser ablation analysis to isotope ratio determinations has been the lack of suitable standards.

The application of laser ablation methods to nuclear forensics is potentially extremely valuable. The rapid measurement of $^{234}\text{U}/^{235}\text{U}/^{238}\text{U}$ in samples collected from nuclear processing plants, nefarious devices, or fallout would enable instantaneous fingerprinting of the samples. However to do this requires standards with suitable uranium contents and known isotopic compositions. At present there are standards with known isotopic ratios but generally not applicable to laser ablation studies. Either the materials are synthetic glasses, typically fabricated using depleted uranium (*e.g.* NIST 600 series – $^{238}\text{U}/^{235}\text{U}=420$), or are glasses made from natural materials with a natural uranium abundance and isotopic composition ($^{238}\text{U}/^{235}\text{U}=137.88$). Although these are useful an array of standards with a continuum of compositions would allow precise determination of unknowns.

We have developed a method for the production of a series of powdered, pelletised standards of varying isotopic ratios, ranging from natural to depleted U abundances. The solid standard MAG-1 is a fine-grained, grey-brown mud certified by the USGS to have 2.7 (± 0.3) ppm naturally occurring U. A 1000ppm SpexCertiprep plasma solution standard, whose isotopic composition was determined to be $^{238}\text{U}/^{235}\text{U}=339$ by comparison with DoE uranium isotope standards, was used as the other mixture end member to produce the solid standard.

In order to produce a range of isotope ratios in the standard, appropriate masses of MAG-1 (*ca.* 50mg) were weighed and mixed with 1mL of solution standard, which had been diluted to a concentration that would give the required U isotope ratio. The mixture was then ground in an agate pestle and mortar and dried in a vacuum oven. The resultant powder was then compressed in a screw devise that produced a 5mm wide pellet. A series of such pellets were produced with varying amounts of solution and MAG mud, leading to a range in U abundance as well as U isotope ratio in the pellets.

The homogenous nature (less than 2% variation) of U isotope ratios and U abundances of these mixtures has been demonstrated by laser ablation ICP-MS analysis.

Analyses of U Isotopes in Glasses, Mud, Dust and Filter Papers

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The rapid production of high quality chemical and isotopic data is essential to successful forensic investigations. We have developed a method for rapid analysis of the U isotopic composition of airborne particulate materials using laser ablation techniques coupled with multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS).

Uranium isotopic measurements provide information concerning the origin and provenance of potentially dangerous materials. The three naturally occurring isotopes of U, namely ²³⁴U, ²³⁵U, and ²³⁸U, are radioactive with half-lives of 2.5×10^5 years, 7.0×10^8 years, and 4.5×10^9 years, respectively. Uranium isotopic ratios of natural materials are normally considered to be invariant showing less than 0.1% variation from the natural ²³⁵U/²³⁸U and ²³⁴U/²³⁸U of 0.72% and 0.0054% respectively. However, as a consequence of refinement for use in nuclear power production or nuclear weapons, the relative abundances of U isotopes are grossly altered in processed nuclear materials (factors of 2 or more enrichments of ²³⁵U/²³⁸U in reactor fuel rods as well as for ²³⁴U/²³⁸U). We report a method for the rapid, accurate and precise determination of the U isotopic composition of airborne particles using a frequency quintupled Nd:YAG laser (213 nm laser pulse) coupled with a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). Isotopic abundances of ²³⁵U and ²³⁴U, the minor isotopes of U, are measured with ion counters, whereas ²³⁸U, the largest ion beam, is measured on a Faraday cup detector. Sample-standard bracketing is employed along with an exponential fractionation law to correct for mass dependent fractionation. Gain corrections between ion counters and Faraday cups are made through the measurement of standard reference materials, NIST 610 and 612 silicate glasses. Experimental procedures can be optimized by the variation of: i) laser spot size (a trade off between spatial resolution and higher count rates); ii) laser repetition rates (a control on sampling depth and count rate); iii) photon fluence (typically between 1.0-3.0 Jcm⁻² [controls fractionation, count rate and photon coupling characteristics]; and iv) sample throughput rate (a trade off between precision and number of analyses). By varying these factors it is possible to control the limits of detection as well as the accuracy and precision of the measurements.

Measurements of filter papers, air particulates and compacted sediments via both solution and *in situ* (i.e., laser ablation) ICP-MS analysis have been carried out. Typical uncertainties for the analysis of materials containing ~2ppm U are on the order of $\pm \sim 2\%$ (2σ external reproducibility) for both ²³⁵U/²³⁸U and ²³⁴U/²³⁸U measurements. Methods presented expand the applicability of LA-ICP-MS towards rapid analysis of easily obtained samples with respect to multiple isotopic systems.

Precise Determination of $^{63}\text{Cu}/^{65}\text{Cu}$, $^{66}\text{Zn}/^{68}\text{Zn}$ and $^{87}\text{Sr}/^{88}\text{Sr}$ in Solid Materials via *in situ* LA-ICP-MS

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Forensic investigations require rapid, reproducible and reliable methods of chemical and isotopic analysis in order to identify the origin of criminal evidence. Laser ablation (LA-) inductively-coupled plasma mass spectrometry (ICP-MS) provides an ideal analytical technique for measuring trace element abundances and isotopic ratios by providing: i) bulk and/or spatially-resolved measurements of micrometer-scale sample specimens; ii) negligible sample processing (which is time-consuming, costly and can introduce impurities and/or isobaric interferences); iii) low analytical blanks and limits of detection; iv) limited oxide production and spectral matrix effects; and, v) the ability to avoid surface and grain-boundary contamination. Additionally, laser ablation methods require smaller quantities of sample ($\leq \mu\text{g}$) compared to traditional solution analyses ($\geq \text{mg}$) and permit both internal or external calibration techniques.

Copper, zinc and strontium represent powerful chemical tracers that can be used for toxicological and/or forensic applications. Distinct isotopic ratios of these elements (i.e., $^{63}\text{Cu}/^{65}\text{Cu}$, $^{66}\text{Zn}/^{68}\text{Zn}$ and $^{87}\text{Sr}/^{88}\text{Sr}$) can provide information regarding the provenance of a variety of sample materials, from ballistic samples and their residues to glass shards to over-the-counter and prescription medicines. We have developed several robust *in situ* LA-ICP-MS analytical techniques to measure the isotopic composition of Cu, Zn and Sr in solid, unprocessed materials. Employing low-resolution mass discrimination ($m/\Delta m = 300$), we can determine $^{63}\text{Cu}/^{65}\text{Cu}$, $^{66}\text{Zn}/^{68}\text{Zn}$ and $^{87}\text{Sr}/^{88}\text{Sr}$ ratios with an analytical precision of $\leq 1\%$ (1σ ; Poisson counting statistics) for concentrations lower than 50 $\mu\text{g/g}$ Cu, 500 $\mu\text{g/g}$ Zn and 50 $\mu\text{g/g}$ Sr. With medium-resolution detection ($m/\Delta m = 4000$), we can determine $^{63}\text{Cu}/^{65}\text{Cu}$, $^{66}\text{Zn}/^{68}\text{Zn}$ and $^{87}\text{Sr}/^{88}\text{Sr}$ with a precision of $\leq 1\%$ (1σ) for concentrations lower than 1000 $\mu\text{g/g}$ Cu, 10,000 $\mu\text{g/g}$ Zn and 1000 $\mu\text{g/g}$ Sr.

In general, LA-ICP-MS provides a rapid and dependable analytical method for measuring isotopic ratios, but a tradeoff exists between the precision of the measurement and the amount of analyte ablated and transmitted through the mass spectrometer, which is limited by the resolution of the mass discrimination. Mass-fractionation correction of any isotopic ratio requires the analysis of matrix-matched standard reference materials under identical analytical conditions for the highest degree of accuracy. Examples will be presented.

Poster Session: 9:50 – 12:00

An Off-Line Method to Eliminate Nitrogen-Oxide Interference for $\delta^{18}\text{O}$ Analysis of Nitro-Organics

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Nitrogen-rich organic compounds, or nitro-organics, are of high importance to forensics in light of their use as explosive stimulants, detonators, or improvised explosive devices. Depending on the origin and processing all explosives acquire signatures amenable to isotopic discrimination. Indeed, analysis of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ has proven useful in determining sources and linking materials to residues (e.g. Pierrini et al., 2007). Though desirable (e.g. Widory et al., 2009), extensive use of $\delta^{18}\text{O}$ in explosives ‘fingerprinting’ has proven difficult and unreliable despite recent instrumentation advances (i.e. TC/EA-IRMS).

Precise and standardized determination of $\delta^{18}\text{O}$ values for nitro-organics is hampered by three fundamental issues: 1) the elevated levels of N_2 produced during online thermal decomposition of these compounds generates NO in the ion source of the IRMS (Gehre and Strauch, 2003), thereby interfering with the CO chromatographic peak, 2) online attempts to eliminate the problem yield mixed results (e.g. Accoe et al., 2008), and 3) no standards exist for inter-laboratory $\delta^{18}\text{O}$ analysis of explosives.

