Isotope Ratio Mass Spectrometry - An Explosive Future in Forensics

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Overview

Isotope ratio mass spectrometry (IRMS) is a relatively new application in forensic science.

The technique has great importance in forensic applications due to it's enormous potential for verifying sources of materials.

Current applications of the technique include archaeology, environmental, drugs, explosives, accelerants, food research and pharmaceuticals, to name a few.

Figure 1. FEL IRMS instrumentation. Thermo Finnigan De Delta^{plus} XP with a Costech Elemental Combustion System, Thermo Finnigan TC/EA and a Thermo Finnigan Conflo III Interface Unit

Background:

Isotopes are uncharged atoms of the same element with different masses. This occurs due to different numbers of neutrons existing in atoms with the same numbers of protons and electrons.

As a result of the differences in mass, some isotopes are incorporated into materials more readily than others causing an isotopic ratio to be established in that material, this process is known as fractionation and may occur by a number of mechanisms.

The ratio of isotopes depends on the environment and processing of a material, and hence measurement of the isotopic signature of a material can give valuable information relating to it's origins. Greater confidence about the origins of a material can be achieved by measuring the isotopic signatures of more than one element to produce multi-dimensional results.

δ (delta) notation is used to represent the ratio of the heavier isotope compared with the lighter isotope in the sample relative to a standard. δ values are expressed in units of ‰ (per mill) according to the following equation which compares the isotope ratio in the sample (R_S) to that of a reference material (R_R). International reference materials are used as a universal calibration source, so results may be directly compared.

$$\delta = \left[\left(\frac{R_S}{R_R}\right) - 1\right] x1000$$

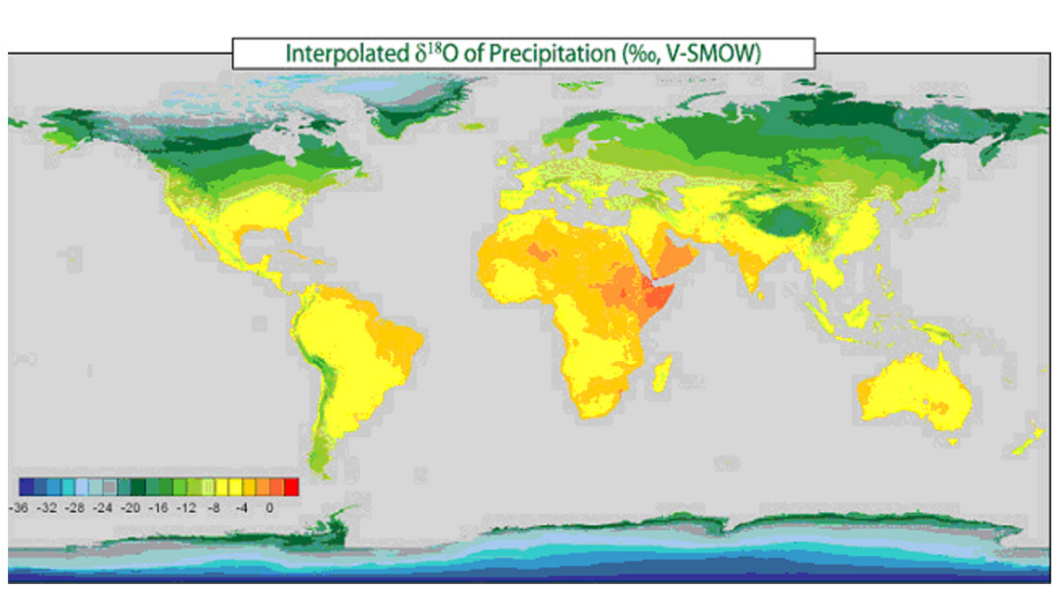
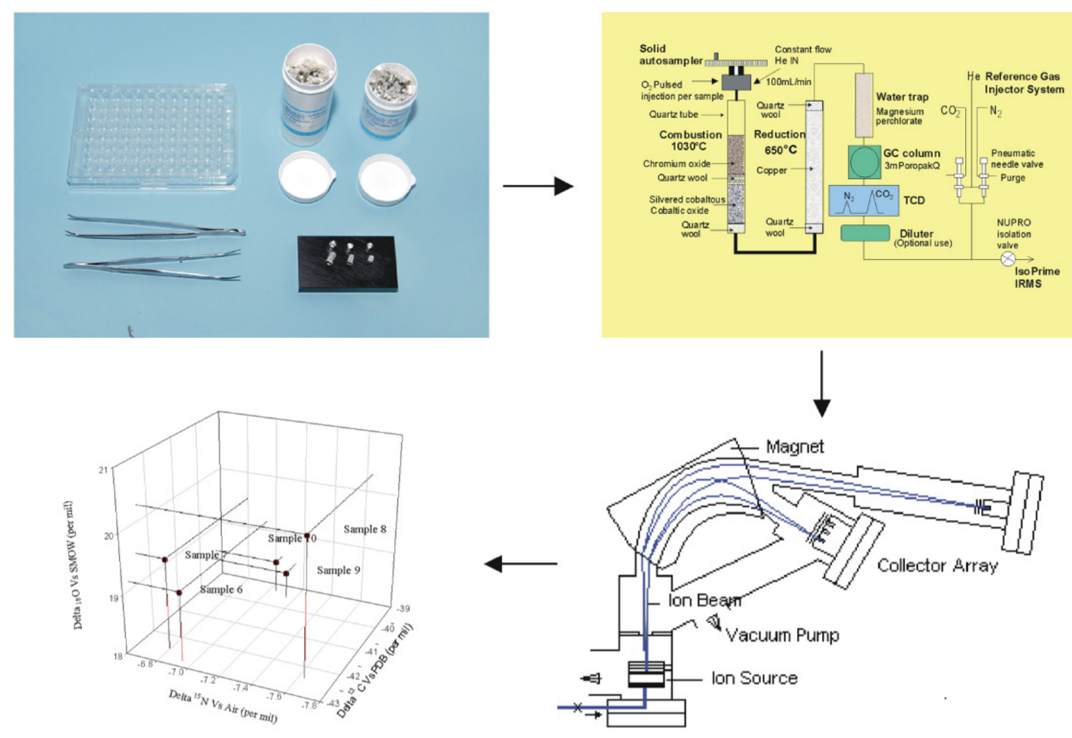


