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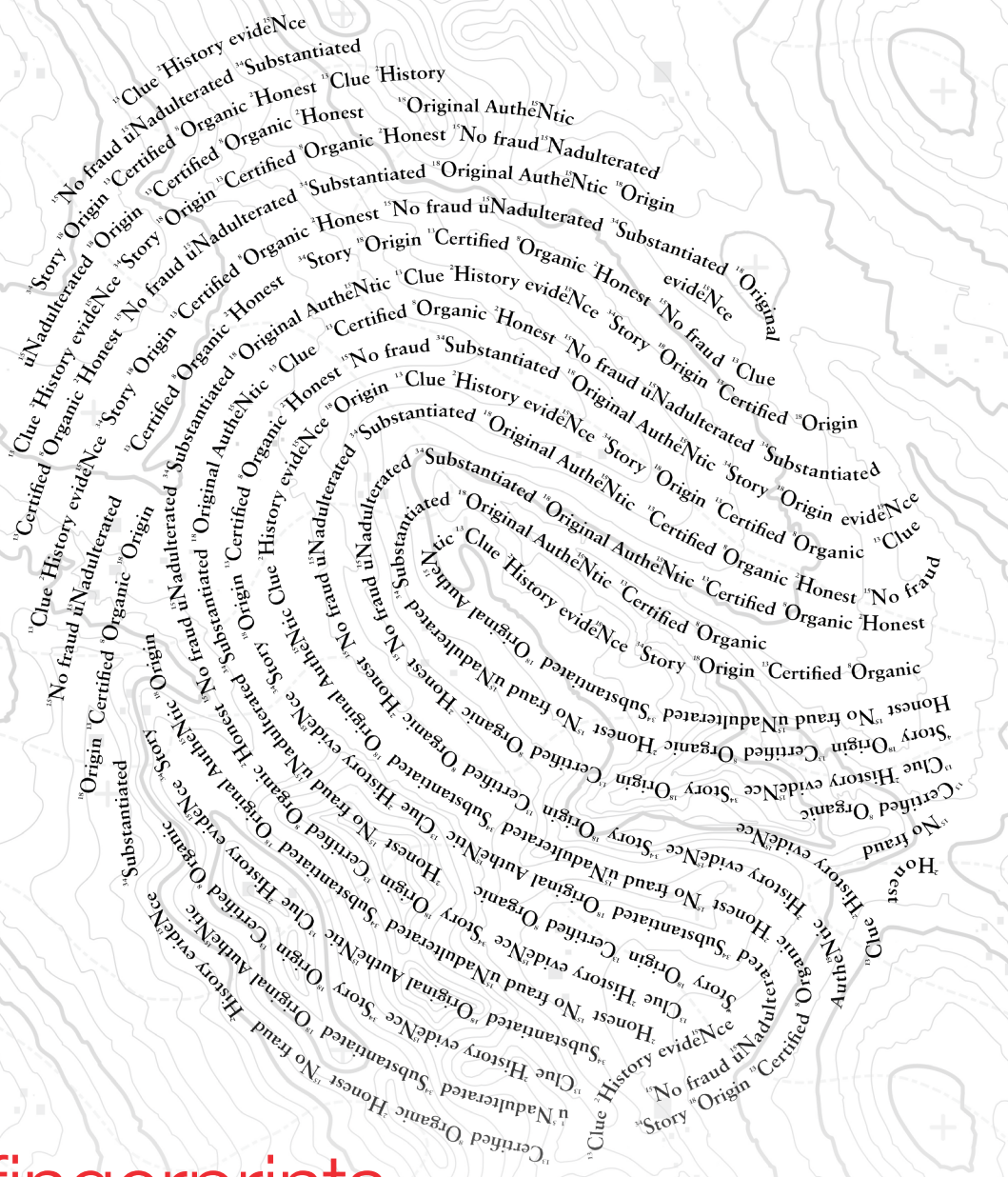

Isotope fingerprints for forensics investigations

Detecting ^{13}Clues, tracking ^{18}Origin, unraveling ^{2}History with isotope fingerprints

