Contents lists available at ScienceDirect



Forensic Chemistry



journal homepage: www.elsevier.com/locate/forc

Isotope ratio mass spectrometry in forensic science applications

Mayara P.V. Matos^a, Glen P. Jackson^{b,c,*}

^a Department of Biology, West Virginia University, Morgantown, WV, United States

^b Department of Forensic and Investigative Science, West Virginia University, Morgantown, WV, United States

^c C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV, United States

HIGHLIGHTS

- Review of forensic applications of isotope ratio mass spectrometry publications since 2009.
- Includes details on good practices for calibration, quality assurance and uncertainty assessments and reporting.
- Review is organized into 10 different forensic science disciplines.

ABSTRACT

This review highlights advances in the application of isotope ratio mass spectrometry (IRMS) to materials of interest to the forensic community. We give special attention to the natural abundance differences in the stable isotopes of carbon, nitrogen, hydrogen and oxygen because they are the most abundant and informative elements in typical forensic casework. We also present some of the recent developments in normalization, error reporting and data analysis, which together provide a more scientific and robust foundation for admissibility in court. The review focusses on research published in the last decade and is organized into 10 major sections, including human provenancing, wildlife forensics, environmental forensics, seized drugs, ignitable liquids, explosives, food forensics, poisoning, questioned documents and miscellaneous applications.

1. Introduction

The ability to unravel the source of chemically indistinguishable substances has made isotope ratio mass spectrometry (IRMS) an indispensable tool in a variety of scientific disciplines, and especially in forensic science [1-3]. There are many excellent reviews and monologs on the theory, development, and application of stable isotope analysis (SIA) in different forensic science areas of study [4-13]. Herein, we do not attempt to be so comprehensive. Instead, we focus on the most recent, novel and impactful forensic applications, including new aspects of data analysis and reporting. In the last decade, IRMS, in combination with improved chromatographic techniques, has provided advances in diverse areas of forensic science, including sample preparation techniques that have enabled more reliable or meaningful discrimination between samples. The review is organized into ten major topical areas of forensic interest. Most of the citations are for applications that involve source provenance and sample classification, but some articles report on better understanding the fractionation of isotopes within or between certain substrates.

Since its foundation in 2002, the Forensic Isotope Ratio Mass Spectrometry Network (FIRMS) has spearheaded the application of IRMS to forensic casework. FIRMS has been organizing triennial conferences, providing forensic practitioner approvals, conducting interlaboratory proficiency tests [2,14], presenting guidance on suitable reference materials (RMs), and offering a "Good Practice Guide for IRMS" (GPG) to assist practitioners with the essential principles of the instrument operation, quality assurance, troubleshooting and data management [15]. The FIRMS Network often publishes a special issue in an analytical or forensic science journal following each triennial conference, and these special editions are a rich source of forensicallyrelevant IRMS literature for anyone interested in the topic.

Relating to the FIRMS Network, Carter and Fry [16] conducted a series of inter-laboratory tests within FIRMS Network members to first assess the variance, quality control and quality assurance protocols of different laboratories, and then to guide improvements in the reproducibility of measurements between laboratories. Problems related to homogeneity in sample preparation, choice of reference materials and internal standards, as well as data reporting relative to delta (δ) scale, are among the identified deficiencies that required improvements to make IRMS results fit-for-purpose. Only a minority of labs were outside the expected range of the results. More recently, another interlaboratory assessment was performed to compare the bulk isotope

https://doi.org/10.1016/j.forc.2019.100154

Received 28 January 2019; Received in revised form 3 March 2019; Accepted 3 March 2019 Available online 06 March 2019 2468-1709/ © 2019 Elsevier B.V. All rights reserved.

^{*} Corresponding author at: Department of Forensic and Investigative Science, West Virginia University, Morgantown, WV, United States. *E-mail address*: glen.jackson@mail.wvu.edu (G.P. Jackson).

analysis of honey coming from diverse metrological institutes [17]. The results derived from forensic stable isotope laboratories within the FIRMS Network [18], and all the participating laboratories, provided δ^{13} C values for bulk honey that were within an acceptable range. The method by which each laboratory calculated and reported their measurement uncertainty was a notable point of discussion, however, because some laboratories report standard deviations instead of expanded measurement uncertainty, such as the 95% confidence interval. To align with international standards, the use of an expanded uncertainty instead of a standard deviation is recommended for reported results.

To assist practitioners in establishing expanding uncertainties, Dunn and coworkers [19] have suggested a simple and straightforward improvement to the Kragten spreadsheet published in the GPG [15], which complements the existing approaches and guidelines used for delta scale [20]. The new spreadsheet is quite practical, and it combines the different sources of isotope uncertainty to multiple samples in one spreadsheet. Note that analytical results can include human errors, which are outside the random errors that are captured in uncertaintybudgeting spreadsheets. All researchers and practitioners should take preventative steps to promptly identify and mitigate sources of occasional mistakes, thereby enhancing the reliability of any reported result [21,22].

One of the biggest challenges in IRMS is the selection and use of appropriate-i.e. matrix matched-and well-characterized reference materials (RMs) [23]. The last few years have witnessed significant developments in RMs for calibration of δ^2 H, δ^{18} O [24–27], δ^{13} C, δ^{15} N, and δ^{34} S values [28–30]. One RM is a mixture of three glycine solutions that are recommended for establishing multiple-point calibration curves for the δ^{13} C scale [29]. Another three sugar RMs (BEET-1, GALT-1 and FRUT-1) were developed for δ^{13} C normalization of sugar-based materials, although it can also be used for other organic materials [31]. The hair RMs USGS-42 and USGS-43 have been developed for measurements of hydrogen and oxygen stable isotopes, but are also appropriate for measurements involving C, N, and S of human and mammalian hair [28]. The use of (at least) a two-point calibration scale is now a minimum requirement for high-quality data [15,23,32,33], and procedures are available with which to provide in-house isotope standards to help preserve the limited stocks of international materials [34].

Beyond the importance of accuracy, it is also important to report measures of precision or confidence intervals for forensic applications and to provide estimates for the power of discrimination of forensic samples [35]. As examples of these approaches, several groups have used Bayesian networks to assess the value of IRMS data [36-38], and several groups have provided a method using likelihood ratios (LRs) as a measure of the strength of IRMS data [39-41]. Such developments in reporting are critical to the future of the forensic community. However, one potential problem with reporting results in terms of LRs is that when an LR weakly favors the prosecution, the LR can be totally misinterpreted by jurors as actually favoring the defense [42]! Another way to interpret this observation is that jurors demand a very high threshold of confidence to find a suspect guilty, so a weakly favorable LR might not pass the cognitive threshold in the jurors' minds to warrant a severe penalty for the defendant. For a contextual understanding of the use of IRMS in legal applications, Ehleringer and Matheson have provided an excellent, comprehensive, clear review article that describes the admissibility of stable isotope analyses in court [43]. This foundational review is a profoundly important document for bridging the gap between the legal community and the research/practitioner communities, and there are many other forensic science disciplines that could benefit from such lucid a foundational document.

2. Human provenance

Many forensic stable isotope studies involve human subjects, and the goal of such investigations is usually to provide an investigative lead, such as insight into a person's geographic origin or travel history. Assisting such investigations, many IRMS studies have examined the relationship between the isotopic composition of human tissues and the geographic origin, health status or dietary interventions of the subjects. Such studies are useful for both paleo-archeological purposes and modern law enforcement investigations because both applications require the prediction of geographic origin of unidentified human remains [10,11,44–46].

A critical factor for strong geo-location inference is the establishment of reliable and high-resolution spatial maps for the precipitation and groundwater values for δ^2 H and δ^{18} O [47,48]. Such isotope landscapes, also known as Isoscapes [49], provide the framework for spatiotemporal movement of humans and other organisms [2,47,50]. In 2014, δ^{2} H and δ^{18} O measurements of 349 US tap water samples were made available in the largest public dataset to date. The samples included a broad geographic sampling and seasonal sampling [51]. Dr. Gabriel Bowen, from the University of Utah, has made the spatial variation metadata for water isotopes fully accessible through the Water Isotopes Database (http://wateriso.utah.edu/waterisotopes/ index.html) and through a recently developed mobile phone application called "wiSamples". Publicly-available data like this are critical for the validation and acceptance of Isoscapes for modern human provenancing, and some groups have successfully started using Isoscapes for such applications [52]. As a word of caution to prospective researchers in this area, one has to be especially careful with the calibration and interpretation of δ^2 H measurements of proteinaceous material like hair, muscle and feathers [53]. The number of exchangeable hydrogens varies greatly depending on the protein composition, so it is critical to use matrix-matched standards to obtain accurate isotope ratio normalization [54].

For geographical provenance determinations, biological samples must be representative of the organism and be chemically robust to provide meaningful isotope ratios, which is why bone, teeth, hair and nails are especially useful matrices. Hair and fingernails have the added advantages that they store a chronological record of diet and health of a person and that they can be non-invasively collected in the presence of a third party; i.e. witnessed [55,56]. Hair and nails are both abundant in α -keratin—a protein that is extremely robust and insoluble in water under normal conditions. As an example of keratin's stability, a study by Koehler and Hobson showed that tanning polar bear hides with sulfuric acid did not alter the δ^{13} C or δ^{15} N values of the hair in the hides but did alter the δ^{34} S values [57]. In another example, isotope ratio values of δ^{13} C, δ^{15} N and δ^{18} O in human hair were shown to be equally stable in a desiccator and freezer as they were spending ten months exposed to the natural environment [58]. However, as cautioned above, some $\delta^2 {\rm H}$ fractionation of hair was observed after prolonged storage times (e.g. 6 months). The general, chemical stability of keratins means that once they are formed, metabolic and chemical changes are minimal, and the isotopes of C, N and O are resistant to external influence.

A global database of δ^{13} C and δ^{15} N in hair and nails was recently compiled [59], and whereas the δ^{13} C values of hair and fingernails were shown to correlate strongly with the amount of C₄ plants in the diet—as determined by latitude and geography—the δ^{15} N values of hair and fingernails showed a much weaker correlation to geography. Instead, the δ^{15} N values correlated more strongly with fish/meat intake and coastal proximity (Fig. 1). Valenzuela *et al.* showed that within the United States the δ^{34} S values of more than 206 human hair samples provided better geographic information than either δ^{13} C or δ^{15} N [60]. However, the samples in this particular study were almost devoid of coastal representation, which is where dietary factors are most likely to influence the δ^{13} C and δ^{15} N values.

Although most of the literature related to human provenancing focuses on the dietary components and geospatial movement of individuals [10,11], non-dietary sources of phenotypic variance, such as sex, BMI and age, also enable the classification of subjects when



Fig. 1. Example of a global isotope database against which questioned samples can be compared. This map shows the spatial distribution of δ^{13} C values collected from more than 4,000 contemporary human hair and nail samples. Equatorial regions, especially on the African continent, are vastly under-represented. Image reprinted from reference [59]: F. Hulsemann, C. Lehn, S. Schneider, G. Jackson, S. Hill, A. Rossmann, N. Scheid, P.J. Dunn, U. Flenker, W. Schanzer, Global spatial distributions of nitrogen and carbon stable isotope ratios of modern human hair, Rapid Commun. Mass Spectrom. 29(22) (2015) 2111–21, Copyright (2015), with permission from John Wiley & Sons, Inc.

performing compound-specific isotope analysis (CSIA) of hair [61]. One note of caution with hair and fingernail comparisons is that human hair is slightly enriched in ¹³C and slightly depleted in ¹⁵N relative to fingernail clippings from the same individual [62–64], so care must be taken when interpreting the isotope values between hair and nails.

3. Wildlife forensics

Studies involving illegal harvesting and the black-market trading of plants and animals are of great interest in the legal community. Illegal wildlife trade is a global problem estimated to circulate US\$5-20 billion annually [65]. The determination of the geographic origin and movement of animals between different landscapes have both been successfully tracked using IRMS. For example, different isotopes are often used to unravel the trophic level of organisms and to establish the various flows of energy inside different food webs [66]. Such studies support a better understanding of the ecological behavior of animals and the development of effective conservational strategies towards endangered species [67]. IRMS can also assist with wildlife crime investigations [67]. Even though IRMS can be very relevant in these particular forensic situations, there is a formal delineation that divides forensic applications from "pure" ecological investigations. As with other cross-disciplinary studies, there are many benefits to maintaining an open dialog between forensic science and ecology application areas.

Carbon, nitrogen and, to a lesser extent, sulfur are the most studied isotopes for diet reconstruction, geographic origin determination, and the study of animal migration/foraging ecology in different habitats [68–72]. These applications also lead to a better understanding of illegal trading of wildlife products. Among these applications, elephant ivory and bone were the first wildlife materials where original source determination via multi-isotope analysis was combined with a forensic application [73–76]. More recently, δ^{13} C and δ^{15} N values were used to discriminate between the breeding of wild and captive Vietnamese endangered crocodile lizards of the taxon *Shinisaurus crocodilurus* [77]. SIA was also successful in determining the differences between wild vs.

illegally traded/captive-bred African grey parrots (*Psittacus erithacus*) [78] and Burmese and reticulated pythons [79]. However, carbon and nitrogen trophic models are not trivial markers of energy flow through an ecosystem because of isotope fractionation. The term fractionation refers to the enrichment or depletion of isotope ratios when a substrate undergoes a physical or chemical transformation. Fractionation occurs when a bond containing a heavier isotope is involved in a rate-limiting chemical transformation, such as when an enzyme decarboxylates an amino acid during metabolism. The heavier isotope has a slightly higher bond dissociation energy than the lighter isotope, so the rate of chemical transformation of the heavier isotope is slightly slower, which leads to the preferential transformation of the lighter light isotope [80,81].

Although measurable, isotopic fractionation between an organism and its food sources is not always predictable, especially in some highly dynamic and complex ecosystems like aquatic food webs [66]. For this reason, some researchers use isoscapes [82], and ⁸⁷Sr/⁸⁶Sr isotope ratios in addition to δ^{13} C and δ^{15} N values to predict an organism's movements. Such studies provide a better understanding of how SIA can be applied for wildlife conservation practices. Extra caution must be taken to ensure that the results are fit-for-purpose and devoid of fractionation [53,54]. Meanwhile, when comparing high-resolution Xray fluorescence (XRF) and δ^{13} C and δ^{15} N values of wild- and zoo-bred specimens of echidnas (*Tachyglossus aculeatus*), Brandis *et al.* reported 100% correct classification using the XRF data compared to 91.3% accuracy from the IRMS data [83]. Such studies are a reminder that IRMS measurements are not always the best or only tool in the analytical chemist's toolbox.