Figure 2. Diagram showing variation of delta values for isotopic abundance of oxygen-18 in rain water. [5]



Scheme 1: How an IRMS system is used for sample analysis 1) Samples weighed into tin capsules, 2) Combustion/Pyrolysis of sample 3) IRMS analysis 4) d values obtained for analysis of results.

Forensic Applications of IRMS

IRMS evidence was first used in a UK court of law in 2002, in a case establishing the identity and batch specificity of ecstasy tablets. This case has paved the way for many future uses in a variety of forensic areas.

Carbon, nitrogen and hydrogen isotopes are all present in the human body along with trace elements such as strontium and lead [1]. The isotopic ratios of these elements vary depending on the region in which a person lives due to the natural variation of isotopic ratios (Figure 2). Diet, and geography affect the isotopic signatures in body tissue such as fingernails, hair, bone and teeth, providing useful data in forensic fields for the determination of geographic origin. For example the diet of person living in America is different to that of a person in Northern Europe, and therefore we would expect samples from these two individuals to have distinguishing delta values for the ratios of 'organic' elements (Figure 3). Isotopic signatures in hair may be representative of changes to environment or diet occurring in a timeframe of months, whereas isotopic signatures in bones may be representative of environment and diet years previously depending on the bone selected. Teeth provide information relating to a persons situation throughout adolescence and can therefore retain geographic information for over half a century depending on the age of the donor.

In a recent murder case IRMS was employed to assist detectives with the identification of the victim's origin. After DNA analysis failed to match a potential relative of the victim, the question of whether the victim originated from Northern Ireland became a key focus in the investigation. Police and scientists used data comparing bone and hair samples to rule out the possibility that the victim originated from Northern Ireland and further determined the approximate origin of the body as a location in Eastern Europe. Further to this, a potential timeline was ascertained from comparisons of water at the suspected origin (location X), water in Northern Ireland and water in the victims hair, suggesting that the victim had arrived in Northern Ireland approximately 10-20 days before their death (Figure 4)[2].

IRMS was also recently employed in the case of 'Adam', the torso found in the Thames River in London. Samples of Adam's bones were used to determine ratios of strontium isotopes. The signature indicated rocks older than 2,500million years and narrowed the search area to West African regions including large areas of Nigeria. Adam's origin was determined to be within a corridor of Nigeria stretching 100 miles by 50 miles [3] [4].