ThermoFisher SCIENTIFIC

Isotope fingerprints for forensic investigations

Forensic investigations examine sample materials to determine how similar or different they are, or to identify the origin of the material. Identifying the difference in a material or where it comes from can be achieved because materials have a unique chemical signature, like a fingerprint. To visualize this fingerprint, Isotope Ratio Mass Spectrometry (IRMS) is used, measuring the stable isotopes of sample material that are essentially chemically identical. Unlike other types of inferential evidence in forensic investigations (e.g., bite marks, impression marks from tires or footwear, handwriting), isotope measurements are quantitative empirical evidence that are reproducible and easy to validate. The application of isotope fingerprints to forensic investigations has become more commonplace because there is a need for a rigorous scientific foundation underpinned by sound analytical techniques. Application areas include forensic investigations on human, criminal, environmental, ecological, food and archaeological materials.

Isotope fingerprints in forensic materials are related to natural processes and geographical regions and can define differences in sample materials. This means that forensic sample materials can be put into a geographical context, so that their origin can be traced, or understood with respect to a specific process or set of processes in nature, such as botanical (timber, food, skeletal remains), dietary and food web variations (skeletal and animal remains, human and animal tissue) and geographical location (skeletal remains, narcotics, explosives, packaging, gemstones). Table 1 provides a non-exhaustive summary of isotope fingerprints in forensic applications. These natural processes can be traced using carbon, nitrogen, sulfur, oxygen and hydrogen isotope fingerprints encoded in the sample materials. However, in the case of explosives, these isotope fingerprints trace factory production efficiency and processes.

Table 1. Isotope fingerprints for forensics investigations.

Isotope Fingerprint	What is the biogeochemical interpretation?	Example forensic interpretation	What sample types can be analyzed?
Carbon	Botanical processes (C3, C4 and CAM Photosynthesis), plant rate of uptake of carbon (differentiate region plant is from, such as tropical vs. temperate), source rock geology, factory production processes/batch processes	Human (dietary preferences, travel history, and provenance), food (labelling authenticity) tracing packaging, arson	Bones, teeth, hair, nails, food, timber origin, oil, narcotics, cellotape, matchsticks
Nitrogen	Nitrogen fixation (trophic level differentiation: herbivore vs. carnivore vs. omnivore), factory production processes	Human (dietary preferences, travel history, and provenance), food (labelling, authenticity)	Bones, teeth, hair, nails, food, explosives, oil, narcotics
Sulfur	Incorporated into plant and animal tissue from bedrock uptake/weathering, atmospheric deposition (sea spray, geological origins, pollution) and microbial activity	Human (dietary preferences and provenance), food (origin)	Bones, teeth, hair, nails, food, timber origin, human and animal tissue, oil
Hydrogen	Principally related to local-regional rainfall, or water transport regimes, and hence geographical area, factory production processes/batch processes	Human (travel history and provenance), synthetic and narcotics (geographical origin), food and beverage (authenticity and origin), tracing packaging, arson	Bones, teeth, hair, nails, animal horn, narcotics, food and beverage, timber origin, oil, matchsticks
Oxygen	Mainly related to local-regional rainfall, or water transport regimes, and hence geographical area, factory production efficiency	Human (travel history and provenance), synthetic and narcotics (geographical origin), food and beverage (authenticity and origin), tracing packaging, arson	Bones, teeth, hair, nails, animal horn, narcotics, food and beverage, timber origin, explosives, matchsticks

The application of isotope fingerprints in forensics brings unique capabilities to the laboratory and to the forensics field that increasingly demands a quantitative empirical evidence base that is reproducible and easy to validate. Applying isotope fingerprints to forensic questions allows investigators to provide a unique characterization of the sample material and so trace reactants, chemical pathways and reaction conditions, relative to natural processes, and then compare materials of interest to others collected, or to an authentic reference material[1]. In addition, investigators may also implement predictive models for environmental parameters, such as rainfall, geological bedrock, temperature, land use, for example[1]. From this basis, using isotope fingerprints makes it possible to determine similarities between different drug seizures and authentic material and to follow trafficking routes to their original source[2]. The same principle can be applied to other criminal materials such as explosives[1], artefacts and gemstones, human remains, human and animal migration and movements, oil spills, food and beverage origin and authenticity, synthetic drugs, arson investigations and plant and wood product origin, and be used to answer questions on material origin and authenticity[1].