In the context of aquatic systems, some studies have investigated the influence of dietary water on the δ^2 H values of different organisms' tissues, as well as how water signatures can be used to trace organic matter and migratory patterns [66,84,85]. For example, Soto and coworkers [86] performed an environmentally controlled experiment where the ambient water, dissolved O₂, food and tissue protein and lipids of two trophic level aquatic species—an insect and a fish—were

Table 1

Examples of instrumental platforms used for compound-specific isotope analysis of organic contaminants. Minimally adapted from reference [103]: T.B. Hofstetter, M. Berg, Assessing transformation processes of organic contaminants by compound-specific stable isotope analysis, Trends Anal. Chem. 30(4) (2011) 618–627, Copyright (2010), with permission from Elsevier.

Instrument	Separation	Interface system	Analyte	Ionization	Mass analysis/ion detection	Isotopes	Reference example
GC/IRMS	GC $GC \times GC^{c}$	Comb ^a Comb/Red ^d Pyr ^e	CO ₂ N ₂ H ₂	EI ^b	Magnetic sector/Faraday cups	¹³ C/ ¹² C ¹⁵ N/ ¹⁴ N ² H/ ¹ H	[112-114113-115114]
LC/IRMS	LC	Wet oxidation	$\tilde{CO_2}$	EI	Magnetic sector/ Faraday cups	¹³ C/ ¹² C	[116,117]
GC/IRMS ^f	GC	none	Organics (PCE, TCE and DCE isomers;CH ₃ Br)	EI	Magnetic sector/ Faraday cups	³⁷ Cl/ ³⁵ Cl ⁸¹ Br/ ⁷⁹ Br	[118119]
GC/qMS	GC	none	Organics (PCE, DDT and PCP)	EI	Quadrupole electron multiplier	³⁷ Cl/ ³⁵ Cl	[120]
GC/MC-ICP-MS	GC	ICP ⁸	Cl Br S	ICP	Magnetic sector/Faraday cups	³⁷ Cl/ ³⁵ Cl ⁸¹ Br/ ⁷⁹ Br ³⁴ S/ ³² S	[121122123]
GC/CRDS ^h	GC	Comb	CO ₂	none	Infrared spectroscopy	$^{13}C/^{12}C$	[124]

GC = Gas Chromatography, LC = Liquid Chromatography, IRMS = Isotope Ratio Mass Spectrometry, qMS = Quadrupole Mass Spectrometry, MC-ICPMS = Multicollector Inductively Coupled Plasma Mass Spectrometry, CRDS = Cavity Ring-Down Spectroscopy, PCE = tetrachloroethene, TCE = trichloroethene, DCE = dichloroethene, DDT = p,p'-dichlorodiphenyltrichloroethane, PCP = pentachlorophenol.

^a Comb = Combustion at 900–950 °C;

^b EI = Electron Ionization;

- ^c Applications reported exclusively for analysis of carbon isotopes;
- ^d Comb/Red = Combustions followed by reduction at 600–650 °C;

^e Pyr = Pyrolysis at 1200–1450 °C;

^f Direct injection GC/IRMS;

- ^g ICP = Inductively Coupled Plasma;
- ^h Also denoted as GC/C/CRDS owing to the use of a combustion interface.

analyzed for $\delta^2 H$ and $\delta^{18} O$ values. The authors demonstrated that hydrogen and oxygen could serve as complementary tracers of diet and provenance in the aquatic ecosystem and pointed out the strengths and weaknesses of this approach. The lipid content of animal tissue is often reported as a source of variation in δ^2 H, δ^{13} C and δ^{15} N values from aquatic animals' tissues [84,87-89]. Independent of the organism, the removal of lipids prior to bulk tissue analysis for their separated analysis or a posterior mathematical lipid normalization is a general recommendation in stable isotope ecology [86,89,90]. However, Patterson and Carmichael recently suggested that lipid extraction may actually not be necessary for all taxa, but more important in glycogen storing species such as the Eastern oyster *Crassostrea virginica* [91]. This overall lipid correction practice should be reviewed in a species-specific and tissue-specific manner to avoid unnecessary sample handling and misinterpretation of isotopic values in trophic ecology studies. In fact, Connan et al.'s recent study with fish samples showed that different pretreatments widely used to remove interfering biological molecules (lipids, urea, TMAO) affect the isotopic data and suggested a more standardized pre-treatment approach to ensure the comparison and reproducibility of bulk SIA [92].

For terrestrial environments, the use of δ^2 H and δ^{18} O analysis of tissues is not always tightly correlated with the precipitation δ^2 H and δ^{18} O isoscapes, which might make geographic determinations more challenging. An example was reported with two North American carnivores, the bobcat (*Lynx rufus*) and the puma (*Puma concolor*), wherein both δ^2 H and δ^{18} O values from hair samples of these felines lacked correlation with local isoscapes [93]. This study highlights the importance of additional investigations into isotopic fractionation and metabolic routing if IRMS is to find a stronger footing in wildlife forensics.

In recent work at the boundary between human provenancing and wildlife forensics, two reports have investigated the light stable isotope composition of blowflies and their diets [94,95]. Both studies showed isotope fractionation between the flesh and the blow flies that was significantly smaller than the isotopic variance that existed between the food sources, thereby enabling the discrimination of potential food

sources. Through CSIA of amino acids in the different life stages of blow flies, the study by Matos *et al.* demonstrated that essential and nonessential amino acids are fractionated differently in the different life stages of the blow flies [95].

Regarding forest studies, Thomas *et al.* analyzed δ^{13} C and δ^{34} S values from red cedar (*Juniperus virginiana* L.) tree rings and presented a recent and gradual recovery of this species from the decades-long acidic pollution that affected the Appalachian region [96]. Despite the direct correlation with forensics, this work revealed the effectiveness of stricter environmental legislation on human activity and also showed the potential of IRMS in forest ecosystems research.

Timber traceability coupled to initiatives against deforestation and illegal logging is another area that can strongly benefit from the use of stable isotope fingerprinting. The combination of δ^{15} N, δ^{34} S, δ^{18} O values, $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios, and radiocarbon dating was successful in identifying relocated South African cycad species removed from the wild, which supports the use of SIA as a prospective method to combat the illegal trading of endangered populations [97]. However, different isotopes have different inferential value depending on the species in question. For wood sourcing, or dendroprovenancing, of two Pinyon pines species in the southwestern United States, the δ^{13} C values from the tree rings proved to be a more precise and successful method than the analysis of ring widths by itself [98]. However, when working with Norway spruces (Picea abies Karst.) in and around the European Alps, carbon isotopes did not work as a proxy for their geolocation. In contrast, δ^2 H and δ^{18} O values were more suitable for European spruces [99]. Stable isotopes have also been successful proxies in archaeological wood sourcing investigations [100], and could even be used for chronology determination of tropical trees with indistinct annual rings [101].

4. Environmental forensics

Environmental forensics covers a broad range of topics and involves the illegal contamination or damage of protected areas, whether intentional or not. A typical example would be the use of δ^{13} C values to determine the point source of an environmental pollutant. Due to the complexity that arises when investigating the source or fate of a contaminant release, it is usually necessary to use a variety of analytical techniques to resolve the issue, as shown in Table 1 [102]. Compound-specific isotope ratio analysis of δ^{13} C, δ^{15} N, δ^{2} H, δ^{18} O, δ^{37} Cl, δ^{34} S, and δ^{81} Br have been comprehensively documented [103–107] alongside the advances and inherent challenges when applied to the micropollutants [108]. IRMS is mostly used in studies involving anthropogenic contamination because most pollutants are man-made and contain an isotope profile that differs significantly from natural sources of the same substance. Examples include chemical leaks and oil spills, which pose a major hazard to marine and coastal environments.

In a weathering simulation experiment of a simulated oil spill, GC-C-IRMS measured the δ^{13} C values of individual *n*-alkanes (C₁₂-C₃₃) in crude oil and showed that δ^{13} C values are generally unaltered by shortterm weathering [109]. The lack of fractionation during mild weathering makes δ^{13} C analysis a suitable tool for oil fingerprinting such complex samples [110]. However, fractionation of hydrocarbons does occur in simulated fire debris samples, so the effects of elevated temperature, pyrolysis and combustion must be better understood before reliable inferences can be made between post-combustion residues and pre-combustion liquids from which they derived [111].

5. Seized drugs

As stated in the 2013 National Survey on Drug Use and Health (NSDUH) report [125], approximately 24.6 million American people aged 12 or more self-declared illicit drug use in the previous year. Given the extent of novel psychoactive substances (NPSs) appearing on the market, IRMS has emerged as a potential technique to infer the cultivation location of drugs of plant origin, to establish trafficking routes, and to establish the synthetic pathways and chemical lots used in clandestine laboratories.

Cannabis sativa L., also known as cannabis or marijuana, is the most common plant-derived illicit drug in the United States and the world [126]. There were are approximately 19.8 million users in the US in 2013 [125], and its use has apparently skyrocketed since the legalization of medical and recreational marijuana in some US states [127]. With the additional announcement that the White House has alleviated restrictions on medical marijuana studies [128], scientists now have more legal support to conduct research in this area. For forensic purposes, IRMS has been mostly applied to infer cannabis source and distribution networks. Most of the data on large-scale drug trafficking samples is collected by the DEA special testing laboratory and it is unclear how much of the available data makes it to the public domain. This is not to criticize the DEA, but to highlight the point that the public domain probably does not contain all that has been learned about the isotopic composition of drug seizures from around the world.

Carbon and nitrogen stable isotopes are the most well-explored isotopes for the origin determination and growth conditions assessment of Cannabis seized in different countries [129-131], and the DEA's database provides insight into trafficking, production and distribution networks [132]. Based on the differences in bulk δ^{13} C and δ^{15} N values from leaves and inflorescences of 554 marijuana samples, West et al. suggested an isotopic framework range to interpret the isotope ratio values [133]. An example is shown in Fig. 2. By combining parameters of indoor or outdoor growth and inorganic or organic fertilizer, West et al. demonstrated a linkage between isotopes and possible cultivation method beyond the correct geographical assignment of known seized samples [126,134]. In a complementary work, Tipple and coworkers found that the study of chain length distributions, concentrations and δ^{13} C values of *n*-alkanes (n-C₂₉) from seized *Cannabis* inflorescences can also provide information about the cultivation settings of marijuana plants [135].

When characterizing marijuana samples seized in Alaska, Booth *et al.* demonstrated that multiple isotopes (δ^{13} C, δ^{15} N, δ^{2} H and δ^{18} O)

can be a useful approach to trace trafficking patterns [136], whereas other authors are exploring the ⁸⁷Sr/⁸⁶Sr ratios retained in marijuana leaves and inflorescences to achieve a similar goal [137]. A subsequent publication from the Jackson group described the comparison of bulk δ^{13} C values of *Cannabis* plant samples to compound-specific δ^{13} C values of cannabinoids extracted from the same samples [138]. Although the advanced age of some of the samples had caused some isomerization and degradation of the cannabinoids, the results effectively showed that individual cannabinoids have unique δ^{13} C values relative to the bulk plant matter, which therefore makes it somewhat challenging to link extracted THC to a particular plant source.

Among all plant-derived drugs, cocaine's production and trafficking routes around the world are of particular interest to law enforcement agencies. In this context, SIA appears to be well-suited to the task because seized cocaine samples closely reflect the growth environment of coca plants. Mallette and coworkers [139] applied a multiple bulk isotope approach (δ^{13} C, δ^{15} N, δ^{2} H and δ^{18} O) combined with trace alkaloids and multivariate statistics to discriminate cocaine coming from 19 major South American growing regions. A similar method was used to differentiate and determine the unique profile of the first illicit coca plantation in Mexico, showing that coca cultivation for cocaine production is expanding its limits outside South America [140]. Under controlled laboratory conditions, those same isotopes were investigated regarding their fractionation patterns in fractionally precipitated cocaine base. Interestingly, the authors observed an opposite trend to the usual Rayleigh fractionation because the earlier fractions of precipitated samples were more depleted than the later ones for all four isotopes. ¹⁵N and ²H were characterized by the largest fractionations [141].

 γ -hydroxybutyric acid (GHB) is another illicit psychoactive drug that became very popular among young people at nightclubs or raves because of the desirable increase in euphoria and disinhibition. GHB use also provides less-desirable effects, including amnesia, which also made GHB attractive for use in drug-facilitated sexual assaults. The popularity caught the authorities' attention because GHB, or its chemical precursors y-butyrolactone (GBL) or 1,4-butanediol (1,4-BD) are colorless and odorless liquids, which makes them easy to spike into beverages of intended victims of drug-assisted sexual assault. Marclay and coworkers used GC/C/IRMS to investigate the effects of in vivo metabolism on $\delta^{13}{\rm C}$ values of GHB [142]. Urinary GHB $\delta^{13}{\rm C}$ values ranged from -25.06‰ to -24.81‰ for patients who had ingested prescribed pharmaceutical GHB, which was indistinguishable from the original δ^{13} C value of -24.99%. Given that metabolism of GHB had no statistical influence on the isotopic ratio, comparison of a seized exogenous GHB and endogenous GHB from a victim can be used as a successful approach to incriminate/acquit a sexual assault suspect. In much the same way, IRMS can distinguish endogenous vs. exogenous sources of performance-enhancing hormones in athletes. Marclay and coworkers had previously used the same instrument to determine the source of 19 GBL samples obtained worldwide by measuring intra and inter-variability of their bulk carbon isotope signatures [143].

In other applications with synthetic drugs, IRMS elucidated different production batches of 23 seized tablets of the piperazine analogs benzylpiperazine (BZP) and trifluoromethylphenylpiperazine (TFMPP) [144], both synthetic stimulants sold as alternatives to ecstasy. In a parallel study, the same group reported the IRMS analysis three batches of benzylpiperazine hydrochloride (BZP·HCl) and its synthetic intermediates, which were synthesized from three different precursor suppliers [145]. Although all the intermediate samples were significantly different and correctly associated with their respective precursor suppliers, the increased variance in the measured δ^{13} C and δ^{15} N values for BZP·HCl meant that not all the BZP·HCl batches could be uniquely linked to the correct precursor suppliers. IRMS has also been used in combination with other profiling techniques to classify carfentanyl seizures [146].

A comprehensive discussion on the application of IRMS to



Fig. 2. Dual isotope approach for the inference of marijuana growth conditions. Image adapted from reference [133]: J.B. West, J.M. Hurley, J.R. Ehleringer, Stable isotope ratios of marijuana. I. Carbon and nitrogen stable isotopes describe growth conditions, J. Forensic Sci. 54(1) (2009) 84–9, Copyright (2008), with permission from John Wiley & Sons, Inc.