We address these concerns via combination of two off-line techniques developed primarily for the analysis $\delta^{18}\text{O}$ in plant cellulose, though amenable to N-containing organics (Schimmelmann and DeNiro, 1985; Sauer and Sternberg, 1993). With this pooled technique, we are able to eliminate all N_2 from the gas products of a chlorinated pyrolysis, resulting in purified CO_2 for analysis via IRMS dual-inlet mode. We test this method sequentially using: 1) N-free compounds (IAEA-CH3 and Sigma cellulose) of certified $\delta^{18}\text{O}$ value, 2) N-doping of IAEA-CH3 standard up to N:O mass ratio of 1:1, and 3) four other $\delta^{18}\text{O}$ certified standards, including caffeine with N:O = 1.8. Our ultimate goal is to determine $\delta^{18}\text{O}$ for a suite of explosives (RDX, PETN, HMX, TNT, NG, and NC; max N:O = 0.9) for cross-laboratory comparison and application as verified-standard values.

To date, we have carefully scrutinized the original methods (Schimmelmann and DeNiro, 1985; Sauer and Sternberg, 1993) resulting in our pooled methodology. Several subtleties of these methods include: 1) Ni reagent purity during disproportionation of CO to CO_2 , 2) Zn reagent purity and temperature control during elimination of HCl gas product, 3) avoiding local water vapor effects, 4) glassware preparation, and 5) lengthy reaction times. Despite these intricacies, preliminary results from our method indicate that the certified $\delta^{18}\text{O}$ value for IAEA-CH3 and Sigma standards is attainable with reproducibility of ~0.1%. Furthermore, initial N-doping of IAEA-CH3 does not appear to exhibit affects on $\delta^{18}\text{O}$ value.

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The Relationship Between HMX and RDX Stable Isotopes Can Reveal Production and Subsequent Mixing Information in Explosive Seizures

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The relative difficulty in producing military-grade explosives and the limited number of production facilities means that source-related information in a seized explosive specimen can be valuable in forensics investigations. In combination with traditional chemical composition analysis, stable isotopic analysis may help narrow the possible sources. Likewise, composition and stable isotopic analysis may suggest that a seized explosive specimen has been altered from its original form through mixing. We present here composition and stable isotopic analysis of nitramine (RDX and HMX) explosive samples that are considered authentic either through direct sampling at the production facility or confirmation through packaging. We found that RDX and HMX synthesized via the Bachmann process have a stable isotope relationship between the HMX and RDX. In these cases carbon and nitrogen isotope ratios are described by the equations $\Delta^{15}\text{N}_{(\text{HMX-RDX})} = -1\text{‰}$ and $\Delta^{13}\text{C}_{(\text{HMX-RDX})} = -1\text{‰}$. When either difference was greater than 1‰, the explosive analyzed is likely the result of the mixing of two different nitramine explosives of different isotopic composition. Combined with component analysis and directed subsampling, stable isotopic analysis of RDX-HMX explosives can be useful in investigating the source and history of an IED.

Forensic Utility of Isotope Ratio Analysis of the Explosive Urea Nitrate and its Precursors

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Urea nitrate is a readily-made improvised terrorist explosive. The component ions of seized and synthesized urea nitrate were separated for nitrogen isotope analysis by dissolving the sample with KOH, drying the sample, followed by removal of the urea by dissolution into 100% methanol. The urea nitrate samples contain an excess of nitric acid making the ionic separation an essential step in the nitrogen isotope analysis. The carbon and nitrogen isotope measurements were determined on the separated component ions, urea and nitrate reagents, and the bulk urea nitrate sample. During urea nitrate synthesis, the nitrogen isotope ratios of the nitrate are preserved and there is a less than 1‰ increase in the urea component. The carbon isotope ratio of the urea is preserved when the bulk urea nitrate sample is measured. The results suggest that isotope ratios may be useful in comparing possible precursors to seized urea nitrate samples in an investigation. There is significant inter-sample urea nitrate variation in both the carbon and nitrogen isotope ratios in collected urea nitrate samples, suggesting forensic utility of this method.

Geographical Region-of-Origin and Cultivation Assignments of Marijuana Seizures in Major Cities Across the United States

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Although marijuana is the most readily available and widely used illicit drug in the United States, there remains significant uncertainty about the importance of different production regions and trafficking patterns as they relate to the supply of marijuana to different markets across the United States. We analyzed 628 “retail” marijuana seizures from over 50 municipalities across the United States for hydrogen and carbon isotope ratios to predict their growth locations and environments. Results are presented for 22 consolidated retail locations across the United States and interpreted in terms of our understanding of the underlying causes of variability in carbon and hydrogen isotope ratios in marijuana. Evaluation of specimens from within these retail locations suggested that marijuana seizures had region-dependent geographic origins, and were often from both domestic and foreign sources. Indoor growth was common in many areas, including in both warm and cool climates, but there was also regional dependence in the proportions cultivated under indoor versus outdoor conditions with northern regions tending to have more indoor-grown marijuana. Both outdoor-cultivated Mexican and indoor-cultivated Canadian marijuana were apparently widely available across the United States, but again regional differences in availability across the conterminous United States were evident consistent with proximity to one foreign source or the other. Based on these observations, we conclude that stable isotope tools provide a useful and independent assessment of street-available marijuana cultivation and trafficking patterns.

High Accuracy Carbon, Magnesium & Sulfur Isotope Ratio Measurements Combined With Trace Metal Profiling for the Detection of Counterfeit Tablets of an Antiviral Drug for HIV/AIDS Treatment

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Pharmaceutical counterfeiting has been detected since 1990 and, more recently, the problem has escalated. The World Health Organization (WHO) has defined counterfeit drugs as those which are “deliberately mislabeled with respect to identity and/or source. Counterfeiting can apply to both branded and generic products with counterfeit products including drugs with the correct ingredients or with the wrong ingredients; without API, with insufficient API or with fake packaging.” The WHO estimates that counterfeits, which now account for >10 % of the global market, cost the pharmaceuticals industry US\$46 billion annually. This value is expected to increase to US\$80 billion by 2014.

Because of its direct impact on health, counterfeit medicines should be combated and regulation should be modified accordingly. Anti-counterfeiting measurements reported so far, range from simple colorimetric methods to more sophisticated techniques such as near-infrared spectroscopy (NIR) and liquid chromatography-mass spectrometric (LC-MS) approaches.

In this work isotopic fingerprinting using IRMS and MC-ICP-MS technologies and trace metal ICP-MS profiling are combined to both identify potential counterfeits of an antiviral drug and to aid classification within the counterfeits. Isotopic authenticity ranges have been obtained for each isotopic system and combined to generate a unique multi-isotopic pattern only present in the genuine tablets. Counterfeit tablets have then been identified as those tablets with an isotopic fingerprint outside the genuine isotopic range.

The combination of those two techniques has therefore great potential as a screening tool for pharmaceutical counterfeit detection. The data from these studies could be presented as evidence in court and therefore methods need to be validated to support their credibility. It is also crucial to be able to produce uncertainty values associated to the isotope amount ratio measurements so that significant differences can be identified and the authenticity of a sample can be assessed.

In-situ Laser Ablation ICP MS Trace Element and Isotope Fingerprinting of Powdered Pharmaceuticals

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) analysis can be used for elemental and isotopic characterization of solid materials. The advantages of this method are that, with suitable standards, accurate and precise data can be obtained rapidly with a 10's to 100's micron spatial resolution.

Variations in the trace element and isotopic composition of pharmaceuticals and other drugs may be the result of two basic effects; source materials and manufacturing. The manufacturing of the active ingredient in pharmaceuticals is carefully controlled and it is to be expected that the majority of the trace elements will be in the filler material used to control dosage and ease consumption. These fillers may be organic (typically lactose, cellulose or acidophilous) or inorganic (*e.g.* calcium carbonate). Although manufacturing processes are carefully controlled, trace element impurities, which have a non-critical role in the performance of the drug, are present in all drugs so far analyzed. The relative abundances of these trace impurities and their isotopic compositions reveal much about the drug's production and provenance.

We have used a combination of laser ablation and standard-addition, solution analysis to measure trace element abundances in powdered Gabapentin. Powdered samples of the drug were compressed, without any added binder material, in a screw device to produce a coherent 4mm pellet capable of being analysed by laser. This pellet production procedure is rapid and has negligible blank contribution. Laser ablation using an ArF excimer laser was carried out with a 400 μ m spot rastered over the sample. The low photon fluence (1.9-2.2Jcm⁻²) and 15Hz repetition rate allowed for appropriate photon coupling characteristics of this friable material, which is a common problem with the analysis of organic materials. Standard addition of the dissolved drug was used to determine elemental abundances for internal calibration during laser ablation.