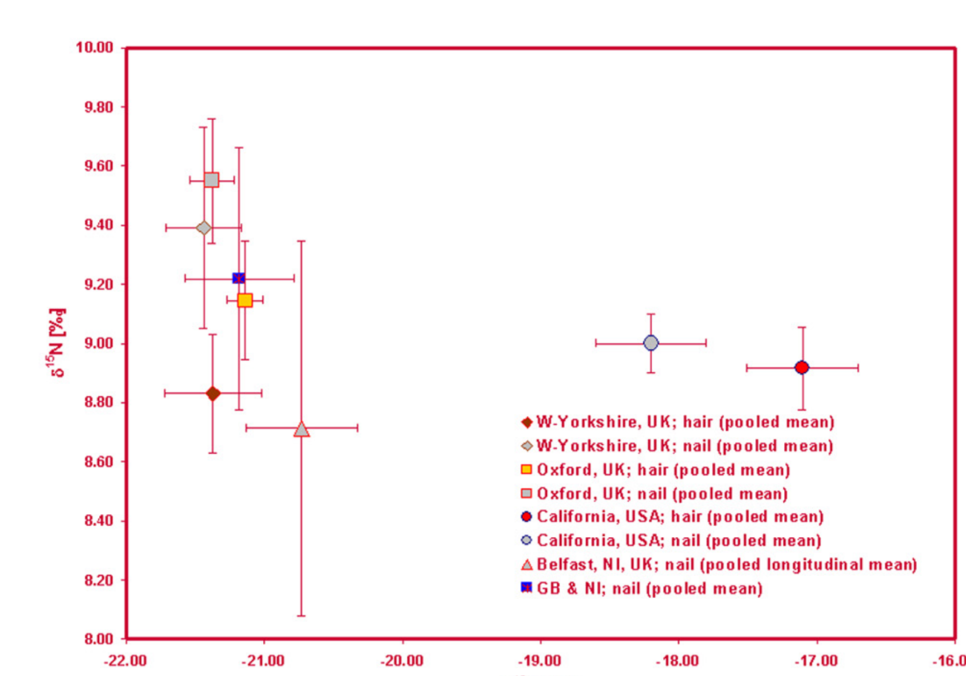


Figure 3. Comparison of carbon and nitrogen isotope ratios in hair and nail samples from donors of different regions. (Belfast, NI, UK pooled longitudinal mean represents 6 measurements taken over a period of 3 months, of people who have lived in Belfast for at least 1 year but have different ethnic origins, over a period of 3 months, all other points measured at one time) [2]

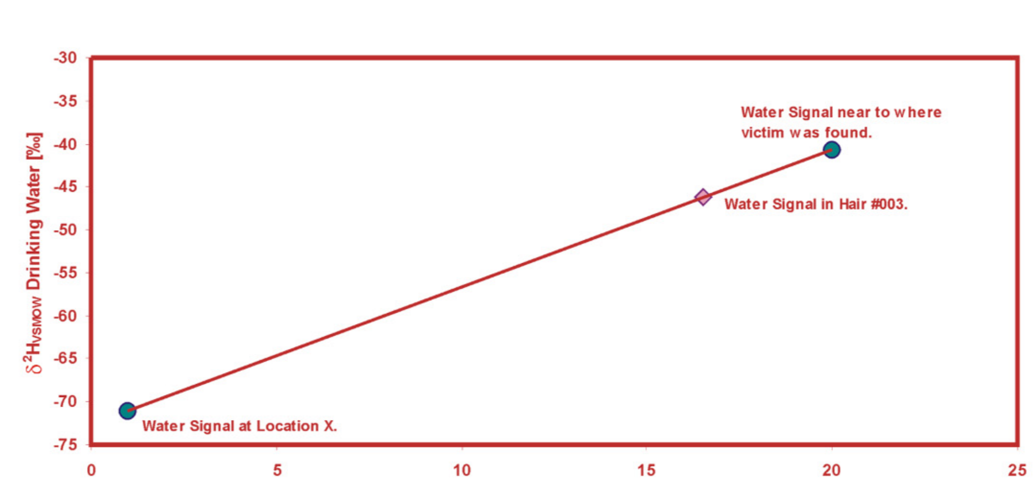


Figure 4. Potential timeline from hair giving an indication of how long the victim had been in Northern Ireland [2]