Fig. 3. Bivariate plot of the δ^{13} C and δ^{2} H values of 782 samples of methylamphetamine seized at the Australian Border. The blue data points in the upper right correspond with samples that were synthesized from ephedrine (pseudoephedrine), which was itself produced through a semi-synthetic process involving the fermentation of a sugar with benzaldehyde. The red data points in the lower left include samples from natural origin (extracted from Ephedra plants) and the entirely-synthetic samples, which start with the bromination of propiophenone. Image reprinted from reference [147]: M. Collins, H. Salouros, A review of some recent studies on the stable isotope profiling of methylamphetamine: Is it a useful adjunct to conventional chemical profiling?, Sci. Justice 55(1) (2015) 2-9, Copyright (2014), with permission from Elsevier.

methylamphetamine (also known as methamphetamine) and its precursors has already been provided by Gentile et al. [7] and will not be repeated in detail here. In another reviews, Collins and Salouros highlight the strategic importance of δ^{13} C, δ^{2} H and δ^{15} N analysis as a complementary profiling technique to impurity profiling for the routine analysis of methylamphetamine seizures [12,147]. Fig. 3 demonstrates the range of δ^{13} C and δ^{2} H values obtained for 782 samples seized at the Australian border and the ability to distinguish semi-synthetic from natural or synthetic methylamphetamine. Other valuable work by Liu et al. compared the isotope ratios of ephedra plants, natural ephedrine, synthetic ephedrine and the partially- or totally-synthetic methamphetamine products [148]. Although the results enabled inferences to be made about the likely source of 987 methamphetamine casework samples, the ground truth for each casework sample was not known, so the casework-specific false positive and false negative rates could not be assessed.

6. Ignitable liquids

According to the National Fire Protection Association (NFPA), around 282,600 intentional fires per year were reported to U.S. fire departments between 2007 and 2011, including 211,500 outside or unclassified fires, 50,800 structure fires and 20,400 vehicle fires [149].

Approximately 160,910 were found to be intentionally set with an ignitable liquid [150]. In spite of these statistics, and in contrast to the extensive use of IRMS on explosives, very few manuscripts have reported the analysis of ignitable liquids with IRMS [7].

Since 2009, diesel fuel has become a more frequently studied ignitable liquid [151–153] even though gasoline is the most commonly used ignitable liquid in arson cases [150]. In one study, Harvey *et al.* first isolated the *n*-alkanes from different diesel samples to ensure baseline resolution between each *n*-alkane and prevent any potential interference between peaks [151]. A following combination of δ^2 H and δ^{13} C CSIA with multivariate statistics was then used to distinguish between the four diesel samples of different sources. Muhammad *et al.* examined a larger dataset of 45 diesel samples from various gas stations in New Zealand [152]. This study showed the difficulty of source attribution when there is only one major supplier of diesel to all the gas stations in the region. Source attribution was scientifically accurate, but of little forensic value.

Weathering and additives are the possible reasons for subtle differences in fuel isotopic compositions. By analyzing the fingerprint pattern of *n*-alkanes (e.g. nC_{12} to nC_{23}) via GC-IRMS, Muhammad *et al.* reaffirmed the discriminant power of CSIA. Moreover, following 21 days of evaporation at room temperature (24 ± 2 °C), hydrogen and carbon isotopic signatures of various *n*-alkanes in a diesel sample [153], the *n*-alkane underwent negligible fractionation for ¹³C and varying degrees of fractionation of ²H. For example, long-chain alkanes were not fractionated during evaporation, but the shorter chain alkanes nC_{12} - nC_{17} underwent significant ²H fractionation.

Several groups have also reported evaporation effects on isotope ratios of different petroleum derivatives [154–156]. Whereas IRMS appears to be a suitable tool to predict potential common sources of pristine flammable liquid samples, Schwartz and coworkers showed that post-combustion residues in simulated fire debris undergo unpredictable extents of ¹³C fractionation ranging from 0 to +10% relative to the same analytes in the pristine, unburned liquid [111]. The absence of any reliable trend in fractionation in simulated fires makes IRMS unsuitable for the comparison of pre-combustion compounds and their post-combustion residues. Not only do the analytes undergo fractionation during evaporation and pyrolysis, but pyrolysis products from the organic substrate (e.g. carpet) also contribute different weighted δ^{13} C values to different residues [157].

7. Explosives

Source determination of explosives has become a growing interest in a variety of government sectors, especially because of the daily use of a broad range of explosive devices in military actions, terrorism and insurgents' attacks. Recently, a combination of IRMS and inductively coupled plasma-mass spectrometry (ICP-MS) was used to provide a better discrimination between ammonium nitrate (AN) samples from distinct AN batches and manufacturers [158]. The low cost and easy access of AN as a fertilizer ensures that ammonium nitrate fuel oil (ANFO), consisting of a mixture of 94% AN and 6% fuel oil, is possibly still one of the most used materials employed in improvised explosive devices (IEDs) [159]. Brust et al. showed that ¹⁵N and ¹⁸O isotopic signatures of AN samples could successfully distinguish between the different samples [158]. Carbon and hydrogen analyses were also performed, but low sample carbon contents and an observed influence of nitrogen on the δ^2 H values made these two isotopes less useful. Benson et al. [160] achieved similar results when the source of Australian AN samples was differentiated based on their δ^2 H, δ^{18} O, and δ^{15} N values [161].

Some challenges in working with nitrogen-rich organic compounds have been reported by other researchers. For example, incomplete reduction might cause the tailing in the N₂ peak of nitrates [162]. Caution must also be used when measuring organic substances against inorganic reference materials like IAEA-N1 and IAEA-N2 [162]. In addition, nitrogen-rich compounds can also influence the accuracy and precision of ²H isotopic analysis [163]. Given that these compounds undergo thermochemical processes that are different from typical organic compounds in EA-IRMS, and that they tend to give lower than expected recoveries of nitrogen, Gentile et al. recommend a thermal decomposition method to remove of any external oxygen [162]. Additional results to this premise indicate that, compared to the usual EA combustion method, thermal decomposition provides more precise δ^{15} N and %N results for both organic and inorganic materials containing oxidized nitrogen. The thermal decomposition procedure did not have a deleterious effect on the measurement of %N, δ^{13} C or δ^{15} N values of materials containing reduced nitrogen [164]. Adjustments to this methodology would allow a more accurate, faster and cheaper way to analyze δ^{15} N materials using EA-IRMS. Other manuscripts have described that isotope analysis of each of the ion components of nitrogenrich explosives (such as ammonium nitrate or urea nitrate) provides additional discriminatory power for the investigation of forensic samples [165–167].

Using samples synthesized in different conditions, Benson *et al.* presented the use of IRMS to differentiate triacetone triperoxide (TATP) samples, another common explosive in many terrorist bombings [168]. Based on bulk δ^{13} C values, the samples were classified according to their synthetic process. Carbon, hydrogen, and oxygen isotopic data

were combined to classify the TATP samples to their common source. A global study by Howa *et al.* showed that δ^{13} C values of TATP correlate strongly with the δ^{13} C values of locally-available liquid acetone, the synthetic precursor to TATP [169].

Using bulk δ^{13} C and δ^{15} N values from a sample set containing the explosive pentaerythritol tetranitrate (PETN), Benson *et al.* showed the discrimination of PETN from detonating cord or cast PETN booster filling [168]. Howa and coworkers [170] investigated the factors that influence the carbon and nitrogen isotopic ratios of commercial PETN by isolating the explosive from the bulk sample of different manufacturers and observing the isotopic linkage between that substance and its reactants, pentaerythritol (PE) and nitric acid. The results showed that, whereas δ^{13} C values from PETN reflect the PE carbon signatures, PETN δ^{15} N values are influenced by both nitric acid δ^{15} N values and the deflagration reaction parameters. The authors suggested further experiments with controlled reaction conditions to provide a better understanding of the results.

The effectiveness and limitations of IRMS were also reported in studies involving RDX, HMX, TNT, HMTD, black powders and other pre- and post-blast materials from explosive devices [113,171–176]. Whereas bulk analyses like these are extremely helpful for linking evidence in pre-detonation scenarios, there are significantly fewer reports linking post-detonation residues with pre-detonation samples. The CSIA of individual analytes in multi-component explosives would be helpful to connect the explosive precursor to the product samples. In this context, Chesson and coworkers provide a very useful step-by-step approach for the extraction and preparation of several explosive mixtures for IRMS (Fig. 4) [177]. The same group established a robust database that helps establish the use of explosive isotopic evidence in court [178].

8. Food forensics

Since the 1990s, the application of SIA in several food adulteration/ safety studies has been recognized as an official method by AOAC International [179]. The use of isotopic techniques has also become prominent among the practiced methods to authenticate and protect citizens and businesses against a variety of legal issues involving foods and brands.

IRMS can provide insight regarding authenticity, provenance, and contamination of foodstuffs, and it has been used in a variety of legal cases [180]. Although counterfeit food is not always dangerous for consumption, counterfeiting is illegal and strongly affects the consumer confidence on the product or brand [181]. Food fraud is most prevalent when products are expensive to produce like premium-brand products. In such cases, black-market suppliers will typically employ cheaper, lower-quality ingredients and less labor-intensive manufacturing methods to produce the final product.

Honey is a commonly counterfeited product. Carbon bulk isotope analysis has been used for the detection of commercial honey adulteration (AOAC-C₄ Sugar Method 998.12) [182] because most authentic honey has a δ^{13} C value close to C₃ plants. However cheap substitutes include syrup sugars made from corn or sugar cane, which shift the δ^{13} C values towards C₄ plants values [183,184]. The AOAC method identifies this adulteration because it requires the extraction of protein from honey and compares the differences between δ^{13} C values of honey protein vs. bulk honey ($\Delta \delta^{13}$ C). Differences greater than 1‰ indicate that the honey has more than 7% adulteration with a C₄ syrup [185,186]. However, elemental analysis by bulk IRMS is not very effective when honey is diluted with cheap C3-plant-derived sugars like sugar beet because the bulk isotope ratio would not be substantially different [186,187]. One exception to the rule is the premium-priced New Zealand manuka honey, which naturally has a high level of C₄ sugar, and therefore has an isotope ratio that is indistinguishable from cane or corn syrup [188]. Because bulk IRMS cannot always identify adulteration in honey, LC-IRMS can provide more selectivity by



Fig. 4. Suggested workflow to isolate and prepare different components from explosive mixtures for measurement by IRMS and other analytical techniques. Image reprinted from reference [177]: L.A. Chesson, J.D. Howa, M.J. Lott, J.R. Ehleringer, Development of a methodological framework for applying isotope ratio mass spectrometry to explosive components, Forensic Chem. 2 (2016) 9–14, Copyright (2016), with permission from Elsevier.

providing compound-specific carbon isotope ratio measurements [189,190]. Furthermore, the use of multi-isotope approaches to classify honey according to their botanical and/or geographical origin has also been reported (Fig. 5) [191,192].

Zhao *et al.* [193] and Camin *et al.* [180,181] have both published thorough reviews about the applications of IRMS in authenticity and traceability of a variety of plant-based and animal-based foods. Another very comprehensive reading on the topic can be found in [194]. Isotope analysis has also contributed to the tracking of animal diets for the protection of premium products as well as for consumer health reasons. IRMS has been used to protect against bovine spongiform encephalopathy (BSE), foot-and-mouth disease (FMD), and even avian influenza

[193]. Most studies involve a multiple isotope approach and sometimes include additional analytical techniques. Applications include the determination of the primary diets of poultry [195–198], pigs [199,200], beef [201], lamb [202,203] and dairy products [204]. Other examples of food applications include the geographic origin of meat [205,206], fish and shellfish [207–211], dairy [212–215], vegetables and fruits [216–219], grain-based food [220–225], chocolate [226], coffee [227], alcoholic and nonalcoholic drinks [228–233] and oils [234–237]. The influence of local ingredients on "global" foods, such as Big Mac[®] patties collected in 26 countries was also accessed via isotope analysis. The δ^{13} C values of hamburgers reflected the diets of the local cattle [238,239].



Fig. 5. Combination of IRMS, ICP-MS and chemometrics to classify Chinese honeys according to their botanical origins. Reprinted with permission from reference [192]: Z. Wu, L. Chen, L. Wu, X. Xue, J. Zhao, Y. Li, Z. Ye, G. Lin, Classification of Chinese honeys according to their floral origins using elemental and stable isotopic compositions, J. Agric. Food. Chem. 63(22) (2015) 5388–94. Copyright (2015) American Chemical Society.

Food fraud is a dynamic activity, however, and it poses a continuous challenge for researchers. Beyond the common use of δ^{13} C values for food authenticity and δ^{15} N values for the distinction of crops raised with organic or synthetic fertilizers, some groups are already incorporating the use of hydrogen and oxygen isotopes as valuable markers for geographic determination. For example, when investigating 436 commonly consumed meat samples from diverse terrestrial and marine animals, Chesson et al. reported that the correlations between δ^{2} H and δ^{18} O values from animal tissues reflect the consumed water similarly, independent of the animal taxa [240]. Hydrogen and oxygen isotopes were also applied to demonstrate that hamburgers sold at local restaurants are more likely to come from regionally raised cattle, while fast food chains rely on beef coming from further regions [13]. Interestingly, most food forensic articles apply some quite advanced chemometrics, which indicates a gradual change in the isotope community towards a more sophisticated interpretation of results.

The effect of cooking on the isotope ratios of foodstuff is not commonly investigated, although many consumed items in a human/animal diet are cooked before consumption. It was recently reported that δ^{13} C and δ^{15} N values of grain-based desserts and yeast bread are not affected by baking or fermentation procedures, and the raw ingredients from processed food can be used to estimate the respective isotopic ratio values [241]. Other research found that steaming, grilling and boiling of two types of fish (mackerel and haddock) did not have a significant effect on the bulk δ^{13} C and δ^{15} N values [242], although a small but significant effect on the δ^{13} C values has been reported for other fish species [243] Cooking processes such as boiling, frying or roasting also did not impact the δ^{13} C and δ^{15} N values of beef samples. However, δ^{2} H values became significantly enriched from 7.2% to 5.9% when compared to raw and processed beef [244]. Studies on how cooking methods affect stable isotope signatures are also a new and interesting venue to understand and reconstruct cultural habits and dietary routine of ancient human populations [245].

Given the increased retail sales and consumer demand for organic products [246], organic produce needs continual certification of authenticity. In this context, the difference between organic and conventionally produced food has become a hot topic in IRMS research. Regarding organic dairy products, chemical analysis of α -linolenic acid (C18:3 ω 3), phytanic acid diastereomer ratios (SRR/RRR), ¹H NMR- and ¹³C NMR-spectroscopy data, δ^{15} N and δ^{13} C values of milk protein and fat identified cases of mislabeled organic dairy products [247–251]. Eggs [252], fish [253] and pork [254] have also been correctly identified by SIA as being produced under organic or conventional methods. The continued growth of organic foodstuff production is likely to continue the expansion in authentication involving IRMS. More information about the principles, applications and limitations of SIA in authenticating organic products from plant or animal origin can be found in [255,256].