Analyses revealed that the level of some trace element impurities reaches tens, to hundreds of micrograms per gram. The distribution of elements and their relative abundances are variable. Some trace elements are uniform in distribution and show little inter- or intra-sample variation; these elements are probably distributed within the bulk of the filler. Other elements show order of magnitude variation in abundance levels, consistent them being impurities heterogeneously distributed a small grains that are incorporated during the manufacturing process. Trace elements, such as Zn, Sr, and Pb, which are in high enough concentration to obtain isotopic analyses, have been examined for their isotopic compositions *via* laser ablation analysis. Isotopic compositional variations come about through fabrication processes (light, volatile elements such as Zn, Cu) and natural variations due to radiogenic decay, such as for Sr and Pb.

Nitrogen Stable Isotope of Ammonia and Nitrate Ion of Atmospheric Particulate Matter

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Suspended particulate matter (SPM), defined to particle size as 100 % cut-off aerodynamic diameter at 10 μm , has adverse effects on human health. The concentration of SPM has been decreased until 1980s, but, 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. Especially, for low SPM (< 30 $\mu\text{g}/\text{m}^3$), ratio of natural source seemed to be low, more complicated artificial source to be high. For decreasing primary direct particle of SPM, the mechanism of the formation of SPM and behavior of gas-particle should be comprehended in greater detail. If the source of SPM is estimated clearly, government can conduct effective policy and strategy of SPM.

In these years, stable isotope ratio of small sample volume can be analyzed high precision by isotope ratio mass spectrometry coupling with elemental analyzer. Recently some fields are using stable isotope ratio. 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 have been limited. We try to analysis $\delta^{15}\text{N}$ -ammonium ($\delta^{15}\text{N}-\text{NH}_4^+$) and nitrate ($\delta^{15}\text{N}-\text{NO}_3^-$) of SPM, to estimate source of NH_4^+ and NO_3^- of SPM.

We analyzed $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{15}\text{N}-\text{NH}_4^+$ of SPM as follows concept for the analytical method. 1. For the same as the general ion measurement, NH_4^+ and NO_3^- in ion-exchanged water were extracted from the sampling filter by supersonic wave for 15 minutes. 2. NH_4^+ was distilled from sample extractions and adsorbed into diluted H_2SO_4 . 3. NO_3^- was reduced to the NH_4^+ using Devarda's alloy (Wako Corp.), and for the same as NH_4^+ were distilled and adsorbed into diluted H_2SO_4 . 4. The both NH_4SO_4 in the distillate were precipitated directly as an insoluble salt of $(\text{C}_6\text{H}_5)_4\text{BNH}_4$ using $(\text{C}_6\text{H}_5)_4\text{BNa}$ (Wako Corp.). 5. The precipitated samples were packed in tin cup after drying, and analyzed by elemental analyzer (Flash EA; Thermo Fisher Scientific K.K.) and isotope ratio mass spectrometry (MAT253; Thermo Fisher Scientific K.K.) for $\delta^{15}\text{N}$ determination. For the validation of the method, we analyzed the soluble mixture of NH_4Cl (Wako Corp.) and KNO_3 (Wako Corp.) as standard sample. $\delta^{15}\text{N}-\text{NH}_4\text{Cl}$ and $\delta^{15}\text{N}-\text{KNO}_3$ were measured individually using elemental analyzer and IRMS.

In this method, the results of the accuracy and the precision were $0.03 \pm 0.04 \text{‰}$ ($\delta^{15}\text{N}-\text{NH}_4^+$) and $-0.15 \pm 0.14 \text{‰}$ ($\delta^{15}\text{N}-\text{NO}_3^-$), respectively. The results were extremely accuracy and precision to compare with other researches. Average $\delta^{15}\text{N}-\text{NH}_4^+$ and $\delta^{15}\text{N}-\text{NO}_3^-$ of SPM in Akita prefecture, Japan were 15.9 ‰ (1.3‰ to 38.5 ‰) and - 0.7 ‰ (-4.6 ‰ to 4.8 ‰), respectively. Although $\delta^{15}\text{N}-\text{NH}_4^+$ do not show seasonal trend, $\delta^{15}\text{N}-\text{NO}_3^-$ 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. Heaton (1990) summarized that $\delta^{15}\text{N}-\text{NO}_x$ is very different by temperature of combustion. They insisted that $\delta^{15}\text{N}-\text{NO}_x$ values are between -13 ‰ to -2 ‰ over 2000 °C (e.g. vehicle engine) and 6 ‰ to 13 ‰ under 1300 °C (e.g. coal combustion). Therefore, 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. In addition, the reason of decreasing in summer seemed to be affected very low $\delta^{15}\text{N}-\text{NO}$ of fertilizer and urea indicated by Li and Wang (2008). Bacteria were activated in summer, and NO from fertilizer and urea was emitted. This summary seemed to be very reasonable.

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Measurement of Stable Hydrogen Isotope Ratio of Atmospheric VOCs

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Volatile Organic Compounds (VOCs) are important precursors of ozone and secondary organic aerosols, some of these compounds have carcinogenic, teratogenic or mutagenic character. Sources of VOCs in ambient air exist very complexly, e.g. vehicle exhausts, gasoline evaporation, solvent use, natural gas emissions, and industrial processes etc. In order to develop efficient air pollution abatement strategies, it is important to identify the emission sources clearly.

In recent years, compound specific isotope analysis (CSIA) is development, and stable carbon isotope ratio of VOCs in air has been measured as a novel method of source identification. However, studies of CSIA of atmospheric VOCs were very few, especially hydrogen of atmospheric VOCs have not been existed. Stable hydrogen isotopes (deuterium) have bigger mass differences than carbon isotope, bigger isotopic distribution might be indicated and caused the differences between sources. If CSIA of hydrogen isotope of atmospheric VOCs can be measured with high accuracy and precision, it might be powerful tool for source identification. In addition, the results might be expanded various fields, forensics field.

This study measured stable hydrogen isotope ratio of VOCs in air using coupling system of Thermal-Desorption and GC/TC/IRMS (TD-GC/TC/IRMS). Analysis of VOCs was carried out with a Trace GC (Thermo Fisher Scientific K.K.) coupled via a GC-combustion-III-interface to a MAT253 (Thermo Fisher Scientific K.K.) coupling with GAS-10 (Tokyo Dylec Corp.), thermal desorption. Precision of TD-GC/C/IRMS was confirmed using standard gas (PAMS-58 (1.0ppm); Takachiho Chemical Industrial Co.,LTD.) diluted by nitrogen gas in tedlar bag. Standard gas was adsorbed at 0 °C for 10 min by TD, and desorbed instantly at about 250 °C and then injected into the GC. The GC was equipped with a fused silica capillary column (150 m × 0.25 mm i.d.) coated with Petrocol DH 150 phase (1.0 μm film thickness). The GC oven was programmed from 35 °C for 22 min to 95 °C for 10 min at 5 °C/min and 140 °C for 0 min at 2 °C/min then, heated 280 °C for 20 min at 40 °C/min. Helium was used as the carrier gas.

The precision (standard deviation; SD) of TD-GC/TC/IRMS was 4.7 ‰, 1.1 ‰, 1.8 ‰, 2.2 ‰, 2.0 ‰ for stable hydrogen isotope ratio of benzene, toluene, ethylbenzene, o-xylene, m,p-xylene, respectively. The results seemed to be reasonable in comparison with other few studies. We can measure 28 VOCs with high precision (avg. of SD; 3.4‰) by TC-GC/TC/IRMS in this study. Additionally, we have tested analytical method such as decomposition and adsorption of VOCs in tedlar bag, temperature of high temperature combustion furnace, flow rate of GC, etc, too. Moreover, some sources (e.g. vehicle exhaust, gas station) have been measured. We would like to discuss the results of TD-GC/C/IRMS in FIRMS 2010 workshop.

Reduction of Sample Size for Oxygen Isotope Analysis in Organic Compounds

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Early descriptions of “cryofocusing” – the controlled release of purified combustion products from a cold-sink located directly upstream of the inlet to the mass spectrometer – promised a reduction in sample size to the 10-1000 nanomole range (Fry et al., 1996). While sample size is rarely limiting for most ecological and geological applications, reduction in sample size is a central issue in forensic analysis. Oxygen stable isotope analysis of organics have shown the utility of $\delta^{18}\text{O}$ as an indicator of geographic origin (Ehleringer et al., 2008). During standard operation of online high-temperature conversion instruments (e.g., TC/EA), approximately 5-10 micromoles of CO are required for these analyses (Gehre and Strauch, 2003). Thus the idealized result of the successful cryofocusing of TC/EA products would lead to a reduction of sample size of three orders of magnitude.

We report here on an online system that converts the CO products of the TC/EA to CO₂ for cryofocusing. We follow the catalytic oxidation approach of Loader and Buhay, (1999) which uses elemental nickel at 550 °C to disproportionate CO to CO₂. However, instead of a Pd:Ag membrane, we use the gas chromatograph of the TC/EA to separate H₂ from the other products in order to avoid the potential for hydrogen to combine with oxygen during the disproportionation. We then apply the cryofocusing method described in Fry et al. (1996), which involves a controlled thaw with no concomitant alteration of He flow. Ultimately this procedure can be optimized by stepping down carrier flow rate in order to amplify the CO₂ peak that reaches the mass spectrometer.