Analytical solution for detecting isotope fingerprints

IRMS works by measuring the "isotope fingerprint" of a sample, a unique chemical signature that changes from sample to sample. There are a number of approaches to preparing sample materials for isotope analysis. However, the fundamental process for IRMS is the conversion of a solid or liquid sample to a gas under high temperature.

In the case of EA-IRMS and GC-IRMS the conversion of the sample to a gas is performed by two processes: combustion and pyrolysis.

Combustion, burning the sample at around 1000 ˚C with oxygen, is used to evolve carbon, nitrogen and sulfur from the sample in the form of N^2, CO_2 and SO_2. Pyrolysis, breaking down the sample at 1400 ˚C in a reductive environment, is used to evolve hydrogen and oxygen from the sample, in the form of H2 and CO. After the gases are produced, they are separated from one another using gas chromatography and then transferred in a continuous gas flow to a detector that measures the isotope fingerprint of the sample. In addition, gas samples can be directly analyzed. The dedicated solutions of the Thermo Fisher Scientific™ stable isotope portfolio are designed to offer different capabilities and performances, with dedicated features for the coupling to the Thermo Scientific™ IRMS Systems, according to the varying analytical needs of laboratories working for routine and research applications:

- the Thermo Scientific™ EA IsoLink™ IRMS System, for analysis of bulk sample material;
- the Thermo Scientific™ GC IsoLink II™ IRMS System, for analyzing specific compounds from a bulk sample material;
- the Thermo Scientific™ LC IsoLink™ IRMS System, for analyzing specific compounds from a bulk sample material in liquid form;
- the Thermo Scientific™ GasBench II System, for the analysis of gas samples evolved from bulk sample materials.

For more information read SN30453

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Application contents

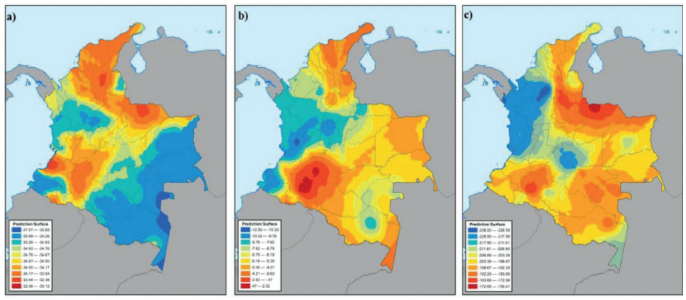
For more information read AB30580

Tracing the geographical origin of cocaine

Cocaine is one of the world's most widely used narcotics and this widespread use and abuse has resulted in more investigations aimed at tracing the coca cultivation regions and identifying exportation routes of the illicitly isolated cocaine. Tracing the origin of cocaine has previously been achieved at the regional scale[1], however, as a result of a significant expansion of coca cultivation and movement for processing and distribution, the identification of cocaine origin at the sub-regional scale has become increasingly difficult. Despite the complexities evident, it has been shown that isotope fingerprints in seized cocaine provide an enhanced insight that allows the coca cultivation region to be identified when combined with trace alkaloids. This application note is a summary of the work by Mallette et al (2016) and focusses on the isotope fingerprint data from coca leaves and seized cocaine samples. Further data on trace compounds, statistical data analysis and the analytical procedures used are presented by the authors in detail in their publication[1] and the interested reader is directed there for full details.