Isotope ratio analysis of δ^{15} N values can provide insight into the

extent of man-made fertilizers. However, other factors can also influence the nitrogen signature in a crop, including soil saturation levels, atmospheric nitrogen deposition, agricultural practices and the plant's internal nitrogen balance [257]. An important factor in food authentication is that the nitrogen isotope signature of cover crops composed of N₂-fixing leguminous plants is often similar to the signature of some synthetic fertilizers. For this reason, δ^{15} N analysis alone not a very suitable parameter for organic authentication [258,259]. A combination of multiple isotopes, multivariate statistics, and other analytical techniques is therefore preferred. Successful multivariate approaches have included IRMS with ICP-MS [257] and IRMS with mid-infrared spectroscopy, (MIS) and Proton Nuclear Magnetic Resonance (¹H NMR) [260] to classify organic vs. conventionally-grown tomatoes. In addition, CSIA has also demonstrated good discriminatory power between plants that are grown under different conditions [258,259,261].

Besides all the benefits listed above, there are still some limitations for IRMS in practical food applications. The high costs to maintain IRM instrument are well known, but the lack of an extensive reference database containing products coming from a range of different diets, production conditions, locations and seasons is possibly the biggest problem [181]. Such a database would also have to be continually updated because of the dynamic nature of global food markets. To our knowledge, wine is the only product with a well stablished isotope databank, which was created in the early 1990s in the European Union [262]. Finally, one challenge in relating food forensics to forensic casework, such as nutritional studies of humans, is that even when controlled studies examine the consumption of large quantities of a certain food, like beer, the isotope signature of the intervention food group is so diluted by the natural variation in a person's diet that the dietary intervention may not be observable [263].

9. Poisoning

Although not as common as food authentication, IRMS is also used in poisoning investigations. Through the use of GC/C/IRMS, researchers in Japan analyzed δ^{13} C values in different samples of methamidophos (O, S-dimethyl phosphoramidothioate). High concentrations of this pesticide were identified in some frozen dumplings imported from China, which caused food poisoning in many Japanese citizens who consumed the product [264]. The comparison of Chinese and Japanese methamidophos isotopic values showed that the pesticide was not added in Japan. Subsequent investigations led a temporary worker in China to admit to the crime. Combining isotopes to investigate food contaminated with pesticides for criminal or suicidal reasons has been reported by others. For example, Ehtesham et al. described the use of SIA in a case study of a deliberate contamination of milk powder with a pesticide (MFA) [265]. In another case, the comparison of δ^{15} N and δ^{13} C values of different methomyl (an insecticide) products and a methomyl-containing Soju collected from a fatal

poisoning incident in Korea was one of the investigative leads that enabled detectives to find the poison source and the suspect responsible for the crime [266]. δ^{15} N and δ^{18} O values were also used to show that a combination of horse manure, urine nitrification and intensive evaporation caused an accumulation of nitrates in a water-filled hole that eventually killed 71 wild horses [267].

In some situations, preventative steps have been taken to establish protocols to determine the isotopic ratios of potential poisons. For example, cyanide salts are easily available and highly toxic. Analyses of δ^{13} C and δ^{15} N values in several commercial NaCN and KCN batches, as well as extracted cyanide from food and medicine matrices, support the use of these two isotopes as forensic tools to distinguish different samples [268,269]. Regarding the toxic protein ricin, which is a Schedule I controlled substance from Ricinus communis (castor beans), the combination of δ^{13} C, δ^{15} N, δ^{18} O, and δ^{2} H values provided powerful discrimination between different sources of castor beans even when the preparation method varied between acetone extraction, salt precipitation or affinity chromatography [270]. When a statistical integration approach was taken to join the four isotopes with ⁸⁷Sr/⁸⁶Sr ratios, the classification accuracy of castor seeds' geographic origin increased [37]. In other work involving the nerve agent, sarin, Moran et al. has shown that when the precursor methylphosphonic dichloride (DC) is converted to methylphosphonic difluoride (DF) during the synthesis, isotopic fractionation of carbon is minimal [271]. For this reason, nerve agents and their intermediates can be included in, or excluded from, the possibility of deriving from certain precursor feedstocks.

10. Questioned documents

Discrimination and source determination of documents remains a severe problem in forensic science. Such examinations include authenticating documents and signatures, document dating and threatening letters, among others [272–276]. Interest in the analysis of paper products was highlighted 2001 during the FBI's investigations of bioterrorist Anthrax letters in 2001 [277]. The likeness of envelopes used to mail the anthrax spores was investigated through SIA [43], but little discrimination was reported in that case.

Regarding paper examinations, in 2013, Jones and coworkers published a series of three manuscripts depicting the effectiveness of δ^{13} C analysis to distinguish the manufacturing source of document papers [278–280]. Using different brands of office papers collected in Australia and New Zealand, the authors evaluated intra and inter-variability of paper reams and suggested a confidence interval to discriminate documents. More recently, the same group has published two additional manuscripts incorporating oxygen isotope values as well [281,282]. Their results once again showed the potential of IRMS to discriminate paper samples, and a dual-isotope approach using carbon and oxygen was indicated as the next investigation step to optimize and ultimately validate an operation protocol suitable for paper document casework analysis. The results were consistent with previous IRMS results in which carbon, oxygen and hydrogen isotopes were able to discriminate 21 out of 25 European paper documents [283]. The combination of IRMS and XRF appeared to be even more effective at distinguishing between paper products. XRF instruments are more affordable and more-readily accessible to forensic labs and could offer an alternative approach to source attribution.

Regarding ink and toner analysis, Raman spectroscopy and Fourier-Transform Infrared Spectroscopy (FTIR) are the most frequent, reliable and non-destructive methods to differentiate variations found in ballpoint and pens [284–286]. IRMS has only just begun to be explored for inks. For example, Chesson *et al.* described the first application of SIA of N, C, H, and O to characterize ballpoint and gel inks from pens purchased in the same package, pens from the same brand purchased in three different states, pens of different ages and ink on paper [287]. According to their results, within-package pens have statistically indistinguishable isotopic signatures, but between-package signatures of the same brand pens from different locations and ages were significantly different. In addition, when investigating ink on paper, nitrogen isotope values allowed the discrimination of the different inks. Additional method development is still required before IRMS can be used in questioned-document casework.

11. Miscellaneous

The implementation of IRMS in trace evidence studies involving clothing fibers is relatively understudied. Given the fact that alternative analytical methods struggle to provide information other than the polymer type and color of fibers, isotope ratio analysis appears to be a prospective method to determine the source of similar fibers. δ^{13} C, δ^{15} N, and δ^{18} O values have enabled the discrimination between valuable natural fibers of cashmere and cheaper synthetic fibers that were used as a substitute for cashmere in the manufacturing process [288]. Using IRMS, a pilot multi-element study of carbon, hydrogen and oxygen isotopes also showed differences in un-dyed spun cotton fabric fibers from different countries [289]. The authors pointed out that for δ^{2} H and δ^{18} O values, a larger number of cotton fiber samples would be required to achieve more robust statistical results of within-region variability. To overcome this issue, a subsequent manuscript used hierarchical cluster analysis to compare the isotopic compositions of 17 raw cotton samples from many US states to 15 cotton fibers from different overseas regions [290]. Despite the promising results, some misidentified samples reaffirmed the necessity of a larger dataset and consideration of additional variables that influence results when IRMS is used. The δ^2 H and δ^{18} O values of cotton can also be used to identify counterfeit currency, since cotton is a primary constituent of paper money. Cerling et al. [8] recently summarized results on how cotton isoscape patterns provide unique geographic information to allow discrimination between genuine US bank notes vs. counterfeit notes.

In recent work by Nienaber *et al.*, SIA showed that within-batch isotope ratio values of cable ties were not significantly different, but that between-batch cable ties were significantly different, especially for δ^2 H and δ^{15} N values of the nylon cable ties [41]. Along with IRMS measurements, other physical and chemical measurements enabled the discrimination of 19 of the 20 samples. The only two samples that could not be distinguished were unintentional replicates that shared the same lot number and supplier. Jones *et al.* surveyed the δ^2 H and δ^{13} C values of 26 cling wraps and 26 packages of resealable bags in Australia [291]. Their work demonstrated a significant difference between the within-sample variance and between-sample variance, the benefit of which was extolled in an example case study.

Plastic bags, cling film and adhesive packaging tapes are examples of other materials often associated with forensic situations. Examples include the packaging of drugs and explosives. SIA of plastic wraps have been demonstrated to contribute to the source elucidation of the illicit materials [292–296].

12. Summary

This review summarizes some of the SIA applications in different fields of forensic science. Good practices are readily available through the FIRMS Network, and they recommend reliable methods for calibration, normalization and the assessment and reporting of measurement uncertainties. In short, best practices require at least two isotopic standards per element and the reporting of confidence intervals instead of standard deviations.

Ecology and wildlife applications are the most challenging areas of interpretation, and species-specific techniques are often necessary to reveal trophic-level and food-web interactions. There are also big gaps in our understanding of how to interpret IRMS data involving migration patterns and foraging behavior of highly mobile animals. In biological applications, the dynamic nature of different organisms and the differences in metabolism within different organs of an organism are complicating factors in the interpretation of IRMS results. Special attention should be given to the type of tissues analyzed and their respective turnover rates [4], particularly if focusing in molecules such as amino acids. These are some of the reasons why amino acid isotope analysis became an active and promising research area in ecogeochemistry [297]. The continuous expansion of Isoscapes metadata and incorporation of other isotope ratios (e.g. ⁸⁷Sr/⁸⁶Sr) show potential to leverage the power of interpretations in multiple forensic areas. We expect this increase in data density to be reflected in future datasets, which, combined with advances in chemometrics, should provide a more solid structure for SIA in future casework.

Magnetic sector IRMS instruments still offer better abundance precision than new high resolution mass spectrometers like the Orbitrap [298], but analytical approaches that include techniques such as XRF, Raman spectroscopy, FTIR, NMR, ICP-MS, cavity ring-down spectroscopy, genetic markers, trace elements and fatty acids profiles tend to provide superior discrimination than IRMS values alone. The benefits derive from the inclusion of additional independent variables. The use of chemometrics and statistics in the data analysis has certainly flourished, but still requires further development.

CSIA is recognized as a more sophisticated, and more complex, approach than bulk IRMS. It provides more variables for discrimination, but these variables oftentimes are not true independent variables but covariates, which means a more careful consideration must be taken when interpreting the results. CSIA results provide additional sourcelevel or metabolic information from the samples in question, which is potentially helpful in distinct forensic contexts [61,95]. Baczynski et al. recently reported the development of a modified GC combustion interface that enables a two-order-of-magnitude reduction in the limits of detection [299]. The CSIA measurement of picomolar levels of organics in a mixture will no doubt open the door to new potential applications [299]. Position-specific isotope analysis (PSIA) of amino acids' carboxyl groups has also been introduced recently [300]. Continued development of PSIA and its applications is likely to provide more in-depth information about the source and metabolism of different amino acids and other metabolites [300]. The value of PSIA to forensic science is questionable at this point, but unless fundamental research continues to push the boundaries of what is possible, we will never move beyond what is currently practicable.

Acknowledgements

This project was supported by grants 2013-DN-BX-K007 and 2018-75-CX-0033, awarded by the National Institute of Justice, Office of Justice Programs, and U.S. Department of Justice. The opinions, findings, and conclusions or recommendations expressed in this publication/program/exhibition are those of the authors and do not necessarily reflect the views of the Department of Justice. This manuscripted has been significantly improved through the excellent advice of two diligent external reviewers to which we are extrmemly grateful.

References

- Z. Muccio, G.P. Jackson, Isotope ratio mass spectrometry, Analyst 134 (2) (2009) 213–222.
- [2] W. Meier-Augenstein, Stable isotope forensics: An introduction to the forensic application of stable isotope analysis, John Wiley & Sons, Chichester, UK, 2010.
- [3] N. nic Daeid, H.A.S. Buchanan, K. Savage, J. Fraser, S.L. Cresswell, Recent advances in the application of stable isotope ratio analysis in forensic chemistry, Aust. J. Chem. 63 (1) (2010) 3–7.
- [4] S.S. Tobe, Determining the geographic origin of animal samples, in: A. Linacre (Ed.), Forensic Science in Wildlife Investigations, Taylor & Francis Group, LLC, Boca Raton, FL, 2009, pp. 127–156.
- [5] J.S. McCullagh, Mixed-mode chromatography/isotope ratio mass spectrometry, Rapid Commun. Mass Spectrom. 24 (5) (2010) 483–494.
- [6] L.A. Chesson, B.J. Tipple, J.D. Howa, G.J. Bowen, J.E. Barnette, T.E. Cerling, J.R. Ehleringer, Stable isotopes in forensics applications, in: H.H. D., T.K. K. (Eds.), Treatise on Geochemistry, Elsevier, Oxford, 2014, pp. 285–317.
- [7] N. Gentile, R.T.W. Siegwolf, P. Esseiva, S. Doyle, K. Zollinger, O. Delemont,

Isotope ratio mass spectrometry as a tool for source inference in forensic science: a critical review, Forensic Sci. Int. 251 (2015) 139–158.