We will report size series analyses of $\delta^{18}\text{O}$ in organic compounds of interest in order to quantify the practical reduction in sample size that can be achieved with this method. In addition to IAEA organic standards such as benzoic acid (C₆H₅COOH; IAEA-601;602) and caffeine (C₈H₁₀N₄O₂; IAEA-600), we will analyze alpha-cellulose (C₆H₇O₂[OH]₃); and sucrose (C₁₂H₂₂O₁₁). Finally, we will also perform a size series on heterogeneous substrates of hair and nail (keratin), insect chitin and plant pollen (sporopollenin) in order to gain insight into the usefulness of this technique for “real world” applications.

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LIAISON: World's First Fully-Automated Universal Interface for Bulk ^{13}C High-Precision Isotope Analysis Using Cavity Ring-Down Spectroscopy

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We have developed the world's first universal interface, named LIAISON, capable of coupling to almost any CO_2 -generating sample preparation front-ends ranging from an elemental analyzer to any dissolved carbon analysis module, which are of significant use in geochemical and biogeochemical studies. In this specific application, we have coupled LIAISON to an elemental analyzer (EA) and to a cavity ring-down spectrometer (CRDS) for ^{13}C isotopic analysis of bulk samples. LIAISON is suited for a high-throughput sample analysis process by running three different gas handling operations in parallel: Admitting combustion gas from the EA into a first gas bag, analyzing the previous sample collected into a second gas bag with CRDS, and flushing and purging a third gas bag in preparation for the upcoming sample collection operation. The sample-to-sample analysis time is 10 minutes and the operation is completely automated for an auto-sampler tray capacity, requiring no operator intervention. The CRDS data is collected, tabulated and saved into an output text file. The memory effect between the L-Glutamic acid standard (USGS 40, $\delta^{13}\text{C} = -26.389 \text{ ‰}$) at natural abundance and the moderately enriched L-Glutamic acid standard (USGS 41, $\delta^{13}\text{C} = 37.626 \text{ ‰}$) is excluded by the selection of the adequate number and duration of flush and purge cycles of the gas sample bags. The system achieved a typical precision equivalent to 0.2 ‰ (1 sigma) or better, including the $\delta^{13}\text{C}$ -enriched samples. The EA-LIAISON-CRDS system presented here provides a fully automated solution for bulk $\delta^{13}\text{C}$ analysis with unprecedented ease-of-use, and possible field-portability with the current availability of a compact combustion module. In addition, LIAISON's universality enables CRDS to supplant IRMS in many continuous flow isotopic analysis applications, for $\delta^{13}\text{C}$ and possibly other stable isotopes, currently employing sample preparation modules in tandem with IRMS.

Continuous Flow – Cavity RingDown Spectroscopy: A Powerful Tool for Food Origin Analysis and Adulteration Detection

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Continuous Flow – Cavity RingDown Spectroscopy CF-CRDS instruments now provide simple access to stable isotope ratios for the three life elements (C, H, O). Once the growing, harvesting and/or processing of natural products is complete, these ratios leave a permanent and characteristic signature that can be easily read and used to screen these products.

In this application, we present data using CF-CRDS for the analysis of the water content in fresh apples and carbon signatures from honey samples collected from various regions were some were purposely mixed with corn syrup. In fact, fresh apples from different growing regions were analyzed for their isotopic water content. A fast sample preparation technique was completed within five minutes and yielded liquid samples which were directly injected into an isotopic CRDS liquid water analyzer for ¹⁸O and D analysis. The high-precision results showed clear differences for the same apple varieties grown in different regions; furthermore, these differences were consistent with the isotopic composition of the region's precipitation. Samples were also analyzed by IRMS which were in good agreement, albeit with additional sample preparation required.

On the other hand, a newly developed Combustion system with a high-throughput interface connected to an isotopic carbon analyzer were used to analyze a host of honey samples collected from various geographical and botanical origins. In one instance, the honey sample was deliberately adulterated with corn syrup at low percentage and successfully analyzed for food fraud detection. Cross analysis with and EA-IRMS system yielded excellent agreement with the CRDS analysis. The results of CRDS analyses precision was at ≤ 0.2 permil.

Micro-Sampling of Organic and Biological Solid Samples for Stable Isotope Measurements Using Laser Ablation Coupled to a Capillary Reactor

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Conventional methods for the introduction of solid samples into an isotope ratio mass spectrometer (IRMS) place a lower bound of approximately ~100 µg per sample depending on the isotope of interest. This precludes detailed spatial profiles that can provide valuable forensic information, for example length-resolved isotope ratios in human hair. We present preliminary data on a system that uses laser ablation to micro-sample organic or biological solids in the form of aerosol particles. Laser ablation of organic polymers and horse hair was performed at 266 nm at pulse lengths of 10 ns or less. These laser parameters have been widely demonstrated to produce chemically representative particles from glass and geological samples, but have not been applied to organic and biological samples. These particles are transferred to a capillary reactor where they are converted to simple gases for isotope ratio analysis. Successful quantitative measurement of isotope ratios using this method requires 1) that the ablated particles represent the isotope ratio of the solid 2) that the ablated particles have a size distribution in the proper range, .1 – 1 micron, to allow quantitative transport from the surface to the reactor and 3) that the conversion of particles to gas in the reactor is complete and quantitative, not introducing any isotopic biases.

An aerosol mass spectrometer (AMS) was used to determine that the size distribution of the particles is in the correct range and that ablation of material from the solid and transfer to the reactor is a quantitative process. The AMS was also used to determine that the molecular composition of particles ablated from these complex samples was constant over the range of particle sizes produced. A complementary measurement using a proton-transfer reaction mass spectrometer (PTR-MS) verified that no material was being released as volatile compounds which could indicate ablation mechanisms that skew isotopic composition. Finally, IRMS was used to make isotopic measurements of hair and polymer samples that agreed with IRMS measurements made with conventional sample introduction, but with a sample size of 2 µg, approximately 50 times smaller than existing methods. It is anticipated that further improvements will substantially reduce the laser ablated sample size to the picomole range. This has prompted a parallel effort in the development of novel optical absorption methods for carbon and oxygen isotope ratio measurements in these micro-sample sizes, these developments also will be presented. The preliminary results presented here support the development of a small system that can perform isotopic imaging on a wide range of sample types of interest to the forensic community.

New Product Developments at Isoprime Ltd.

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Two new products have been released by Isoprime that increases ease and performance of forensic sample analysis. The first product development is the 100V head amplifier with computer switchable gains of the Isoprime100. The new head amplifier will increase the range of sample size that we can analyze, but still enable small sample analysis. The second product development is a new addition to Elementar's vario CUBE series. It is a new elemental analyzer with maximum temperature of 1500°C for high temperature pyrolysis applications. It has an additional furnace to enable a two tube solution for simultaneous NCS isotope analysis, and a purge and trap CO separation resulting in improved oxygen analysis for high nitrogen samples (such as hair). The Isoprime100 and vario PYRO cube complement the existing product range and address customer's needs for flexible and high performance EA-IRMS solutions.

High Precision Isotopic Reference Material Program

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Recent developments in thermal ionization and inductively coupled plasma multi-collector mass spectrometry instrumentation have led to “high precision” isotope ratio measurements with uncertainties approaching a few parts in 10^6 . These new measurement capabilities have revolutionized the study of isotopic variations in nature by increasing the number of elements showing natural variations by almost a factor of two, and new research areas are actively opening up in climate change, health, ecology, geology and in particular forensic studies.

Standard reference materials are essential not only for assessing the accuracy and precision of chemical and isotopic analyses but also for underpinning inter-laboratory comparisons and measurements to be used in forensic applications. Because the isotopic applications are impacting very diverse fields (e.g. food authentication, crime investigation, trafficking, provenance estimation, dirty bomb origin), there is at present little effective coordination between research laboratories over reference materials and the values to apply to those materials. NIST had originally developed the techniques for producing accurate isotopic characterizations, culminating in the NIST Isotopic SRM series. Unfortunately, the values certified for all these isotopic SRMs produced by NIST, using techniques developed in the 1960's, are two or more orders of magnitude too imprecise compared with the new measurements. Worse yet, there are no reference materials available for many of the new elements and some of the existing SRMs (e.g. SRM 980) have proved to be inhomogeneous at these new levels of precision. A new generation of isotopic standards is urgently needed and will directly affect the quality and scope of all emergent applications and ensure that the results being derived are comparable.

A series of new isotopic reference materials the NIST 8300 Isotopic SRM series is being designed with the goal of producing standards in a pure liquid form that are isotopically suitable and homogeneous and have been ampouled/bottled for assessment of long term stability. The majority of the solutions will be made from NIST Primary Materials that are the high purity metal basis for the NIST Single Element Spectrometric Solutions (SRM 3100 series). These materials will be initially released as Reference Materials (RMs) and are expected to become the basis for artifact based δ -scales.

Initial focus has been on the three elements: Pb, Hg, and Tl. The Hg isotopic standard will address ongoing concerns of Hg standardization for both mass-dependent and independent investigations. The Tl isotopic standard is used for mass bias corrections for Hg and Pb isotopic measurements and should be released at the same time. Pb isotopic measurements are among the most common isotopic measurements performed world wide and have applications in diverse fields including medical, environmental, and earth systems science and the forensic community.

Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) To Provide Forensic Isotopic Evidence: An Overview

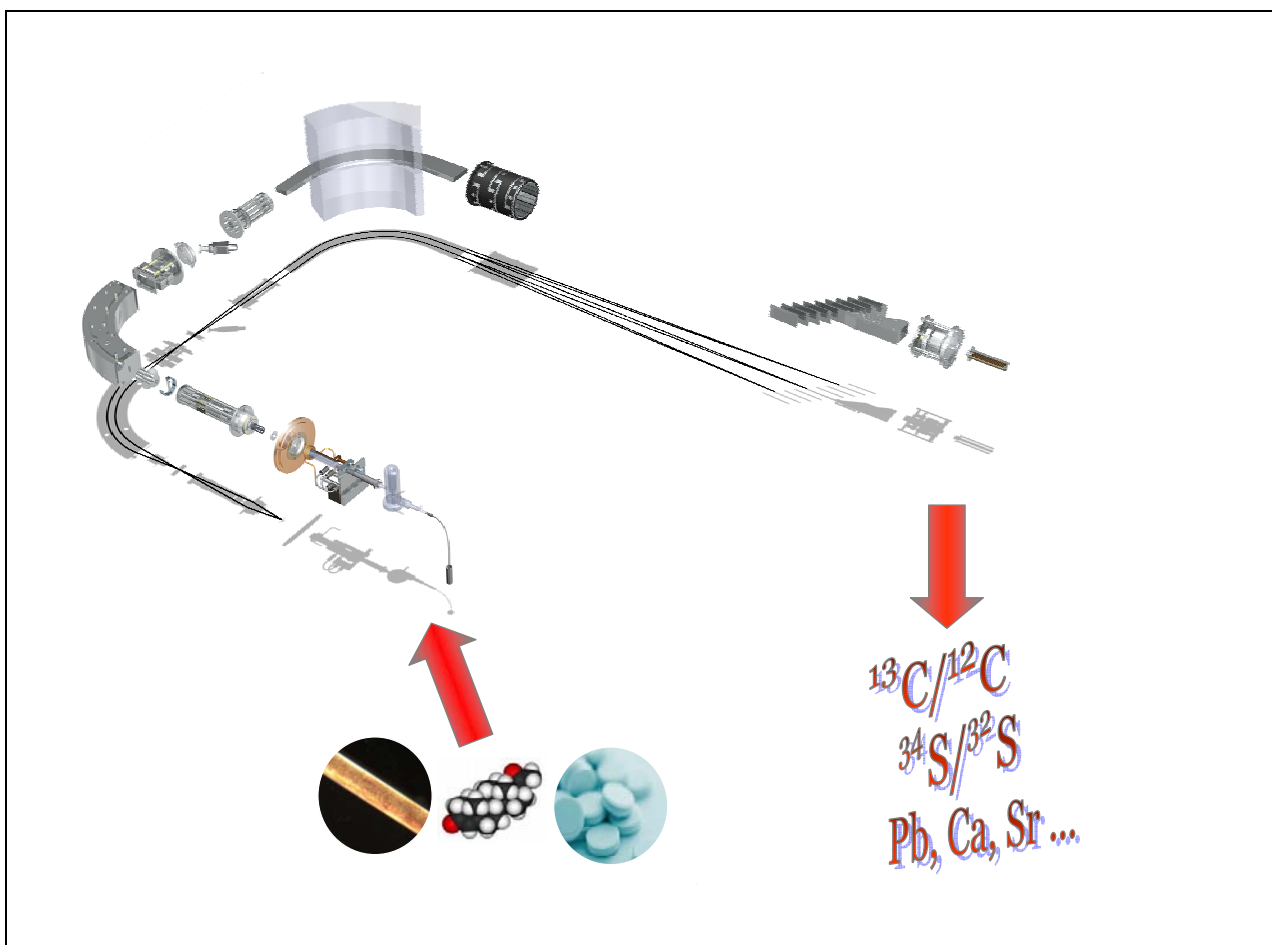
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The role of stable isotope ratios in forensic investigations has been previously highlighted. To be able to use isotopic data as evidence, methods must be validated, reference samples characterized and uncertainties evaluated.

In this work, an overview of methodology, which has been developed 'in house' for the measurement of high precision carbon and sulfur isotope ratios by multicollector ICP-MS in samples of forensic interest such as counterfeit drugs, hair samples, steroids, pharmaceutical packaging etc. will be given.

The application of calcium and lead isotope ratio measurements by LA-MC-ICP-MS to discriminate counterfeit drug packaging and the use of longitudinal sulfur isotopic variation measurements in hair strands by LA-MC-ICP-MS to track geographical movements will be discussed. Finally, evaluation of the feasibility of a novel method for carbon isotope ratio measurements by MC-ICP-MS for the production of isotopic standards of metrological and forensic interest will be presented.



A Laser Desorption Resonance Ionization Mass Spectrometer for Geolocation and Source Attribution

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We are developing a portable laser desorption resonance ionization mass spectrometer (LDRIMS) enabling fast, sensitive elemental and isotopic measurements for two FIRMS relevant applications: 1) to constrain the origins and movements of humans [e.g. *Juarez, 2008*] and materials such as explosives [e.g. *McGuire, 2005*], and 2) for identifying enriched nuclear materials and the characteristic isotopic signatures of the source reactor. Our current prototype focuses on strontium (Sr) detection, though in principle we could apply the same technique to many other elements. In the first case, humans and animals take on the environmental isotopic signatures, such as $^{87}\text{Sr}/^{86}\text{Sr}$, through the consumption of food and water. Sr signatures are derived from the underlying geology and vary as a function of age and composition of the rocks. For example, point measurements of Sr in Europe have been used to constrain the provenance of the Sr signatures in teeth and bones of the “Iceman”, a frozen mummy found in Europe [*Hoogerwerff et al, 2001*]. The home territory of prehistoric humans can typically be distinguished using $^{87}\text{Sr}/^{86}\text{Sr}$ if their teeth or bones can be determined to a precision of $\pm 0.1\text{-}0.01\%$, in samples commonly with Sr abundance of 50-2000 ppm [*Bentley et al, 2006*]. In the modern era food and water signatures may be removed from their original source due to mass production and shipping practices, however, isotopic relationships continue to exist due to regional and/or cultural preferences for food sources. For example, **Figure 1** [*Juarez, 2008*] illustrates three isotopically distinct regions determined from $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in teeth for individuals from Mexico. These isotopically distinct regions are influenced by local hydrology and geology, despite potentially imported strontium sources [*Montgomery et al, 2006*], but remain distinct due to regional or cultural food preferences [*Juarez, 2008*]. Our LARIMS instrument potentially could be carried to the scene of an investigation, or used real-time at an entrance portal. In the second case, the high sensitivity and precision of LDRIMS enables us to potentially measure nuclear materials at lower abundances with moderate precision. This enables the LDRIMS instrument to also rapidly assess nuclear enrichment, which commonly requires low precision, but high abundance sensitivity, as well as potentially identify isotopic signatures of a source reactor.

Figure 1: Map of isotopically distinct regions determined from $^{87}\text{Sr}/^{86}\text{Sr}$ from teeth of modern citizens of Mexico. Close proximity of isotopically distinct locales suggests moderately high resolution global determination of individual provenance may be possible.

Currently, we can measure the isotope ratio of lab standards with 10 ppm net Sr to a precision of $\pm 0.5\%$ (1σ), with a sensitivity of $1:10^{10}$ in less than 1 minute, with virtually no sample preparation. Increasing the measurement time to 15 minutes improves the precision to 0.1% (1σ). The speed of the LDRIMS measurement allows thousands of samples to be measured in significantly shorter periods of time than traditional methods, with little or no sample preparation. These results were obtained using low laser powers ($\sim 10\ \mu\text{J}$ for resonance, $< 1\ \text{mJ}$ for photoionization), consistent with a fast, portable instrument. Currently, the mass spectrometer has been miniaturized, though the laser systems have not.

Figure 2: Example of data analysis showing improved sensitivity ($< 50\ \text{ppb}$)

Stable Isotope and Ultratrace Metal Impurity Analysis for Forensic Characterization of Cyanides

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Cyanides are globally produced for large-scale use in mining and chemical industries. Whether it is mixed with water to form vapor HCN or its powder is ingested directly, cyanide is highly toxic due to its ability to inhibit cellular energy production. The combination of cyanide's high production quantities (50,000 tons per year in the US alone) and high intrinsic toxicity make it a potential chemical threat agent. We used a dual approach strategy focused on cyanide stable isotope content and trace constituent analysis to reveal signatures for both sample matching and potentially revealing information about manufacturing and handling histories to assist in forensic investigations.