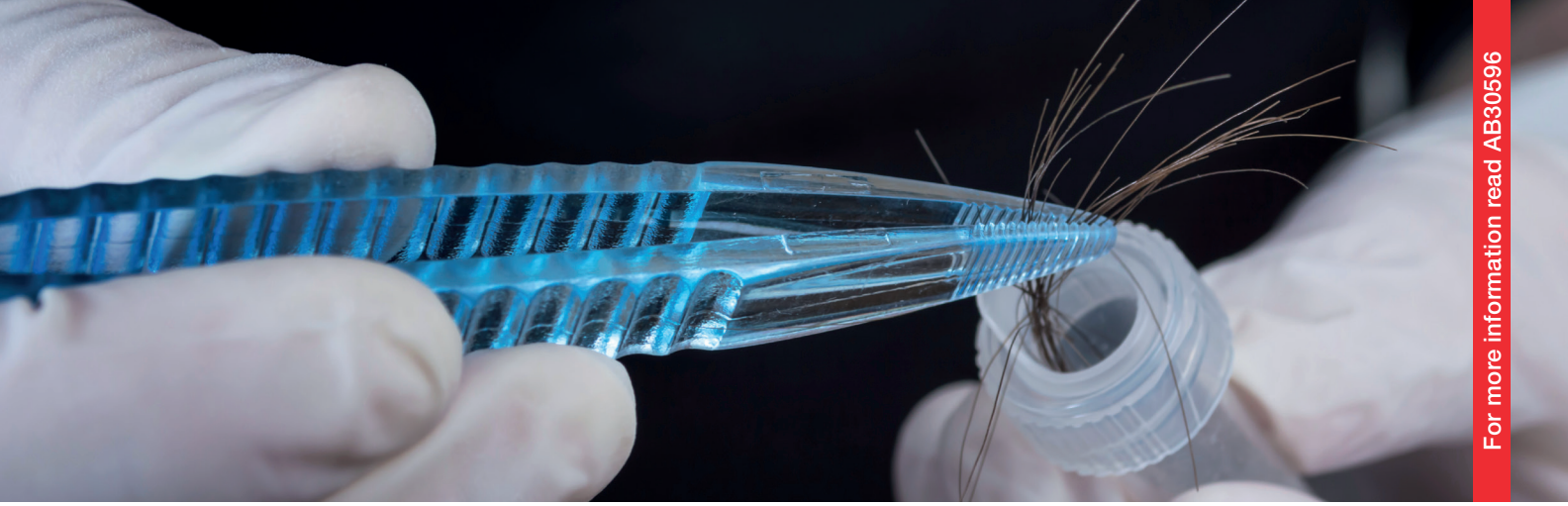
Isotope fingerprints of coca plants and cocaine

The carbon and nitrogen isotope fingerprints ($\delta^{13}C$ and $\delta^{15}N$ values) in coca plants follow the predicted pattern as they relate to environmental factors. The carbon fingerprints generally follow changes in elevation associated with temperature and partial pressure of CO_2 along the altitudinal transect, whilst nitrogen fingerprints vary according to changes in local precipitation and soil type, and conditions therein, that directly affect local nitrogen cycling. The hydrogen and oxygen isotope fingerprints ($\delta^{2}H$ and $\delta^{18}O$ values) of seized cocaine can be utilized to help trace geographical origin. The coca plants, from which cocaine is illicitly produced, carry a local-regional fingerprint primarily derived from the



Example of cocaine isoscapes from Colombia showing carbon (a), nitrogen (b) and hydrogen (c) isotope fingerprints.

hydrological cycle, which is associated with local-regional rainfall, but can also be influenced by cultivation practices, soil processes and geological characteristics of the local area, altitude and proximity to the shoreline[3]. The oxygen and hydrogen isotope fingerprints change in rainfall as you move further inland from the shoreline and with increasing altitude because the heavier isotopes are the first to be released from the clouds. This effect can be tracked in the oxygen and hydrogen isotopic fingerprints of leaves of the coca plants. Importantly, the isotope fingerprint does not change during the isolation of cocaine from the coca leave itself, meaning that the isotope fingerprint of the isolated cocaine reflects the environment from which the coca cultivation occurred. This, therefore, provides a framework for tracing the seized cocaine back to its origin.