- [8] T.E. Cerling, J.E. Barnette, G.J. Bowen, L.A. Chesson, J.R. Ehleringer, C.H. Remien, P. Shea, B.J. Tipple, J.B. West, Forensic stable isotope biogeochemistry, Annu. Rev. Earth Planet. Sci. 44 (1) (2016) 175–206.
- [9] L.A. Chesson, J.E. Barnette, G.J. Bowen, J.R. Brooks, J.F. Casale, T.E. Cerling, C.S. Cook, C.B. Douthitt, J.D. Howa, J.M. Hurley, H.W. Kreuzer, M.J. Lott, L.A. Martinelli, S.P. O'Grady, D.W. Podlesak, B.J. Tipple, L.O. Valenzuela, J.B. West, Applying the principles of isotope analysis in plant and animal ecology to forensic science in the Americas, Oecologia 187 (4) (2018) 1077–1094.
- [10] E.J. Bartelink, G.E. Berg, L.A. Chesson, B.J. Tipple, M.M. Beasley, J.R. Prince-Buitenhuys, H. MacInnes, A.T. MacKinnon, K.E. Latham, Applications of stable isotope forensics for geolocating unidentified human remains from past conflict situations and large-scale humanitarian efforts, in: K.E. Latham, E.J. Bartelink, M. Finnegan (Eds.), New Perspectives in Forensic Human Skeletal Identification, Academic Press, 2018, pp. 175–184.
- [11] L.A. Chesson, B.J. Tipple, L.V. Youmans, M.A. O'Brien, M.M. Harmon, Forensic identification of human skeletal remains using isotopes: a brief history of applications from archaeological dig sites to modern crime scenes, in: K.E. Latham, E.J. Bartelink, M. Finnegan (Eds.), New Perspectives in Forensic Human Skeletal Identification, Elsevier, 2018, pp. 157–173.
- [12] H. Salouros, Illicit drug chemical profiling: current and future state, Aust. J. Forensic Sci. 50 (6) (2018) 689–696.
- [13] J.R. Ehleringer, L.A. Chesson, L.O. Valenzuela, B.J. Tipple, L.A. Martinelli, Stable isotopes trace the truth: from adulterated foods to crime scenes, Elements 11 (4) (2015) 259–264.
- [14] < http://www.forensic-isotopes.org/ > , 2016 (accessed August 20. 2016).
- [15] P.J.H. Dunn, J.F. Carter, Good Practice Guide for Isotope Ratio Mass Spectrometry, 2nd ed., FIRMS 2018.
- [16] J.F. Carter, B. Fry, Ensuring the reliability of stable isotope ratio data-beyond the principle of identical treatment, Anal. Bioanal. Chem. 405 (9) (2013) 2799–2814.
- [17] P.J.H. Dunn, H. Goenaga-Infante, A.C. Goren, A. Şimşek, M. Bilsel, N. Ogrinc, P. Armishaw, L. Hai, CCQM-K140: Carbon stable isotope ratio delta values in honey, Metrologia 54 (08005) (2017).
- [18] P.J.H. Dunn, S. Hill, S. Cowen, H. Goenaga-Infante, M. Sargent, A.C. Gören, M. Bilsel, A. Şimşek, N. Ogrinc, D. Potočnik, P. Armishaw, L. Hai, L. Konopelko, Y. Chubchenko, L.A. Chesson, G. van der Peijl, C. Blaga, R. Posey, F. Camin, A. Chernyshev, S.A. Chowdhury, Lessons learned from inter-laboratory studies of carbon isotope analysis of honey, Sci. Justice 59 (1) (2019) 9–19.
- [19] P.J. Dunn, L. Hai, D. Malinovsky, H. Goenaga-Infante, Simple spreadsheet templates for the determination of the measurement uncertainty of stable isotope ratio delta values, Rapid Commun. Mass Spectrom. 29 (22) (2015) 2184–2186.
- [20] T.B. Coplen, Guidelines and recommended terms for expression of stable-isotoperatio and gas-ratio measurement results, Rapid Commun. Mass Spectrom. 25 (2011) 2538–2560.
- [21] D.J. Hawke, J.C.S. Brown, S.J. Bury, B. Pracheil, The prevention and detection of human error in ecological stable isotope analysis, Methods Ecol. Evol., 2018.
- [22] A.L. Plant, C.A. Becker, R.J. Hanisch, R.F. Boisvert, A.M. Possolo, J.T. Elliott, How measurement science can improve confidence in research results, PLoS Biol. 16 (4) (2018) e2004299.
- [23] W.A. Brand, T.B. Coplen, J. Vogl, M. Rosner, T. Prohaska, Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report), Pure Appl. Chem. 86 (3) (2014) 425–467.
- [24] T.B. Coplen, H. Qi, L. Tarbox, J. Lorenz, B. Buck, USGS46 Greenland ice core water - a new isotopic reference material for ^{3²}H and ^{3¹⁸O} measurements of water, Geostand. Geoanalytical Res. 38 (2) (2013) 153–157.
- [25] H. Qi, T.B. Coplen, L. Tarbox, J.M. Lorenz, M. Scholl, USGS48 Puerto Rico precipitation - a new isotopic reference material for δ²H and δ¹⁸O measurements of water, Isotopes Environ. Health Stud. 50 (4) (2014) 442–447.
- [26] H. Qi, J.M. Lorenz, T.B. Coplen, L. Tarbox, B. Mayer, S. Taylor, Lake Louise water (USGS47): a new isotopic reference water for stable hydrogen and oxygen isotope measurements, Rapid Commun. Mass Spectrom. 28 (4) (2014) 351–354.
- [27] V. Faghihi, B.M.A.A. Verstappen-Dumoulin, H.G. Jansen, G. van Dijk, A.T. Aerts-Bijma, E.R.T. Kerstel, M. Gröning, H.A.J. Meijer, A new high-quality set of singly (²H) and doubly (²H and ¹⁸O) stable isotope labeled reference waters for biomedical and other isotope-labeled research, Rapid Commun. Mass Spectrom. 29 (4) (2015) 311–321.
- [28] T.B. Coplen, H.P. Qi, USGS42 and USGS43: Human-hair stable hydrogen and oxygen isotopic reference materials and analytical methods for forensic science and implications for published measurement results, Forensic Sci. Int. 214 (1–3) (2012) 135–141.
- [29] D. Malinovsky, P.J.H. Dunn, G. Holcombe, S. Cowen, H. Goenaga-Infante, Development and characterisation of new glycine certified reference materials for SI-traceable ¹³C/¹²C isotope amount ratio measurements, J. Anal. At. Spectrom. 34 (1) (2019) 147–159.
- [30] H. Qi, T.B. Coplen, S.J. Mroczkowski, W.A. Brand, L. Brandes, H. Geilmann, A. Schimmelmann, A new organic reference material, l-glutamic acid, USGS41a, for δ¹³C and δ¹⁵N measurements - a replacement for USGS41, Rapid Commun. Mass Spectrom. 30 (7) (2016) 859–866.
- [31] M.M.G. Chartrand, J. Meija, P. Kumkrong, Z. Mester, Three certified sugar reference materials for carbon isotope delta measurements, Rapid Commun. Mass Spectrom. 33 (3) (2019) 272–280.
- [32] T.B. Coplen, W.A. Brand, M. Gehre, M. Groning, H.A.J. Meijer, B. Toman, R.M. Verkouteren, New Guidelines for δ^{13} C Measurements, Anal. Chem. 78 (7) (2006) 2439–2441.

- [33] W. Meier-Augenstein, A. Schimmelmann, A guide for proper utilisation of stable isotope reference materials, Isotopes Environ. Health Stud. (2018) 1–16.
- [34] J.F. Carter, B. Fry, "Do it yourself" reference materials for δ¹³C determinations by isotope ratio mass spectrometry, Anal. Bioanal. Chem. 405 (14) (2013) 4959–4962.
- [35] Strengthening forensic science in the United States: Committee on Identifying the Needs of the Forensic Sciences Community, A path forward, National Research Council, The National Academy Press, 2009.
- [36] C.D. Kennedy, G.J. Bowen, J.R. Ehleringer, Temporal variation of oxygen isotope ratios (δ¹⁸O) in drinking water: implications for specifying location of origin with human scalp hair, Forensic Sci. Int. 208 (1–3) (2011) 156–166.
- [37] B.J. Webb-Robertson, H. Kreuzer, G. Hart, J. Ehleringer, J. West, G. Gill, D. Duckworth, Bayesian integration of isotope ratio for geographic sourcing of castor beans, J. Biomed. Biotechnol. 2012 (2012) 1–8.
- [38] G.J. Bowen, Z.F. Liu, H.B. Vander Zanden, L. Zhao, G. Takahashi, Geographic assignment with stable isotopes in IsoMAP, Methods Ecol. Evol. 5 (3) (2014) 201–206.
- [39] N. Farmer, W. Meier-Augenstein, D. Lucy, Stable isotope analysis of white paints and likelihood ratios, Sci. Justice 49 (2) (2009) 114–119.
- [40] J.F. Carter, S. Doyle, B.L. Phasumane, N. nic Daeid, The role of isotope ratio mass spectrometry as a tool for the comparison of physical evidence, Sci. Justice 54 (5) (2014) 327–334.
- [41] L.M. Nienaber, S.L. Cresswell, J.F. Carter, T. Peter, A comparison of plastic cable ties based on physical, chemical and stable isotopic measurements, Sci. Justice 58 (1) (2018) 67–75.
- [42] K.A. Martire, R.I. Kemp, M. Sayle, B.R. Newell, On the interpretation of likelihood ratios in forensic science evidence: presentation formats and the weak evidence effect, Forensic Sci. Int. 240 (2014) 61–68.
- [43] J.R. Ehleringer, S.M. Matheson Jr., Stable isotopes and courts, Utah Law Review No. 2 (2010) 385–442.
- [44] E. Mutzel Rauch, C. Lehn, O. Peschel, S. Holzl, A. Rossmann, Assignment of unknown persons to their geographical origin by determination of stable isotopes in hair samples, Int. J. Legal Med. 123 (1) (2009) 35–40.
- [45] L. Font, G. van der Peijl, C. van Leuwen, I. van Wetten, G.R. Davies, Identification of the geographical place of origin of an unidentified individual by multi-isotope analysis, Sci. Justice 55 (1) (2015) 34–42.
- [46] C.A.M. France, D.W. Owsley, L.A.C. Hayek, Stable isotope indicators of provenance and demographics in 18th and 19th century North Americans, J. Archaeol. Sci. 42 (2014) 356–366.
- [47] J.B. West, G.J. Bowen, T.E. Dawson, K.P. Tu, Isoscapes Understanding movement, pattern, and process on Earth through isotope mapping, Springer Science + Business Media B.V, Springer, Dordrecht Heidelberg London New York, 2010.
- [48] A.G. West, E.C. February, G.J. Bowen, Spatial analysis of hydrogen and oxygen stable isotopes ("isoscapes") in ground water and tap water across South Africa, J. Geochem. Explor. 145 (2014) 213–222.
- [49] G.J. Bowen, Isoscapes: Spatial pattern in isotopic biogeochemistry, Annu. Rev. Earth Planet. Sci. 38 (2010) 161–187.
- [50] M.M. Warner, A.M. Plemons, N.P. Herrmann, L.A. Regan, Refining stable oxygen and hydrogen isoscapes for the identification of human remains in Mississippi, J. Forensic Sci. 63 (2) (2018) 395–402.
- [51] J.M. Landwehr, T.B. Coplen, D.W. Stewart, Spatial, seasonal, and source variability in the stable oxygen and hydrogen isotopic composition of tap waters throughout the USA, Hydrol. Process. 28 (21) (2014) 5382–5422.
- [52] C.J. Mancuso, J.R. Ehleringer, Resident and nonresident fingernail isotopes reveal diet and travel patterns, J. Forensic Sci. 64 (1) (2019) 77–87.
- [53] H.B. Vander Zanden, A. Reid, T. Katzner, D.M. Nelson, Effect of heat and singeing on stable hydrogen isotope ratios of bird feathers and implications for their use in determining geographic origin, Rapid Commun. Mass Spectrom. 32 (21) (2018) 1859–1866.
- [54] W. Meier-Augenstein, K.A. Hobson, L.I. Wassenaar, Critique: measuring hydrogen stable isotope abundance of proteins to infer origins of wildlife, food and people, Bioanalysis 5 (7) (2013) 751–767.
- [55] W. Meier-Augenstein, H.F. Kemp, Stable isotope analysis: hair and nails, Wiley Encyclopedia of Forensic Science, John Wiley & Sons Ltd, 2012.
- [56] I.M. Kempson, E. Lombi, Hair analysis as a biomonitor for toxicology, disease and health status, Chem. Soc. Rev. 40 (7) (2011) 3915–3940.
- [57] G. Koehler, K.A. Hobson, Effects of tanning on the stable isotopic compositions of hair, Forensic Sci. Int. 292 (2018) 78–82.
- [58] G.W. Gordon, T.B. Saul, D. Steadman, D.J. Wescott, K. Knudson, Preservation of hair stable isotope signatures during freezing and law enforcement evidence packaging, Forensic Chem. 11 (2018) 108–119.
- [59] F. Hulsemann, C. Lehn, S. Schneider, G. Jackson, S. Hill, A. Rossmann, N. Scheid, P.J. Dunn, U. Flenker, W. Schanzer, Global spatial distributions of nitrogen and carbon stable isotope ratios of modern human hair, Rapid Commun. Mass Spectrom. 29 (22) (2015) 2111–2121.
- [60] L.O. Valenzuela, L.A. Chesson, S.P. O'Grady, T.E. Cerling, J.R. Ehleringer, Spatial distributions of carbon, nitrogen and sulfur isotope ratios in human hair across the central United States, Rapid Commun. Mass Spectrom. 25 (7) (2011) 861–868.
- [61] G.P. Jackson, Y. An, K.I. Konstantynova, A.H.B. Rashaid, Biometrics from the carbon isotope ratio analysis of amino acids in human hair, Sci. Justice 55 (2015) 43–50.
- [62] T.C. O'Connell, R.E.M. Hedges, M.A. Healey, A.H.R.W. Simpson, Isotopic comparison of hair, nail and bone: modern analyses, J. Archaeol. Sci. 28 (11) (2001) 1247–1255.
- [63] C. Lehn, E. Mutzel, A. Rossmann, Multi-element stable isotope analysis of H, C, N and S in hair and nails of contemporary human remains, Int. J. Legal Med. 125 (5)

(2011) 695–706.