IRMS work at the Forensic Explosives Laboratory

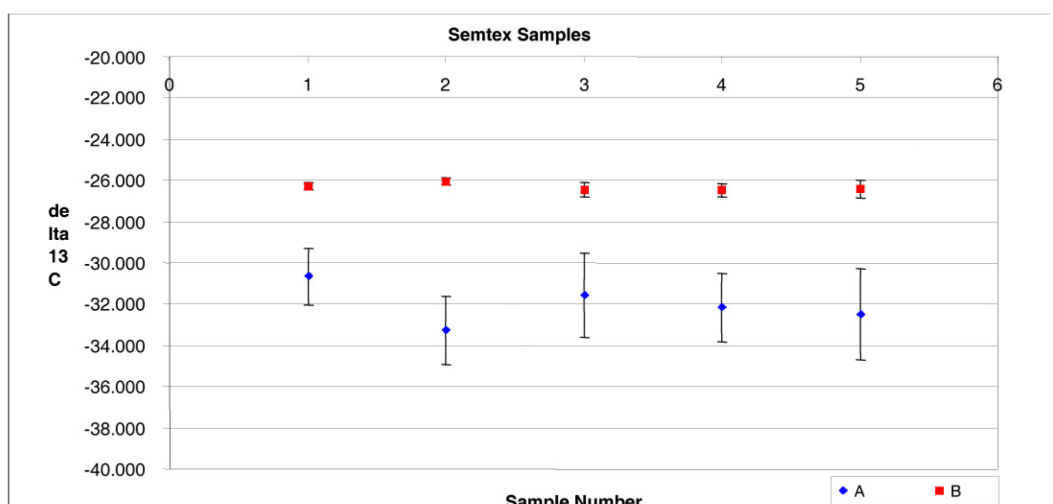
The Forensic Explosives Laboratory (FEL) is currently optimising and validating methods for analysis of carbon, nitrogen, oxygen and hydrogen isotopes in energetinc materials. The instrumentation at the FEL is a Thermo Finnigan Delaplus XP, with two Costech elemental combustion systems (C, N & S), a Thermo Finnigan TC/EA (H & O) and a Conflo III Interface. (Figure 1)

Studies so far have included:

- Bulk analysis of explosives from a number of different sources
- Homogeneity studies (Sticks of PE4, casts of TNT, chlorate)
- Blind study using PE4 (unknown sample correctly identified)
- Batch Variation (RDX, Semtex)

Future work at the FEL:

A study of the effects of recovery, extraction and clean-up techniques on the isotopic signatures in a sample is planned as well as the determination of whether pre-explosion material can be directly compared with the same material post explosion.
In addition to this the FEL plans to develop a database of IRMS analyses of a wide range of explosives from different locations and batches, to assist with future identifications. It is hoped that this database will be extended internationally through work and collaboration between forensic laboratories and manufacturers, with the assistance of the FIRMS network, referred to below.



BATCH		HC	BIND	PETN	RDX	EXP	δ n=6	s
A	1	11.5	2.7	47.9	37.9	85.8	-30.661	0.692
	2	11.2	3.4	47.1	38.3	85.4	-33.285	0.819
	3	11.1	2.9	46.5	39.5	86.0	-31.585	1.017
	4	10.8	3.1	48.4	37.7	86.1	-32.180	0.838
	5	11.1	2.7	46.7	39.6	86.3	-32.519	1.101
						x	**-32.046**	
						s	**0.988**	
						%	**-3.084**	
B	1	11.4	2.6	0.0	86.0	88.0	-26.282	0.075
	2	11.4	2.5	0.0	86.1	86.1	-26.045	0.093
	3	10.8	2.5	0.0	86.8	86.8	-26.466	0.173
	4	10.7	2.6	0.0	86.8	86.8	-26.476	0.152
	5	11.1	2.6	0.0	86.3	86.3	-26.424	0.225
						x	**-26.339**	
						s	**0.18153**	
						%	**-0.6892**	

Figure 5. Semtex sample analysis. Five independent sources of each of the batches of Semtex samples were run with 6 replicates of each giving details of homogeinity and batch specificity.

The FIRMS Network

The Forensic Isotope Ratio Mass Spectrometry (FIRMS) Network was established in 2002, uniting researchers, end users, instrument manufacturers, police and legal representatives in the task of developing this powerful technique and raising awareness in the scientific community. In September 2002 the first international FIRMS network conference was held which concentrated the areas of IRMS research, on meeting the end users requirements. Part of the outcome of the conference was the establishment of three working groups in the fields of explosives, drugs and general forensics. Members are kept informed about international progress through the network website and newsletter.

Further information about the FIRMS network and the conference can be found at http://www.forensic-isotopes.rdg.ac.uk or by contacting the network co-ordinator at firms@dstl.gov.uk

Acknowledgements and References:

[1] "Forensic applications of 'Isotope DNA'". Discussion document written for NCF. Wolfram Meier-Augenstein, Environmental Engineering Research Centre, Queen's University Belfast.

[2] "Forensic Applications of Stable Isotope Technologies". Conference presentation. Wolfram Meier-Augenstein, Environmental Engineering Research Centre, Queen's University Belfast.

[3] "Torso in the Thames, Scientist helps murder case" Cambridgeshire Constabulary Press Release (http://www.cambs.police.uk/camops/press_releases/press_releases.asp?ID=1028)

[4] RedNova News 08 August 2003. (http://www.rednova.com/news/stories/2/2003/08/08/story102.html)

[5] "Spatial distribution of d18O in meteoric precipitation." Bowen, G. J. and Wilkinson, B. (2002) Geology 30 (4): 315 - 318.

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