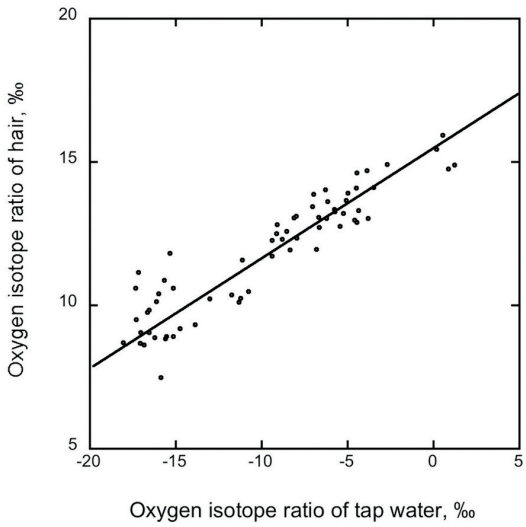
For more information read AB30596

Tracing human provenance using hydrogen and oxygen isotope fingerprints

One investigation area that is part of criminal forensics is human provenance: where has a person been and what were their movements? This is a critical question that sometimes cannot be answered completely with traditional evidence gathered by law enforcement agencies. In such instances, stable isotope analysis, or isotope fingerprinting, has been shown to provide vital important additional evidence that has been able to successfully trace human movements and even bring clarity to homicide cases. Generally, this is achieved by being able to detect the oxygen isotope fingerprints locked in the hair, teeth and bones of humans, which has a strong relationship with local drinking water. By extension, the same concept can be applied to anthropological studies.

Isotope fingerprints of human hair

The hydrogen and oxygen isotope fingerprints ($\delta^{2}H$ and $\delta^{18}O$ values) of human hair can be utilized to help with human provenance, tracing where a human has been based on their dietary intake of water, either via drinking water or water consumed within food stuffs. The primary protein in hair is keratin and during keratin synthesis in the hair follicle, the protein $\delta^{2}H$ and $\delta^{18}O$ values should be influenced by several factors, including dietary (water intake), atmospheric oxygen, and water derived from metabolism. In this study it was hypothesized that variations in the nonexchangeable $\delta^{2}H$ and $\delta^{18}O$ values in human keratin could provide insights into water and human diet across geographical regions if the hydrogen and/or oxygen isotopes from these tap water sources were recorded in the keratin of human hair.



A plot of oxygen isotope ratios in local tap drinking water versus human scalp hair from 18 states across the USA.

Local tap water fundamentally carries a local-regional fingerprint primarily derived from the hydrological cycle, which is directly associated with local-regional snowfall or rainfall, but can also be influenced in arid regions by water transferred across basins. The oxygen and hydrogen isotope fingerprints change in rainfall as you move further inland from the coast and with increasing altitude because the heavier isotopes are the first to be released from the clouds[3,4]. Consequently, there is a variation in $\delta^{2}H$ and $\delta^{18}O$ values across geographical regions, which subsequently relates to local-regional tap water. The consequence of this is that the $\delta^{2}H$ and $\delta^{18}O$ values in human hair are highly correlated with tap water, providing a strong framework for human provenance research.

Tracing origin of explosives using carbon, hydrogen and oxygen isotope fingerprints

The Bureau of Alcohol, Tobacco, Firearms and Explosives (ATF) states that "tracing is the systematic tracking of explosives from manufacturer to purchaser (and/or possessor) for the purpose of aiding law enforcement officials in identifying suspects involved in criminal violations, establishing stolen status, and proving ownership". Over the years, stable isotope analysis, or isotope fingerprinting, has shown to be a valuable technique to provide unique information on the origin of sample material, though their application in the investigations requiring the provision of evidence to a Court is very limited in criminal cases. However, identifying and tracking explosives to support counter-terrorism efforts is critical for national and international security.

Benson et al. (2009) employed isotope fingerprints in their study on organic peroxide explosives, with a particular focus on triacetone triperoxide (TATP) and pentaerythritoltetranitrate (PETN). The objective was to assess whether isotope fingerprints could differentiate samples of TATP that had been manufactured utilizing different starting materials and/or manufacturing processes and, with respect to the use of PETN in detonators, detonating cord, and boosters, to differentiate PETN samples from different sources.

This application note is a summary of the work by Benson et al. on the studies on origin of explosives. Specifically, it focuses on carbon, hydrogen and oxygen isotope fingerprint data. Further data and data analysis, alongside the full analytical procedures used are presented by the authors in detail in their publication.