We used continuous flow isotope ratio mass spectrometry to measure the carbon and nitrogen stable isotope content of 65 cyanide samples from 24 different suppliers to assess the isotopic ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) variability amongst commercially available cyanide sources. The isotopic content of each cyanide sample should reflect that of the starting material used in the synthesis and potentially provide a fingerprint unique to those feedstocks. For instance, methane displays high $\delta^{13}\text{C}$ variability and is frequently used as the carbon source for synthetic cyanide production. We observed variability of 20 ‰ in $\delta^{13}\text{C}$ and 6.5 ‰ in $\delta^{15}\text{N}$ with a wide spread of data between these extremes. Simultaneously utilizing both isotopes minimized overlap between samples and highlights the potential of this technique to link cyanide samples collected at different locations. To assist in future work, we also calibrated three cyanide samples for use as isotopic standards using different mass spectrometers at two different locations (Pacific Northwest National Laboratory and Oak Ridge National Laboratory). Use of these standards may minimize analysis variations when compared to using a host of previously developed organic and inorganic stable isotope standards that have vastly different structures and may therefore react differently in combustion reactions.

We used a combination of inductively coupled plasma optical emission spectroscopy (ICP-OES) and high performance ion chromatography (HPIC) and to assess trace constituents of eight potassium cyanide samples. ICP-OES highlighted a number of metals, including Rb, Sr, Mg, Ca, Cs, Fe, and Ba that showed high variability between samples that would permit sample matching and potentially reveal aspect of the sample's manufacturing and handling history. In particular, exploiting ratios of different elements (ie: Rb/Sr versus Na/Ca) segregated the eight samples analyzed into distinct groups that correlated to vendor providing the sample (samples from the same vendor plotted together and apart from other samples).

Casework IRMS/ICPMS Examples in The Netherlands

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In this poster a number of forensic IRMS/(LA-)ICPMS applications will be discussed. The IRMS/(LA-)ICPMS technique combination is used for forensic casework investigations within the NFI since 2003. Various applications were developed that demonstrate the strong discriminating power of this technique combination.

IRMS and (LA-)ICPMS, alone or in combination, were used for various tape types, adhesives, paper, safe wall filling materials (combination of potassium alum and saw dust), jeans, motor oils, polyester trousers, polypropylene rope, polymethyl methacrylate objects, candles, jerry cans, remnants of burnt jerry cans, ink, glass, bullet lead and other metals.

Some applications will be discussed in the presentation. Presently we intend to focus on

- a tape investigation as part of an explosive device ,
- a series of arson investigations in which police cars were burnt using a modus operandi of placing polythene jerry cans filled with petrol on top of a car and lighting it. The investigation focused on comparing burnt jerry can remnants with other jerry cans,
- a comparison of skimmer materials as encountered at a crime scene and with a suspect.

Discrimination of Candle Wax Materials by Gas Chromatography (GC) and Isotope Ratio Mass Spectrometry (IRMS)

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Candles or candle wax materials are sometimes encountered in arson investigations where they are used in devices to initiate a fire. In this situation often a request is made to compare these candle wax materials with visually similar candles retrieved during *e.g.* a search at a suspect's house. In the past, this was limited to infrared spectrometric (IR) and gas chromatography (GC) characterisation of both wax materials to be compared. If materials could not be discriminated, this was stated but no conclusion could be provided on a common source since the background variation of these characteristics was unknown to us.

In a specific Dutch high profile serial arson investigation it was deemed necessary to both use more techniques as well as obtain a measure of the background variation of the characteristics used. Techniques used at first were visual investigation (colour, structure, morphology, layer thickness, hardness), X-ray fluorescence (XRF) to assess low levels of heavier elements, GC to determine aliphatic hydrocarbon profiles and fatty acid levels, GC-MS to identify additional (low-level) compounds that could be used for characterisation and Isotope Ratio Mass Spectrometry (IRMS) to determine isotope ratios of the light hydrogen (H) and carbon (C) elements of the wax samples. In this first part of the investigation it was found that the combination of visual techniques, GC and IRMS was the most informative, apparently discriminating best.

The focus in this investigation was on white or ivory coloured common candles without further outside decorations such as embossing. Both tapered as well as cylindrical candles were relevant. These are sold under designations such as household, table, dinner or gothic candles. Depending on *e.g.* the manufacturing process as well as market preferences candles in general consist of a white or light coloured body of candle wax around the central wick and a thin outer layer that may be white or otherwise coloured. One of the advantages of this combination is that a manufacturer can use a single type of candle body and cater to market demands for variation (both directly from consumers as well as from chain stores ordering batches of private label candles) by applying a variation of coloured outer layers. Larger producers may in this way produce thousands of colours for their candles. This outside layer will in general have a different composition and a higher melting point than the main candle wax body. When the candle is lit, the outside layer will then melt later than the main body and act as a container for the molten wax material layer from the main body.

The differences in material composition between the main body and the outside layer in principle offer additional characteristics for discrimination. The main wax body typically will be a mixture of paraffins and saturated fatty acids, mostly stearic and palmitic acid. The outside layer almost exclusively consists of paraffins only.

In the second part of the investigation, 130 different boxes of candles were bought in a variety of consumer shops throughout the Netherlands during a short period of three weeks in February/March 2008. The main brands encountered are Bolsius and Gouda (two different brands from a single Dutch company) as well as a number of private label brands from Dutch chain stores. In addition to the direct acquisition of candle materials from the shops, manufacturers and managers at the headquarters of the chain stores were interviewed on potential handles for candle discrimination as well as on buying policies that may influence characteristics variability.

The IRMS and GC analytical methods were validated for these wax materials and candle wax composition variation was determined, both along the length of single candles, within candle boxes and in between candle boxes from a single brand. Apart from the variation in candle wax composition also visual characteristics were determined and it was recognized that candles had been produced using a number of different industrial candle manufacturing processes (extrusion, drawing, molding). The drawing process results *e.g.* in a typical layered structure (tree ring effect) of the candle cross section and in the extruded candle visual inhomogeneities may be observed reflecting the granular nature of the extruder feed.

From the IRMS and GC analytical results it was observed that variation was highest in between brands. For boxes of a single brand, inter box variation was much higher for private label brands than for the main single brand producers. These results reflect buying policies of chain stores for their private label brands. A few manufacturers are selected for a single private label brand to encourage competition and otherwise selected batches of candles may be acquired from other manufacturers.

Time dependency of results was investigated by acquiring another 27 boxes with similar candles a year after the first study, analyse these candles also by IRMS and compare results to the earlier results.

Compound-Specific IRMS of *n*-alkanes for Fingerprinting Stolen Diesel

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Background. Diesel theft in New Zealand is an increasing problem. Contractors working in remote locations are having machinery tampered with and mini-tankers drained. These incidents are very often accompanied by further crime such as willful damage and theft of tools and small items of equipment. The present case involved theft of diesel from a ski field. The ski field was burgled 4 times over 11 months. Two of those burglaries involved the theft of a large amount of diesel (2 700 litres). The offender appeared to be forensically aware, leaving very little evidence at the scene.

Police investigation led to a suspects house where several containers of diesel were found. The majority of diesel supplied in New Zealand comes from the single refinery at Marsden Point and so conventional GC-MS fingerprinting was considered to provide insufficient resolution for this case. Samples were therefore submitted to Isotracer Research at the University of Otago for IRMS analysis.

Results. The GC-C-IRMS of the *n*-alkanes provided a consistent fingerprint whereby samples of a common origin clustered together and were distinguished from samples of differing origin. One sample from the suspects house fell within the specifications of the samples from the ski field.

Conclusion. The evidence was accepted in court and the suspect subsequently pled guilty on all charges.

Oral Session on Controlled Materials – Drugs, Microbes and Plants

Stable Isotope Ratios of Marijuana from Brazil and Paraguay: Carbon and Nitrogen as Guides for Growth Conditions. Strontium Isotopes as References for Possible Geographic Origin

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Eleven marijuana samples from different localities in Brazil and one from Paraguay were processed and then submitted to IRMS to obtain $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ data. Results permit to conclude that all samples were outdoor-grown, using industrial fertilizers.

Replicas from the same samples were chemically processed before obtaining $^{87}\text{Sr}/^{86}\text{Sr}$. The aim is to compare these data to modeled $^{87}\text{Sr}/^{86}\text{Sr}$ rock data from growth localities in order to discuss the possibility to use these data for the geographical determination of plant growth.

Presentation
Withdrawn

Integrating Stable Isotope Ratio and Other Mass Spectral Data for Microbial Forensics

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The nascent field of microbial forensics requires the development of signatures to indicate various aspects of the production environment of microorganisms. We have characterized isotopic relationships between *B. subtilis* ATCC® 6051 spores and their growth environment using as a database the carbon, nitrogen, oxygen and hydrogen stable isotope ratios of a total of 247 separate cultures of spores produced on a total of 32 different culture media. We have analyzed variation within individual samples, between cultures produced in tandem, and between cultures produced in the same medium but at different times in the context of using stable isotope ratios as a signature for sample matching. We have correlated the stable isotope ratios of carbon, nitrogen, oxygen, and hydrogen of growth medium nutrients or water and spores and show examples of how these relationships can be used to exclude nutrient or water samples as possible growth substrates for specific cultures.