- [64] T.C. O'Connell, C.J. Kneale, N. Tasevska, G.G. Kuhnle, The diet-body offset in human nitrogen isotopic values: a controlled dietary study, Am. J. Phys. Anthropol. 149 (3) (2012) 426–434.
- [65] G.E. Rosen, K.F. Smith, Summarizing the evidence on the international trade in illegal wildlife, EcoHealth 7 (1) (2010) 24–32.
- [66] J.C. Finlay, R.R. Doucett, C. McNeely, Tracing energy flow in stream food webs using stable isotopes of hydrogen, Freshw. Biol. 55 (5) (2010) 941–951.
- [67] J.A. Seminoff, S.R. Benson, K.E. Arthur, T. Eguchi, P.H. Dutton, R.F. Tapilatu, B.N. Popp, Stable isotope tracking of endangered sea turtles: validation with satellite telemetry and δ¹⁵N analysis of amino acids, PLoS One 7 (5) (2012) e37403.
- [68] B.S. Graham, P.L. Koch, S.D. Newsome, K.W. McMahon, D. Aurioles, Using isoscapes to trace the movements and foraging behavior of top predators in oceanic ecosystems, in: J.B. West, G.J. Bowen, T.E. Dawson, K.P. Tu (Eds.), Isoscapes: Understanding Movement, Pattern, and Process on Earth Through Isotope Mapping, Springer Science + Business Media B.V., 2010, pp. 299–318.
- [69] R. Ramos, J. González-Solís, Trace me if you can: the use of intrinsic biogeochemical markers in marine top predators, Front. Ecol. Environ. 10 (5) (2012) 258–266.
- [70] H.B.V. Zanden, A.D. Tucker, K.M. Hart, M.M. Lamont, I. Fujisaki, D.S. Addison, K.L. Mansfield, K.F. Phillips, M.B. Wunder, G.J. Bowen, M. Pajuelo, A.B. Bolten, K.A. Bjorndal, Determining origin in a migratory marine vertebrate: a novel method to integrate stable isotopes and satellite tracking, Ecol. Appl. 25 (2) (2015) 320–335.
- [71] T. Tsutaya, Y. Fujimori, M. Hayashi, M. Yoneda, T. Miyabe-Nishiwaki, Carbon and nitrogen stable isotopic offsets between diet and hair/feces in captive chimpanzees, Rapid Commun. Mass Spectrom. 31 (1) (2017) 59–67.
- [72] T.E. Cerling, S.A. Andanje, F. Gakuya, J.M. Kariuki, L. Kariuki, J.W. Kingoo, C. Khayale, I. Lekolool, A.N. Macharia, C.R. Anderson, D.P. Fernandez, L. Hu, S.J. Thomas, Stable isotope ecology of black rhinos (*Diceros bicornis*) in Kenya, Oecologia 187 (4) (2018) 1095–1105.
- [73] N.J. van der Merwe, J.A. Lee-Thorp, J.F. Thackeray, A. Hall-Martin, F.J. Kruger, H. Coetzee, R.H.V. Bell, M. Lindeque, Source-area determination of elephant ivory by isotopic analysis, Nature 346 (1990) 744–746.
- [74] T.E. Cerling, P. Omondi, A.N. Macharia, Diets of Kenyan elephants from stable isotopes and the origin of confiscated ivory in Kenya, Afr. J. Ecol. 45 (2007) 614–623.
- [75] S. Ziegler, S. Merker, B. Streit, M. Boner, D.E. Jacob, Towards understanding isotope variability in elephant ivory to establish isotopic profiling and source-area determination, Biol. Conserv. 197 (2016) 154–163.
- [76] J.C. Vogel, B. Eglington, J.M. Auret, Isotope fingerprints in elephant bone and ivory, Nature 346 (1990) 747–749.
- [77] M. van Schingen, T. Ziegler, M. Boner, B. Streit, T.Q. Nguyen, V. Crook, S. Ziegler, Can isotope markers differentiate between wild and captive reptile populations? A case study based on crocodile lizards (*Shinisaurus crocodilurus*) from Vietnam, Glob. Ecol. Conserv. 6 (2016) 232–241.
- [78] J. Alexander, C.T. Downs, M. Butler, S. Woodborne, C.T. Symes, Stable isotope analyses as a forensic tool to monitor illegally traded African grey parrots, Anim. Conserv., 2018.
- [79] D.J.D. Natusch, J.F. Carter, P.W. Aust, N. Van Tri, U. Tinggi, A. Mumpuni, J.A. Lyons Riyanto, Serpent's source: determining the source and geographic origin of traded python skins using isotopic and elemental markers, Biol. Conserv. 209 (2017) 406–414.
- [80] D.A. Schoeller, Isotope fractionation: why aren't we what we eat? J. Archaeol. Sci. 26 (1999) 667–673.
- [81] Z.D. Sharp, Principles of Stable Isotope Geochemistry, 2nd ed. 2017.
- [82] H.B. Vander Zanden, D.M. Nelson, M.B. Wunder, T.J. Conkling, T. Katzner, Application of isoscapes to determine geographic origin of terrestrial wildlife for conservation and management, Biol. Conserv. 228 (2018) 268–280.
- [83] K.J. Brandis, P.J.B. Meagher, L.J. Tong, M. Shaw, D. Mazumder, P. Gadd, D. Ramp, Novel detection of provenance in the illegal wildlife trade using elemental data, Sci. Rep. 8 (1) (2018) 15380.
- [84] C.T. Graham, S.S.C. Harrison, C. Harrod, Differences in the contributions of dietary water to the hydrogen stable isotope ratios of cultured Atlantic salmon and Arctic charr tissues, Hydrobiologia 721 (1) (2013) 45–55.
- [85] H.B.V. Zanden, M.B. Wunder, K.A. Hobson, S.L. Van Wilgenburg, L.I. Wassenaar, J.M. Welker, G.J. Bowen, Contrasting assignment of migratory organisms to geographic origins using long-term versus year-specific precipitation isotope maps, Methods Ecol. Evol. 5 (9) (2014) 891–900.
- [86] D.X. Soto, L.I. Wassenaar, K.A. Hobson, Stable hydrogen and oxygen isotopes in aquatic food webs are tracers of diet and provenance, Funct. Ecol. 27 (2) (2013) 535–543.
- [87] I.C. Ansmann, J.M. Lanyon, J.M. Seddon, G.J. Parra, Habitat and resource partitioning among Indo-Pacific bottlenose dolphins in Moreton Bay, Australia, Mar. Mamm. Sci. 31 (1) (2015) 211–230.
- [88] F.A. Aya, I. Kudo, Isotopic shifts with size, culture habitat, and enrichment between the diet and tissues of the Japanese scallop *Mizuhopecten yessoensis* (Jay, 1857), Mar. Biol. 157 (10) (2010) 2157–2167.
- [89] W.J. Boecklen, C.T. Yarnes, B.A. Cook, A.C. James, On the use of stable isotopes in trophic ecology, Annu. Rev. Ecol. Evol. Syst. 42 (1) (2011) 411–440.
- [90] C.K. Weldrick, R. Trebilco, K.M. Swadling, Can lipid removal affect interpretation of resource partitioning from stable isotopes in Southern Ocean pteropods? Rapid Commun. Mass Spectrom., 2019.
- [91] H.K. Patterson, R.H. Carmichael, The effect of lipid extraction on carbon and nitrogen stable isotope ratios in oyster tissues: implications for glycogen-rich species, Rapid Commun. Mass Spectrom. 30 (24) (2016) 2594–2600.

- [92] M. Connan, G. Hall, M. Smale, Effects of pre-treatments on bulk stable isotope ratios in fish samples: a cautionary note for studies comparisons, Rapid Commun. Mass Spectrom. 33 (3) (2019) 291–302.
- [93] S.J. Pietsch, K.A. Hobson, L.I. Wassenaar, T. Tutken, Tracking cats: problems with placing feline carnivores on δ^{18} O, δ D isoscapes, PLoS One 6 (9) (2011) e24601.
- [94] V. Bernhardt, T. Holdermann, N. Scheid, T. Schafer, M.A. Verhoff, J. Amendt, Same, same but different!-matching entomological traces to a human food source by stable isotope analysis, Int. J. Legal Med. 132 (3) (2018) 915–921.
- [95] M.P.V. Matos, K.I. Konstantynova, R.M. Mohr, G.P. Jackson, Analysis of the ¹³C isotope ratios of amino acids in the larvae, pupae and adult stages of *Calliphora vicina* blow flies and their carrion food sources, Anal. Bioanal. Chem. 410 (30) (2018) 7943–7954.
- [96] R.B. Thomas, S.E. Spal, K.R. Smith, J.B. Nippert, Evidence of recovery of *Juniperus virginiana* trees from sulfur pollution after the Clean Air Act, Proc. Natl. Acad. Sci. USA 110 (38) (2013) 15319–15324.
- [97] K. Retief, A.G. West, M.F. Pfab, Can stable isotopes and radiocarbon dating provide a forensic solution for curbing illegal harvesting of threatened cycads? J. Forensic Sci. 59 (6) (2014) 1541–1551.
- [98] A. Kagawa, S.W. Leavitt, Stable carbon isotopes of tree rings as a tool to pinpoint the geographic origin of timber, J. Wood Sci. 56 (3) (2010) 175–183.
- [99] Y. Gori, R. Wehrens, N. La Porta, F. Camin, Oxygen and hydrogen stable isotope ratios of bulk needles reveal the geographic origin of Norway spruce in the European Alps, PLoS One 10 (3) (2015) 14.
- [100] M. Bridge, Locating the origins of wood resources: a review of dendroprovenancing, J. Archaeological Sci. 39 (8) (2012) 2828–2834.
- [101] P.F. Poussart, M.N. Evans, D.P. Schrag, Resolving seasonality in tropical trees: multi-decade, high-resolution oxygen and carbon isotope records from Indonesia and Thailand, Earth. Planet. Sci. Lett. 218 (3–4) (2004) 301–316.
- [102] R.P. Philp, An overview of environmental forensics, Geol. Acta 12 (4) (2014) 363–374.
- [103] T.B. Hofstetter, M. Berg, Assessing transformation processes of organic contaminants by compound-specific stable isotope analysis, Trends Anal. Chem. 30 (4) (2011) 618–627.
- [104] T.B. Hofstetter, J. Bolotin, M. Skarpeli-Liati, R. Wijker, Z. Kurt, S.F. Nishino, J.C. Spain, Tracking transformation processes of organic micropollutants in aquatic environments using multi-element isotope fractionation analysis, Appl. Geochem. 26 (2011) S334–S336.
- [105] A. Cincinelli, F. Pieri, Y. Zhang, M. Seed, K.C. Jones, Compound specific isotope analysis (CSIA) for chlorine and bromine: a review of techniques and applications to elucidate environmental sources and processes, Environ. Pollut. 169 (2012) 112–127.
- [106] M. Thullner, F. Centler, H.-H. Richnow, A. Fischer, Quantification of organic pollutant degradation in contaminated aquifers using compound specific stable isotope analysis – review of recent developments, Org. Geochem. 42 (12) (2012) 1440–1460.
- [107] W.J. Shin, S.W. Lee, S.Y. Heo, K.S. Lee, Stable isotopic fingerprinting for identification of the methyl tert-butyl ether (MTBE) manufacturer, Environ. Forensics 14 (1) (2013) 36–41.
- [108] M. Elsner, G. Imfeld, Compound-specific isotope analysis (CSIA) of micropollutants in the environment - current developments and future challenges, Curr. Opin. Biotechnol. 41 (2016) 60–72.
- [109] Y. Li, Y. Xiong, W. Yang, Y. Xie, S. Li, Y. Sun, Compound-specific stable carbon isotopic composition of petroleum hydrocarbons as a tool for tracing the source of oil spills, Mar. Pollut. Bull. 58 (1) (2009) 114–117.
- [110] U.H. Yim, M. Kim, S.Y. Ha, S. Kim, W.J. Shim, Oil spill environmental forensics: the Hebei Spirit oil spill case, Environ. Sci. Technol. 46 (12) (2012) 6431–6437.
- [111] Z. Schwartz, Y. An, K.I. Konstantynova, G.P. Jackson, Analysis of household ignitable liquids and their post-combustion weathered residues using compoundspecific gas chromatography-combustion-isotope ratio mass spectrometry, Forensic Sci. Int. 233 (1–3) (2013) 365–373.
- [112] H.J. Tobias, G.L. Sacks, Y. Zhang, J.T. Brenna, Comprehensive two-dimensional gas chromatography combustion isotope ratio mass spectrometry, Anal. Chem. 80 (22) (2008) 8613–8621.
- [113] F. Gelman, A. Kotlyar, D. Chiguala, Z. Ronen, Precise and accurate compoundspecific carbon and nitrogen isotope analysis of RDX by GC-IRMS, Int. J. Environ. Anal. Chem. 91 (14) (2011) 1392–1400.
- [114] S. Spahr, J. Bolotin, J. Schleucher, I. Ehlers, U. von Gunten, T.B. Hofstetter, Compound-specific carbon, nitrogen, and hydrogen isotope analysis of *N*-nitrosodimethylamine in aqueous solutions, Anal. Chem. 87 (5) (2015) 2916–2924.
- [115] K. Schreglmann, M. Hoeche, S. Steinbeiss, S. Reinnicke, M. Elsner, Carbon and nitrogen isotope analysis of atrazine and desethylatrazine at sub-microgram per liter concentrations in groundwater, Anal. Bioanal. Chem. 405 (9) (2013) 2857–2867.
- [116] D.M. Kujawinski, L. Zhang, T.C. Schmidt, M.A. Jochmann, When other separation techniques fail: compound-specific carbon isotope ratio analysis of sulfonamide containing pharmaceuticals by high-temperature-liquid chromatography-isotope ratio mass spectrometry, Anal. Chem. 84 (18) (2012) 7656–7663.
- [117] D.M. Kujawinski, J.B. Wolbert, L. Zhang, M.A. Jochmann, D. Widory, N. Baran, T.C. Schmidt, Carbon isotope ratio measurements of glyphosate and AMPA by liquid chromatography coupled to isotope ratio mass spectrometry, Anal. Bioanal. Chem. 405 (9) (2013) 2869–2878.
- [118] O. Shouakar-Stash, R.J. Drimmie, M. Zhang, S.K. Frape, Compound-specific chlorine isotope ratios of TCE, PCE and DCE isomers by direct injection using CF-IRMS, Appl. Geochem. 21 (5) (2006) 766–781.
- [119] O. Shouakar-Stash, S.K. Frape, R.J. Drimmie, Determination of bromine stable isotopes using continuous-flow isotope ratio mass spectrometry, Anal. Chem. 77

(2005) 4027-4033.