Isotope fingerprints of explosives

TATP can be derived from household chemicals - acetone, hydrogen peroxide, and strong acids - all of which are easily obtained at hardware and beauty supply stores. Its use in improvised explosive devices, alongside other peroxide-based explosives such as hexamethylene triperoxide diamine (HMTD), is becoming more prevalent, as seen in recent high-profile incidents. As the use of homemade explosives, such as TATP, in improvised explosive devices becomes more prevalent, the ability of law enforcement to link a precursor, such as acetone, to a clandestine lab or possibly to the explosive itself is of forensic interest. The carbon and hydrogen isotope fingerprints in TATP are closely linked to the carbon and hydrogen isotope fingerprints in the precursor acetone, indicating that acetone may well be a good proxy for generating a background dataset for TATP. Further, the oxygen isotope fingerprints derive from the hydrogen peroxide precursor.

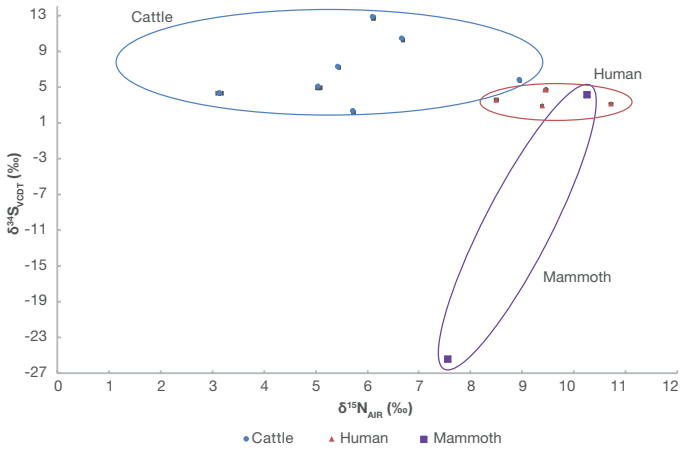
For more information read AB30550

Tracking human and animal dietary habits using isotope fingerprints recorded in bone collagen

Measurements of nitrogen and carbon stable isotopes (hereafter $\delta^{13}C$ and $\delta^{15}N$) in bone collagen have been interpreted reliably as an indicator of human and animal diets because they primarily reflect the protein fraction of the consumer's diet. It may also be possible to use $\delta^{13}C$ and $\delta^{15}N$ from mammal bone collagen records to track movement and past climate changes as vegetation sources (and hence food sources) change with temperature and aridity. More recently, sulfur stable isotopes (hereafter $\delta^{34}S$) have also been employed in dietary studies and may also be used to trace geographic origins of humans and animals because of their relationship to the underlying geology. Most research, however, has focused on $\delta^{13}C$ and $\delta^{15}N$, with far fewer studies incorporating $\delta^{34}S$. A key challenge to simultaneous $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ analysis in bone collagen was the accurate and precise analysis of small concentrations of sulfur (around 0.2-0.3%). In this application note, we show $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ data from bone collagen measured using the Thermo Scientific EA IsoLink IRMS System. The challenge of sulfur analysis is overcome and an insight on animal and human diet trends is observed.

$\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ isotope fingerprints of bone

The $\delta^{13}C$ and $\delta^{15}N$ fingerprints in bone reflect the isotopic composition of the diet of the consumer, implying that it can be used as a way to reconstruct or trace diet. In addition, $\delta^{34}S$ fingerprints are used to account for the amount and origin of protein in the diet, which reflects the environment form which the plants/tissue was grown.



$\delta^{15}N$ and $\delta^{34}S$ showing separation of collagen type as a function of diet.

Therefore, in conjunction with $\delta^{13}C$ and $\delta^{15}N$ fingerprints, $\delta^{34}S$ fingerprints can provide an overview of the consumer diet and the source location of the foods. Here, our data suggest a diet strongly influenced by C3 and C4 plants derived from terrestrial habitats (cattle). However, the $\delta^{15}N$ fingerprints in the human bones indicate a diet influenced by marine based fauna, particularly fish.

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