While stable isotope ratios of microorganisms provide a powerful tool for both sample matching and characterization of the growth medium, the power of stable isotope ratio data can be greatly enhanced by combining it with orthogonal datasets that speak to different aspects of an organism's production environment. The objective of our long-term effort is to develop Bayesian statistical frameworks for integrating disparate analytical measurements to characterize the production method of a microbiological sample without the need for comparison to known samples.

To construct such a framework, it is necessary to develop causal relationships between aspects of the growth environment and individual signatures obtainable from a microbiological sample. To date, in addition to establishing causal relationships relating spore stable isotope ratios to growth environment, we have also characterized the relationship between the elemental content of spores and the addition of certain metal salts to the growth medium by secondary ion mass spectrometry (SIMS), and developed targeted electrospray ionization (ESI) and matrix-assisted laser desorption-ionization (MALDI) mass spectrometric analyses that detect residual agar and blood components in spore samples.

We developed a Bayesian network that follows these causal relationships from culture medium recipe to spore signatures. The network was developed and tested on data from three replicate cultures of *B. subtilis* ATCC 49760 in broth and agar-containing versions of four different nutrient media. To test the network, data from SIMS analyses of *B. subtilis* 49760 produced in a different medium, from approximately 200 ESI MS analyses of *B. thuringensis* ATCC 58890 and *B. anthracis* Sterne grown in five additional media, and the stable isotope data from the 247 cultures of *B. subtilis* 6051 spores were used. This network was able to characterize *Bacillus* spores of varying species grown under multiple culture conditions with an error rate of less than 0.07 in characterizing carbon and nitrogen source, addition of metals, and presence of agar, and an error rate of 0.19 in characterizing the culture medium recipe.

The integration of multiple analytical techniques allowed us to maximize the amount of information obtained from unknown source microorganisms. The Bayesian network approach allowed us to combine scientific understanding with well established statistical methodologies to characterize a microbe's growth environment without the need for reference signatures. Similar approaches could be applied to data from other scientific disciplines, as well as to other problems of attribution.

Comparison of P2P Seizures Using GC/MS Impurity Profiling and IRMS

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Recreational use of illicit drugs as amphetamine is not uncommon in the Netherlands. Associated clandestine production of amphetamine takes place in illegal factories. 1-phenyl-2-propanone (P2P, benzylmethylketone) as precursor of amphetamine is often encountered at production sites and appears to be of interest for forensic investigations into production and trading networks. P2P seized in the Netherlands generally enters the country by smuggling from international operating organisations.

Characterization of P2P is commonly performed by organic impurity profiling using GC/MS. With this technique much information can be gained about the potential source, synthesis routes and quality of the precursor. However, when the seized P2P samples are of high quality, impurity profiling information diminishes. To obtain additional information from high quality P2P samples a pilot study is set up using IRMS to analyse the stable isotope ratios for a series of seized P2P materials. The combination of GC/MS and IRMS is a step forward for forensic source investigation of P2P as two independent techniques are used to chemically characterize P2P on different properties of the P2P samples providing additional information to interpret the results

Where impurity profiling is based on the presence of minor components, is IRMS based on analyses of the major P2P elements carbon, oxygen and hydrogen. A collection of P2P samples from ~80 different seizures was analyzed for their GC/MS spectra as well as their $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values. The measured samples cover different types of seizures, from complete factories to large scale smuggling from different European countries and possession. The isotope homogeneity of 'production batches' has been determined, based on large scale seizures with quantities of multiple 10 to 50 litre jerry cans of P2P. Within and between these drums no difference in the isotopic composition was detected, suggesting large (industrial) scale production. Overall a large spread was found for the stable isotope values indicating that discrimination between different batches and seizures is possible. Vice versa, for a similarity found in the stable isotope data and impurity profiling strengthens a potential link between cases. For intelligence purposes potential links can be used to map border crossing P2P trafficking routes.

Our study shows that impurity profiling data and IRMS data are often complementary. The strength of combining these two techniques is that whereas GC/MS results are most useful for higher amounts of impurities, IRMS results can still be used to discriminate pure P2P samples or samples with very low amounts of impurities. For intermediate amounts of impurities both techniques contribute to discrimination. For example if stable isotope ratios deviate, impurity profiles show a different GC spectra or signs of degradation/oxidation of the P2P.

Comprehensive Two Dimensional Gas Chromatography-Combustion IRMS (GC×GCC-IRMS) Instrument Principles for Rapid Isotope Analysis

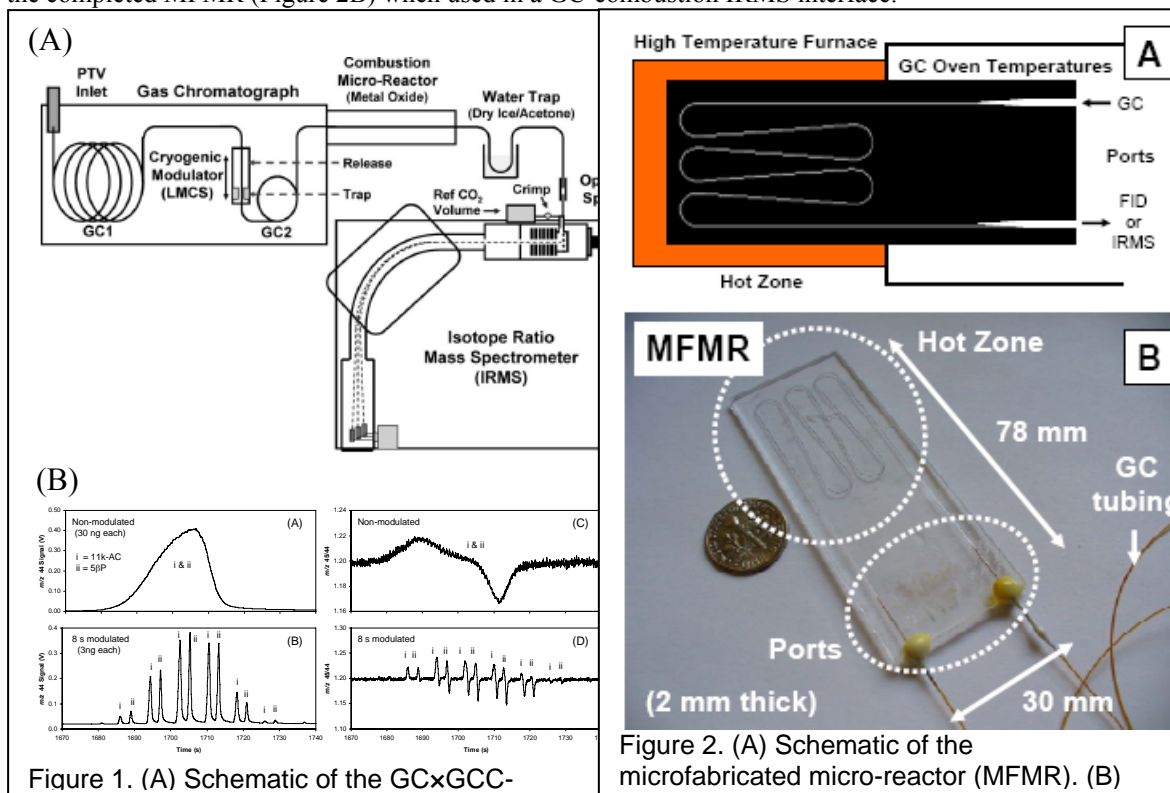
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Our laboratory is currently interested in advancing Gas Chromatography Combustion (GCC) IRMS for the measurement of ¹³C/¹²C in urinary steroids for sport doping. Traditional GC has insufficient resolution to separate many components in such complex mixtures; however, Comprehensive 2D GC (GC×GC) has substantially greater chromatographic peak number capacity, facilitating rapid sample cleanup. GC×GC has also been applied to molecular analysis of forensic samples, and its coupling to IRMS is expected to apply to forensic sourcing problems.

Generally, GC×GC employs two chromatographic columns with different properties operating in tandem, where the first column (GC1) separates normally (~30-60 min) and the second column (GC2) separates cryogenic slices from the first column very rapidly (~2-10 seconds). Challenges interfacing GC×GC to C-IRMS include the preservation of narrow peak widths required for fast GC separation in the second column and reconstruction of “sliced peaks” for precise isotope ratio calculation. A prototype GC×GCC-IRMS system was built (Figure 1A) by joining a GC and IRMS with a low dead volume interface and integration of a Longitudinal Modulation Cryogenic System (LMCS). Feasibility was initially demonstrated using a narrow inner diameter capillary tube combustion reactor, where peak shapes required for GC×GC were preserved (Figure 1B), with good precision and accuracy after sliced peak reconstruction.