- [120] C. Aeppli, H. Holmstrand, P. Andersson, O. Gustafsson, Direct compound-specific stable chlorine isotope analysis of organic compounds with quadrupole GC/MS using standard isotope bracketing, Anal. Chem. 82 (1) (2010) 420–426.
- [121] M.R.M.D. Van Acker, A. Shahar, E.D. Young, M.L. Coleman, GC/multiple collector-ICPMS method for chlorine stable isotope analysis of chlorinated aliphatic hydrocarbons, Anal. Chem. 78 (13) (2006) 4663–4667.
- [122] D. Carrizo, M. Unger, H. Holmstrand, P. Andersson, Ö. Gustafsson, S.P. Sylva, C.M. Reddy, Compound-specific bromine isotope compositions of one natural and six industrially synthesised organobromine substances, Environ. Chem. 8 (2) (2011) 127.
- [123] A. Amrani, A.L. Sessions, J.F. Adkins, Compound-specific δ^{34} S analysis of volatile organics by coupled GC/multicollector-ICPMS, Anal. Chem. 81 (21) (2009) 9027–9034.
- [124] R.N. Zare, D.S. Kuramoto, C. Haase, S.M. Tan, E.R. Crosson, N.M. Saad, Highprecision optical measurements of ¹³C/¹²C isotope ratios in organic compounds at natural abundance, Proc. Natl. Acad. Sci. USA 106 (27) (2009) 10928–10932.
- [125] Results from the 2013 national survey on drug use and health: mental health findings NSDUH Series H-49, HHS Publication No. (SMA) 14-4887. Rockville, MD: Substance Abuse and Mental Health Services Administration, 2014, p. 142.
- [126] J.M. Hurley, J.B. West, J.R. Ehleringer, Tracing retail cannabis in the United States: geographic origin and cultivation patterns, Int. J. Drug Policy 21 (3) (2010) 222–228.
- [127] E.J. D'Amico, A. Rodriguez, J.S. Tucker, E.R. Pedersen, R.A. Shih, Planting the seed for marijuana use: changes in exposure to medical marijuana advertising and subsequent adolescent marijuana use, cognitions, and consequences over seven years, Drug Alcohol Depend. 188 (2018) 385–391.
- [128] Announcement of revision to the department of Health and Human Services guidance on procedures for the provision of marijuana for medical research as published on May 21, 1999, in: D.o.H.a.H. Services (Ed.) Federal Register 2015, pp. 35960–35961.
- [129] T.M. Denton, S. Schmidt, C. Critchley, G.R. Stewart, Natural abundance of stable carbon and nitrogen isotopes in *Cannabis sativa* reflects growth conditions, Funct. Plant Biol. 28 (10) (2001) 1005.
- [130] E.K. Shibuya, J.E. Souza Sarkis, O.N. Neto, M.Z. Moreira, R.L. Victoria, Sourcing Brazilian marijuana by applying IRMS analysis to seized samples, Forensic Sci. Int. 160 (1) (2006) 35–43.
- [131] E.K. Shibuya, J.E. Sarkis, O. Negrini-Neto, L.A. Martinelli, Carbon and nitrogen stable isotopes as indicative of geographical origin of marijuana samples seized in the city of Sao Paulo (Brazil), Forensic Sci. Int. 167 (1) (2007) 8–15.
- [132] https://www.courier-journal.com/story/news/crime/2019/02/28/covert-deadrug-testing-lab-what-know-virginia-facility/3005848002/ (accessed February 2019.).
- [133] J.B. West, J.M. Hurley, J.R. Ehleringer, Stable isotope ratios of marijuana. I. Carbon and nitrogen stable isotopes describe growth conditions, J. Forensic Sci. 54 (1) (2009) 84–89.
- [134] J.M. Hurley, J.B. West, J.R. Ehleringer, Stable isotope models to predict geographic origin and cultivation conditions of marijuana, Sci. Justice 50 (2) (2010) 86–93.
- [135] B.J. Tipple, B. Hambach, J.E. Barnette, L.A. Chesson, J.R. Ehleringer, The influences of cultivation setting on inflorescence lipid distributions, concentrations, and carbon isotope ratios of *Cannabis sp*, Forensic Sci. Int. 262 (2016) 233–241.
- [136] A.L. Booth, M.J. Wooller, T. Howe, N. Haubenstock, Tracing geographic and temporal trafficking patterns for marijuana in Alaska using stable isotopes (C, N, O and H), Forensic Sci. Int. 202 (1–3) (2010) 45–53.
- [137] J.B. West, J.M. Hurley, F.O. Dudas, J.R. Ehleringer, The stable isotope ratios of marijuana. II. Strontium isotopes relate to geographic origin, J. Forensic Sci. 54 (6) (2009) 1261–1269.
- [138] Z. Muccio, C. Wockel, Y. An, G.P. Jackson, Comparison of bulk and compound-specific δ^{13} C isotope ratio analyses for the discrimination between Cannabis samples, J. Forensic Sci. 57 (3) (2012) 757–764.
- [139] J.R. Mallette, J.F. Casale, J. Jordan, D.R. Morello, P.M. Beyer, Geographically sourcing cocaine's origin - delineation of the nineteen major coca growing regions in South America, Sci. Rep. 6 (2016) 23520.
- [140] J.F. Casale, J.R. Mallette, Illicit coca grown in Mexico: An alkaloid and isotope profile unlike coca grown in South America, Forensic Chem. 1 (2016) 1–5.
- [141] J.R. Mallette, J.F. Casale, L.M. Jones, D.R. Morello, The isotopic fractionation of carbon, nitrogen, hydrogen, and oxygen during illicit production of cocaine base in South America, Forensic Sci. Int. 270 (2017) 255–260.
- [142] F. Marclay, C. Saudan, J. Vienne, M. Tafti, M. Saugy, Source inference of exogenous gamma-hydroxybutyric acid (GHB) administered to humans by means of carbon isotopic ratio analysis: novel perspectives regarding forensic investigation and intelligence issues, Anal. Bioanal. Chem. 400 (2011) 1105–1112.
- [143] F. Marclay, D. Pazos, O. Delemont, P. Esseiva, C. Saudan, Potential of IRMS technology for tracing gamma-butyrolactone (GBL), Forensic Sci. Int. 198 (1–3) (2010) 46–52.
- [144] N.M. Beckett, S.L. Cresswell, D.I. Grice, J.F. Carter, Isotopic profiling of seized benzylpiperazine and trifluoromethylphenylpiperazine tablets using δ^{13} C and δ^{15} N stable isotopes, Sci. Justice 55 (1) (2015) 51–56.
- [145] N.M. Beckett, D.I. Grice, J.F. Carter, S.L. Cresswell, Precursor discrimination of designer drug benzylpiperazine using δ¹³C and δ¹⁵N stable isotopes, Sci. Justice 55 (1) (2015) 57–62.
- [146] J.F. Casale, J.R. Mallette, E.M. Guest, Analysis of illicit carfentanil: Emergence of the death dragon, Forensic Chem. 3 (2017) 74–80.
- [147] M. Collins, H. Salouros, A review of some recent studies on the stable isotope profiling of methylamphetamine: is it a useful adjunct to conventional chemical

profiling? Sci. Justice 55 (1) (2015) 2-9.

- [148] C.M. Liu, P.P. Liu, W. Jia, Y.F. Fan, Carbon and nitrogen stable isotope analyses of Ephedra plant and Ephedrine samples and their application for methamphetamine profiling, J. Forensic Sci. 63 (4) (2018) 1053–1058.
- [149] R. Campbell, Intentional fires, National Fire Protection Association Fire Analysis and Research Division (2014) 81.
- [150] J.R. Hall Jr., Fires starting with flammable gas or flammable or combustible liquid, National Fire Protection Association - Fire Analysis and Research Division (2014) 187.
- [151] S.D. Harvey, K.H. Jarman, J.J. Moran, C.M. Sorensen, B.W. Wright, Characterization of diesel fuel by chemical separation combined with capillary gas chromatography (GC) isotope ratio mass spectrometry (IRMS), Talanta 99 (2012) 262–269.
- [152] S.A. Muhammad, R.D. Frew, A.R. Hayman, Forensic differentiation of diesel fuels using hydrocarbon isotope fingerprints, Central European Geol. 56 (1) (2013) 19–37.
- [153] S.A. Muhammad, A.R. Hayman, R. Van Hale, R.D. Frew, Assessing carbon and hydrogen isotopic fractionation of diesel fuel *n*-alkanes during progressive evaporation, J. Forensic Sci. 60 (S1) (2015) S56–S65.
- [154] T. Kuder, P. Philp, J. Allen, Effects of volatilization on carbon and hydrogen isotope ratios of MTBE, Environ. Sci. Technol. 43 (6) (2009) 1763–1768.
- [155] W.J. Shin, K.S. Lee, Carbon isotope fractionation of benzene and toluene by progressive evaporation, Rapid Commun. Mass Spectrom. 24 (11) (2010) 1636–1640.
- [156] Q. Xiao, Y. Sun, Y. Zhang, P. Chai, Stable carbon isotope fractionation of individual light hydrocarbons in the C_6-C_8 range in crude oil as induced by natural evaporation: experimental results and geological implications, Org. Geochem. 50 (2012) 44–56.
- [157] M.R. Williams, M.E. Sigman, J. Lewis, K.M. Pitan, Combined target factor analysis and Bayesian soft-classification of interference-contaminated samples: forensic fire debris analysis, Forensic Sci. Int. 222 (1–3) (2012) 373–386.
- [158] H. Brust, M. Koeberg, A. van der Heijden, W. Wiarda, I. Mugler, M. Schrader, G. Vivo-Truyols, P. Schoenmakers, A. van Asten, Isotopic and elemental profiling of ammonium nitrate in forensic explosives investigations, Forensic Sci. Int. 248 (2015) 101–112.
- [159] A. Beveridge, Forensic investigation of explosions, 2nd ed., CRC Press, Taylor & Francis Group, LLC, 2012.
- [160] S.J. Benson, C.J. Lennard, P. Maynard, D.M. Hill, A.S. Andrew, C. Roux, Forensic analysis of explosives using isotope ratio mass spectrometry (IRMS)-discrimination of ammonium nitrate sources, Sci. Justice 49 (2) (2009) 73–80.
- [161] S.J. Benson, C.J. Lennard, D.M. Hill, P. Maynard, C. Roux, Forensic analysis of explosives using isotope ratio mass spectrometry (IRMS)-Part 1: instrument validation of the DELTA^{plus}XP IRMS for bulk nitrogen isotope ratio measurements, J. Forensic Sci. 55 (1) (2010) 193–204.
- [162] N. Gentile, M.J. Rossi, O. Delemont, R.T.W. Siegwolf, 8¹⁵N measurement of organic and inorganic substances by EA-IRMS: a speciation-dependent procedure, Anal. Bioanal. Chem. 405 (1) (2013) 159–176.
- [163] W. Meier-Augenstein, H.F. Kemp, C.M. Lock, N₂: a potential pitfall for bulk ²H isotope analysis of explosives and other nitrogen-rich compounds by continuous-flow isotope-ratio mass spectrometry, Rapid Commun. Mass Spectrom. 23 (13) (2009) 2011–2016.
- **[164]** M.J. Lott, J.D. Howa, L.A. Chesson, J.R. Ehleringer, Improved accuracy and precision in δ^{15} _{NAI}R measurements of explosives, urea, and inorganic nitrates by elemental analyzer/isotope ratio mass spectrometry using thermal decomposition, Rapid Commun. Mass Spectrom. 29 (15) (2015) 1381–1388.
- [165] R. Aranda IV, L.A. Stern, M.E. Dietz, M.C. McCormick, J.A. Barrow, R.F. Mothershead II, Forensic utility of isotope ratio analysis of the explosive urea nitrate and its precursors, Forensic Sci. Int. 206 (1–3) (2011) 143–149.
- [166] J.D. Howa, M.J. Lott, J.R. Ehleringer, Isolation and stable nitrogen isotope analysis of ammonium ions in ammonium nitrate prills using sodium tetraphenylborate, Rapid Commun. Mass Spectrom. 28 (13) (2014) 1530–1534.
- [167] B.L. Grimm, L.A. Stern, A.J. Lowe, Forensic utility of a nitrogen and oxygen isotope ratio time series of ammonium nitrate and its isolated ions, Talanta 178 (2018) 94–101.
- [168] S.J. Benson, C.J. Lennard, P. Maynard, D.M. Hill, A.S. Andrew, C. Roux, Forensic analysis of explosives using isotope ratio mass spectrometry (IRMS)-preliminary study on TATP and PETN, Sci. Justice 49 (2) (2009) 81–86.
- [169] J.D. Howa, J.E. Barnette, L.A. Chesson, M.J. Lott, J.R. Ehleringer, TATP isotope ratios as influenced by worldwide acetone variation, Talanta 181 (2018) 125–131.
- [170] J.D. Howa, M.J. Lott, J.R. Ehleringer, Observations and sources of carbon and nitrogen isotope ratio variation of pentaerythritol tetranitrate (PETN), Forensic Sci. Int. 244 (2014) 152–157.
- [171] N. Gentile, R.T.W. Siegwolf, O. Delémont, Study of isotopic variations in black powder: reflections on the use of stable isotopes in forensic science for source inference, Rapid Commun. Mass Spectrom. 23 (2009) 2559–2567.
- [172] A.T. Quirk, J.M. Bellerby, J.F. Carter, F.A. Thomas, J.C. Hill, An initial evaluation of stable isotopic characterisation of post-blast plastic debris from improvised explosive devices, Sci. Justice 49 (2) (2009) 87–93.
- [173] D. Widory, J.J. Minet, M. Barbe-Leborgne, Sourcing explosives: a multi-isotope approach, Sci. Justice 49 (2) (2009) 62–72.
- [174] C.M. Lock, H. Brust, M. van Breukelen, J. Dalmolen, M. Koeberg, D.A. Stoker, Investigation of isotopic linkages between precursor materials and the improvised high explosive product hexamethylene triperoxide diamine, Anal. Chem. 84 (11) (2012) 4984–4992.
- [175] J.D. Howa, M.J. Lott, L.A. Chesson, J.R. Ehleringer, Carbon and nitrogen isotope ratios of factory-produced RDX and HMX, Forensic Sci. Int. 240 (2014) 80–87.
- [176] K. Bezemer, R. Woortmeijer, M. Koeberg, W. Wiarda, P. Schoenmakers, A. van

Asten, Multicomponent characterization and differentiation of flash bangers - part II: elemental profiling of plastic caps, Forensic Sci. Int. 290 (2018) 336–348.