Robustness to facilitate reliable, high performance operation requires further reduction of the i.d. of the reactor to reduce band broadening and improvement of the physical stability of the reactor at high temperatures. These issues were addressed by microfabrication of a micro-reactor (MFMR) in high purity fused silica. Microfabrication allowed the creation of long, narrow-diameter (56–209 μm) reactor channels in a relatively small surface area by using a serpentine design pattern (Figure 2A). The channels were filled with a Cu/Ni alloy, which was then oxidized. Integrity of the reactor at ~1000°C was maintained leak-free over a large temperature gradient and temperature cycling. Also, the peak shapes of fast GC plugs of CO₂ gas and methane were evaluated through the completed MFMR (Figure 2B) when used in a GC-combustion IRMS interface.



Stable Isotope Ratio Methodologies for Illicit Drug Intelligence Programs

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Illicit drug profiling provides law enforcement with information about the geographical origin of cultivated drugs such as cocaine and heroin, and the synthetic origin of amphetamine type stimulants such as methylamphetamine and 3,4-methylenedioxymethylamphetamine (MDMA). The Australian Illicit Drug Intelligence Program (AIDIP) – a collaboration between the National Measurement Institute and the Australian Federal Police – aims to assist the disruption of drug trafficking operations across the Australian border and monitor the diversion of legitimate industrial chemicals for illegal purposes.

Recent work has been undertaken to investigate the complementary application of Isotope Ratio Mass Spectrometry (IRMS) to profiling cocaine, heroin, methylamphetamine and MDMA. IRMS has the potential to be a strong discriminator of samples and give the ability to more accurately identify relationships between samples.

The effect of environmental conditions on the isotopic composition ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^2\text{H}$ and $\delta^{18}\text{O}$) of plants and their constituents has provided valuable strategic intelligence for determining the origin of cocaine. In addition to conventional profiling of minor tropane alkaloids and truxillines, the combination of bulk stable isotope ratio values obtained by EA/TC-IRMS allows the country of origin to be determined for the primary coca (*Erythroxylum*) growing regions along the Andean Ridge in South America.

Tactical comparison of samples within and between seizures is a further advantage of IRMS applied to the profiling of cultivated drugs. For heroin, studies demonstrating links between samples seized from different individuals will be presented that measured $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values by GC-C/TC-IRMS of diacetylmorphine, acetylcodeine and caffeine – a common adulterant used in the manufacture of South West Asian heroin.

The isotopic composition of synthetic illicit drugs is characteristic of the starting materials used and the synthetic processes employed. The AIDIP has extended previous work on methylamphetamine to include $\delta^2\text{H}$ analysis, as well as $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, in ephedrine and pseudoephedrine from different origins. Methylamphetamine samples synthesized via a number of common routes from ephedrine hydrochloride originating from natural *ephedra* extracts were found to have negative $\delta^2\text{H}$ values while those originating from the fermentation of benzaldehyde had positive $\delta^2\text{H}$ values.¹ Coupled with previous reports of fully-synthetic ephedrine having depleted ^{15}N content,² it is possible to determine the source of chemical precursors used in illicit methylamphetamine manufacture using EA/TC-IRMS.

Case studies illustrate the additional value of strategic and tactical intelligence derived from multi-element EA/TC-IRMS analysis of high purity (>95% as HCl form) amphetamine-type stimulants for which limited information was obtained using conventional profiling techniques.

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2. Makino, Y. *et al.*, *Bull. Narc.*, **57** (2005) 63.

Author Index

Agon, V.....	51	Doyle, S.....	54
Al Na'imi, K.....	29	Ehleringer, J....	9, 13, 14, 17, 18, 19, 20, 21, 22, 26, 36, 38, 39, 45, 60, 62
Alexander, M.....	70	Enright, L.....	13, 20, 21
Almond, M.....	16	Erkkila, B.....	36
Anderson, F.....	74	Farmer, O.....	75
Andrews, J.....	30	Fava, N.....	79
Aranda, R.....	34, 61	Fessenden, J.....	41
Arevalo, R.....	57, 58	Font, L.....	24
Armstrong, K.....	28	Frew, R.....	28, 35, 78
Asfaha, D.....	31	Galimov, E.....	32
Ash, R.....	48, 56, 57, 58, 64	Goren, Y.....	47
Ayalon, A.....	47	Hagopian, W.....	59, 67
Baker, A.....	53	Hayman, A.....	78
Baker, J.....	28	Hays, P.....	42
Bar-Matthews, M.....	47	Heagney, A.....	83
Barnette, J.....	45	Hearn, R.....	10, 63
Barrow, J.....	61	Heikoop, J.....	41
Bastos, M.....	79	Hendrikse, J.....	77
Bathgate, H.....	30	Hjernquist, M.....	24
Baxter, M.....	31	Hobbs Mehlretter, L.....	34
Becker, S.....	11	Hoitink, M.....	81
Bellucci, J.....	48	Holder, P.....	28
Benson, S.....	27, 43	Holdermann, T.....	11
Black, S.....	16	Hoogewerff, J.....	29, 30, 31
Blackledge, R.....	52	Horita, J.....	75
Bond, E.....	41	Howa, J.....	45, 60
Bowen, G.....	14, 18, 19, 26	Hsiao, G.....	69
Brenna, J.....	82	Hughes, S.....	71
Brooker, L.....	51	Hunsinger, G.....	59
Butler, T.....	72	Hurley, J.....	39, 62
Carman, A.....	75	Iñanez, J.....	48
Cawley, A.....	51, 83	Jahren, A.....	59, 67
Cerling, T.13, 17, 18, 19, 20, 21, 22, 36, 38, 39		Jarman, K.....	80
Chartrand, M.....	12	Jayatilake, M.....	56
Chesson, L.....	13, 17, 18, 19, 20, 21, 22, 36, 38	Jones, K.....	27
Clarke, J.....	30	Jordan, J.....	49
Clough, T.....	28	Jorgensen, M.....	13
Collins, M.....	83	Kaplan, J.....	13
Coplen, T.....	15, 49	Kawashima, H.....	65, 66
Dale, M.....	41	Kazlauskas, R.....	51
Dalpé, C.....	12	Kelly, J.....	70
Davies, G.....	24	Kennedy, C.....	14, 26
Davis, P.....	41	Kikuchi, N.....	66
Dekant, C.....	31	Klaassen, M.....	24
Dietz, M.....	34, 61	Koch, P.....	23
Dogger, J.....	77	Koeberg, M.....	44
		Kreuzer, H.....	39, 70, 75, 80

Kuder, T.	40	Salouros, H.	83
Kurahashi, T.	65	Sams, R.	70
Kuznetsova, O.	32	Santamaria-Fernandez, R.	10, 63, 73
Laincz, J.	42	Santos, R.	79
Landwehr, J.	15	Scheid, N.	11
Larson, T.	41	Schneiders, S.	11
Lima, B.	79	Schrader, M.	33, 77
Liu, Z.	26	Sevastyanov, V.	32
Lock, C.	44	Simmons, T.	29
Longmire, P.	41	Simpson, T.	43
Lott, M.	45, 60	Singleton, G.	49
Lovett, A.	30	Smith, A.	25
Mancini, L.	79	Stern, L.	34, 61
Mann, J.	72	St-Jean, G.	12
Martinez-Sierra, J.	10	Stroud, M.	41
McComb, K.	35	Sutka, R.	71
McCormick, M.	61	Swan, H.	83
McDonough, W.	48, 56, 57, 58, 64	Tipple, B.	36
McKinstry, C.	80	Tobias, H.	82
McLasky, V.	34	Tompkins, B.	75
Millet, M.	28	Ueckermann, H.	29, 30, 31
Millot, R.	37, 46	Valenzuela, L. 13, 17, 18, 19, 20, 21, 22, 38	
Moran, J.	70, 75	van Bocxstaele, M.	31
Mothershead, R.	61	van Breukelen, M.	33, 44, 50, 76, 77, 81
Muhammad, S.	78	van der Peijl, G.	33, 50, 76, 77
Mumaw, B.	57	van der Veer, G.	31
Négrel, P.	37	van Es, A.	33, 50, 76
Newburn, M.	70	van Grol, M.	77
Nic Daéid, N.	54	Van Hale, R.	28, 78
Nowell, G.	24	Veen, T.	24
Nowicki, K.	74	Vocke, R.	72
O’Grady, S.	13, 17, 18, 20, 21, 22, 38	Vogelpoel, F.	33
O’Reilly, W.	53	Vonhof, H.	24
Pacheco, W.	79	Vujic, S.	83
Parish, A.	34	Wagner, J.	13
Pearson, G.	24	Wahl, K.	80
Perkins, G.	41	Walker, S.	55
<u>Philp, R.</u>	40	Webb-Robertson, B.	80
Podlesak, D.	19, 20, 21	West, J.	39, 62
Poortman, A.	81	Wheatley, P.	23
Posey, R.	29	Wiarda, W.	33, 50, 76
Qi, H.	49	Widory, D.	46
Quetel, C.	31	Willis, S.	24
Raynaud, S.	16	Winston, B.	42
Rearick, M.	41	Wojtyk, J.	12
Remien, C.	13, 20, 21	Wolff, J.	63
Richman, B.	68	Zacca, J.	79
Roux, C.	27	Zhang, Y.	82
Rummel, S.	31	Ziegler, S.	42
Saad, N.	68, 69		