- [177] L.A. Chesson, J.D. Howa, M.J. Lott, J.R. Ehleringer, Development of a methodological framework for applying isotope ratio mass spectrometry to explosive components, Forensic Chem. 2 (2016) 9–14.
- [178] J.D. Howa, M.J. Lott, L.A. Chesson, J.R. Ehleringer, Isolation of components of plastic explosives for isotope ratio mass spectrometry, Forensic Chem. 1 (2016) 6–12.
- [179] G.P. Danezis, A.S. Tsagkaris, F. Camin, V. Brusic, C.A. Georgiou, Food authentication: Techniques, trends & emerging approaches, TrAC, Trends Anal. Chem. 85 (2016) 123–132.
- [180] F. Camin, M. Boner, L. Bontempo, C. Fauhl-Hassek, S.D. Kelly, J. Riedl, A. Rossmann, Stable isotope techniques for verifying the declared geographical origin of food in legal cases, Trends Food Sci. Technol. 61 (2017) 176–187.
- [181] F. Camin, L. Bontempo, M. Perini, E. Piasentier, Stable isotope ratio analysis for assessing the authenticity of food of animal origin, Compr. Rev. Food Sci. Food Saf. 15 (5) (2016) 868–877.
- [182] AOAC, Official Method 998.12. C4 plant sugars in honey, Official Methods of Analysis of AOAC International 2 (1999) 27–30.
- [183] A. Simsek, M. Bilsel, A.C. Goren, ¹³C/¹²C pattern of honey from Turkey and determination of adulteration in commercially available honey samples using EA-IRMS, Food Chem. 130 (4) (2012) 1115–1121.
- [184] V. Berriel, C. Perdomo, Determination of high fructose corn syrup concentration in Uruguayan honey by ¹³C analyses, LWT Food Sci. Technol. 73 (2016) 649–653.
- [185] A.I. Cabanero, J.L. Recio, M. Ruperez, Liquid chromatography coupled to isotope ratio mass spectrometry: a new perspective on honey adulteration detection, J. Agric. Food. Chem. 54 (26) (2006) 9719–9727.
- [186] A. Guler, H. Kocaokutgen, A.V. Garipoglu, H. Onder, D. Ekinci, S. Biyik, Detection of adulterated honey produced by honeybee (*Apis mellifera L.*) colonies fed with different levels of commercial industrial sugar (C₃ and C₄ plants) syrups by the carbon isotope ratio analysis, Food Chem. 155 (2014) 155–160.
- [187] M. Tosun, Detection of adulteration in honey samples added various sugar syrups with ¹³C/¹²C isotope ratio analysis method, Food Chem. 138 (2–3) (2013) 1629–1632.
- [188] K.M. Rogers, M. Grainger, M. Manley-Harris, The unique manuka effect: why New Zealand manuka honey fails the AOAC 998.12 C₄ sugar method, J. Agric. Food. Chem. 62 (12) (2014) 2615–2622.
- [189] L. Elflein, K.-P. Raezke, Improved detection of honey adulteration by measuring differences between ¹³C/¹²C stable carbon isotope ratios of protein and sugar compounds with a combination of elemental analyzer - isotope ratio mass spectrometry and liquid chromatography - isotope ratio mass spectrometry (δ¹³C-EA/ LC-IRMS), Apidologie 39 (5) (2008) 574–587.
- [190] H. Dong, K. Xiao, Y. Xian, Y. Wu, Authenticity determination of honeys with nonextractable proteins by means of elemental analyzer (EA) and liquid chromatography (LC) coupled to isotope ratio mass spectroscopy (IRMS), Food Chem. 240 (2018) 717–724.
- [191] A. Schellenberg, S. Chmielus, C. Schlicht, F. Camin, M. Perini, L. Bontempo, K. Heinrich, S.D. Kelly, A. Rossmann, F. Thomas, E. Jamin, M. Horacek, Multielement stable isotope ratios (H, C, N, S) of honey from different European regions, Food Chem. 121 (3) (2010) 770–777.
- [192] Z. Wu, L. Chen, L. Wu, X. Xue, J. Zhao, Y. Li, Z. Ye, G. Lin, Classification of Chinese honeys according to their floral origins using elemental and stable isotopic compositions, J. Agric. Food. Chem. 63 (22) (2015) 5388–5394.
- [193] Y. Zhao, B. Zhang, G. Chen, A. Chen, S. Yang, Z. Ye, Recent developments in application of stable isotope analysis on agro-product authenticity and traceability, Food Chem. 145 (2014) 300–305.
- [194] J.F. Carter, L.A. Chesson, Food forensics: stable isotopes as a guide to authenticity and origin, CRC Press, Boca Raton, 2017.
- [195] L.D. Coletta, A.L. Pereira, A.A.D. Coelho, V.J.M. Savino, J.F.M. Menten, E. Correr, L.C. França, L.A. Martinelli, Barn vs. free-range chickens: differences in their diets determined by stable isotopes, Food Chem. 131 (1) (2012) 155–160.
- [196] R.P. Oliveira, C. Ducatti, A.C. Pezzato, J.C. Denadai, V.C. Cruz, J.R. Sartori, A.S. Carrijo, F.R. Caldara, Traceability of poultry offal meal in broiler feeding using isotopic analysis (δ^{13} C and δ^{15} N) of different tissues, Brazilian J. Poultry Sci. 12 (1) (2010) 13–20.
- [197] C.N. Rhodes, J.H. Lofthouse, S. Hird, P. Rose, P. Reece, J. Christy, R. Macarthur, P.A. Brereton, The use of stable carbon isotopes to authenticate claims that poultry have been corn-fed, Food Chem. 118 (4) (2010) 927–932.
- [198] V.C. Cruz, P.C. Araujo, J.R. Sartori, A.C. Pezzato, J.C. Denadai, G.V. Polycarpo, L.H. Zanetti, C. Ducatti, Poultry offal meal in chicken: traceability using the technique of carbon (¹³C/¹²C)- and nitrogen (¹⁵N/¹⁴N)-stable isotopes, Poult. Sci. 91 (2) (2012) 478–486.
- [199] I. González-Martin, C. González-Pérez, M.J. Hernández, E. Marqués-Macias, S.F. Poveda, Use of isotope analysis to characterize meat from Iberian-breed swine, Meat Sci. 52 (1999) 437–441.
- [200] I. González-Martin, C. González-Pérez, J.H. Méndez, C.S. González, Differentiation of dietary regimene of Iberian swine by means of isotopic analysis of carbon and sulphur in hepatic tissue, Meat Sci. 58 (2001) 25–30.
- [201] M.T. Osorio, G. Downey, A.P. Moloney, F.T. Rohrle, G. Luciano, O. Schmidt, F.J. Monahan, Beef authentication using dietary markers: chemometric selection and modelling of significant beef biomarkers using concatenated data from multiple analytical methods, Food Chem. 141 (3) (2013) 2795–2801.
- [202] T. Devincenzi, O. Delfosse, D. Andueza, C. Nabinger, S. Prache, Dose-dependent response of nitrogen stable isotope ratio to proportion of legumes in diet to authenticate lamb meat produced from legume-rich diets, Food Chem. 152 (2014) 456–461.

- [203] L. Bontempo, F. Camin, L. Ziller, L. Biondi, M.G. D'Urso, V. Vasta, G. Luciano, Variations in stable isotope ratios in lamb blood fractions following dietary changes: a preliminary study, Rapid Commun. Mass Spectrom. 30 (1) (2016) 170–174.
- [204] E. Ehtesham, A. Hayman, R. Van Hale, R. Frew, Influence of feed and water on the stable isotopic composition of dairy milk, Int. Dairy J. 47 (2015) 37–45.
- [205] B.L. Guo, Y.M. Wei, J.R. Pan, Y. Li, Stable C and N isotope ratio analysis for regional geographical traceability of cattle in China, Food Chem. 118 (4) (2010) 915–920.
- [206] G. Rees, S.D. Kelly, P. Cairns, H. Ueckermann, S. Hoelzl, A. Rossmann, M.J. Scotter, Verifying the geographical origin of poultry: the application of stable isotope and trace element (SITE) analysis, Food Control 67 (2016) 144–154.
- [207] A. Trembaczowski, Use of sulphur and carbon stable-isotope composition of fish scales and muscles to identify the origin of fish, Mineralogia 42 (1) (2011).
- [208] J.F. Carter, U. Tinggi, X. Yang, B. Fry, Stable isotope and trace metal compositions of Australian prawns as a guide to authenticity and wholesomeness, Food Chem. 170 (2015) 241–248.
- [209] M.P. Chaguri, A.L. Maulvault, M.L. Nunes, D.A. Santiago, J.C. Denadai, F.H. Fogaça, L.S. Sant'Ana, C. Ducatti, N. Bandarra, M.L. Carvalho, A. Marques, Different tools to trace geographic origin and seasonality of croaker (*Micropogonias furnieri*), LWT Food Sci. Technol. 61 (1) (2015) 194–200.
- [210] H. Kim, K. Suresh Kumar, K.-H. Shin, Applicability of stable C and N isotope analysis in inferring the geographical origin and authentication of commercial fish (Mackerel, Yellow Croaker and Pollock), Food Chem. 172C (2015) 523–527.
- [211] I. Ortea, J.M. Gallardo, Investigation of production method, geographical origin and species authentication in commercially relevant shrimps using stable isotope ratio and/or multi-element analyses combined with chemometrics: an exploratory analysis, Food Chem. 170 (2015) 145–153.
- [212] L.A. Chesson, L.O. Valenzuela, S.P. O'Grady, T.E. Cerling, J.R. Ehleringer, Hydrogen and oxygen stable isotope ratios of milk in the United States, J. Agric. Food. Chem. 58 (4) (2010) 2358–2363.
- [213] E. Ehtesham, A.R. Hayman, K.A. McComb, R. Van Hale, R.D. Frew, Correlation of geographical location with stable isotope values of hydrogen and carbon of fatty acids from New Zealand milk and bulk milk powder, J. Agric. Food. Chem. 61 (37) (2013) 8914–8923.
- [214] R. Stevenson, S. Desrochers, J.-F. Hélie, Stable and radiogenic isotopes as indicators of agri-food provenance: insights from artisanal cheeses from Quebec, Canada, Int. Dairy J. 49 (2015) 37–45.
- [215] M. Nečemer, D. Potočnik, N. Ogrinc, Discrimination between Slovenian cow, goat and sheep milk and cheese according to geographical origin using a combination of elemental content and stable isotope data, J. Food Compost. Anal. 52 (2016) 16–23.
- [216] F. Longobardi, G. Casiello, M. Cortese, M. Perini, F. Camin, L. Catucci, A. Agostiano, Discrimination of geographical origin of lentils (*Lens culinaris* Medik.) using isotope ratio mass spectrometry combined with chemometrics, Food Chem. 188 (2015) 343–349.
- T. Mimmo, F. Camin, L. Bontempo, C. Capici, M. Tagliavini, S. Cesco,
 M. Scampicchio, Traceability of different apple varieties by multivariate analysis of isotope ratio mass spectrometry data, Rapid Commun. Mass Spectrom. 29 (21) (2015) 1984–1990.
- [218] E. de Rijke, J.C. Schoorl, C. Cerli, H.B. Vonhof, S.J. Verdegaal, G. Vivo-Truyols, M. Lopatka, R. Dekter, D. Bakker, M.J. Sjerps, M. Ebskamp, C.G. de Koster, The use of δ²H and δ¹⁸O isotopic analyses combined with chemometrics as a traceability tool for the geographical origin of bell peppers, Food Chem. 204 (2016) 122–128.
- [219] M. Perini, L. Giongo, M. Grisenti, L. Bontempo, F. Camin, Stable isotope ratio analysis of different European raspberries, blackberries, blueberries, currants and strawberries, Food Chem. 239 (2018) 48–55.
- [220] N.S. Podio, M.V. Baroni, R.G. Badini, M. Inga, H.A. Ostera, M. Cagnoni, E.A. Gautier, P.P. Garcia, J. Hoogewerff, D.A. Wunderlin, Elemental and isotopic fingerprint of Argentinean wheat. Matching soil, water, and crop composition to differentiate provenance, J. Agric. Food. Chem. 61 (16) (2013) 3763–3773.
- [221] D. Luo, H. Dong, H. Luo, Y. Xian, J. Wan, X. Guo, Y. Wu, The application of stable isotope ratio analysis to determine the geographical origin of wheat, Food Chem. 174 (2015) 197–201.
- [222] Y. Wu, D. Luo, H. Dong, J. Wan, H. Luo, Y. Xian, X. Guo, F. Qin, W. Han, L. Wang, B. Wang, Geographical origin of cereal grains based on element analyser-stable isotope ratio mass spectrometry (EA-SIRMS), Food Chem. 174 (2015) 553–557.
- [223] I.M. Chung, J.K. Kim, M. Prabakaran, J.H. Yang, S.H. Kim, Authenticity of rice (Oryza sativa L.) geographical origin based on analysis of C, N, O and S stable isotope ratios: a preliminary case report in Korea, China and Philippine, J. Sci. Food Agric. 96(7) (2016) 2433–2439.
- [224] I.M. Chung, J.K. Kim, K.J. Lee, S.K. Park, J.H. Lee, N.Y. Son, Y.I. Jin, S.H. Kim, Geographic authentication of Asian rice (*Oryza sativa* L.) using multi-elemental and stable isotopic data combined with multivariate analysis, Food Chem. 240 (2018) 840–849.
- [225] L. Bontempo, F. Camin, M. Paolini, C. Micheloni, K.H. Laursen, Multi-isotopic signatures of organic and conventional Italian pasta along the production chain, J. Mass Spectrom. 51 (9) (2016) 675–683.
- [226] M. Bononi, G. Quaglia, F. Tateo, Easy extraction method to evaluate δ^{13} C vanillin by liquid chromatography-isotopic ratio mass spectrometry in chocolate bars and chocolate snack foods, J. Agric. Food. Chem. 63 (19) (2015) 4777–4781.
- [227] J.F. Carter, H.S. Yates, U. Tinggi, Isotopic and elemental composition of roasted coffee as a guide to authenticity and origin, J. Agric. Food. Chem. 63 (24) (2015) 5771–5779.
- [228] L.A. Chesson, L.O. Valenzuela, S.P. O'Grady, T.E. Cerling, J.R. Ehleringer, Links between purchase location and stable isotope ratios of bottled water, soda, and

beer in the United States, J. Agric. Food. Chem. 58 (12) (2010) 7311-7316.

- [229] S. Rummel, S. Hoelzl, P. Horn, A. Rossmann, C. Schlicht, The combination of stable isotope abundance ratios of H, C, N and S with ⁸⁷Sr/⁸⁶Sr for geographical origin assignment of orange juices, Food Chem. 118 (4) (2010) 890–900.
- [230] S.V. Dutra, L. Adami, A.R. Marcon, G.J. Carnieli, C.A. Roani, F.R. Spinelli, S. Leonardelli, R. Vanderlinde, Characterization of wines according the geographical origin by analysis of isotopes and minerals and the influence of harvest on the isotope values, Food Chem. 141 (3) (2013) 2148–2153.
- [231] M. Perini, F. Camin, δ¹⁸O of ethanol in wine and spirits for authentication purposes, J. Food Sci. 78 (6) (2013) C839–C844.
- [232] J.F. Carter, H.S. Yates, U. Tinggi, A global survey of the stable isotope and chemical compositions of bottled and canned beers as a guide to authenticity, Sci. Justice 55 (1) (2015) 18–26.
- [233] J.F. Carter, H.S. Yates, U. Tinggi, Stable isotope and chemical compositions of European and Australasian ciders as a guide to authenticity, J. Agric. Food. Chem. 63 (3) (2015) 975–982.
- [234] M. Horacek, K. Hansel-Hohl, K. Burg, G. Soja, W. Okello-Anyanga, S. Fluch, Control of origin of sesame oil from various countries by stable isotope analysis and DNA based markers-A pilot study, PLoS One 10 (4) (2015) 12.
- [235] H. Jeon, S.C. Lee, Y.J. Cho, J.H. Oh, K. Kwon, B.H. Kim, A triple-isotope approach for discriminating the geographic origin of Asian sesame oils, Food Chem. 167 (2015) 363–369.
- [236] F. Camin, A. Pavone, L. Bontempo, R. Wehrens, M. Paolini, A. Faberi, R.M. Marianella, D. Capitani, S. Vista, L. Mannina, The use of IRMS, ¹H NMR and chemical analysis to characterise Italian and imported Tunisian olive oils, Food Chem. 196 (2016) 98–105.
- [237] F. Chiocchini, S. Portarena, M. Ciolfi, E. Brugnoli, M. Lauteri, Isoscapes of carbon and oxygen stable isotope compositions in tracing authenticity and geographical origin of Italian extra-virgin olive oils, Food Chem. 202 (2016) 291–301.
- [238] L.A. Martinelli, G.B. Nardoto, L.A. Chesson, F.D. Rinaldi, J.P.H.B. Ometto, T.E. Cerling, J.R. Ehleringer, Worldwide stable carbon and nitrogen isotopes of Big Mac⁶ patties: an example of a truly "glocal" food, Food Chem. 127 (4) (2011) 1712–1718.
- [239] L.A. Chesson, Flesh foods, or What can stable isotope analysis reveal about the meat you eat? in: J.F. Carter, L.A. Chesson (Eds.), Food forensics: stable isotopes as a guide to authenticity and origin, CRC Press, Boca Raton, 2017, pp. 115–152.
- [240] L.A. Chesson, L.O. Valenzuela, G.J. Bowen, T.E. Cerling, J.R. Ehleringer, Consistent predictable patterns in the hydrogen and oxygen stable isotope ratios of animal proteins consumed by modern humans in the USA, Rapid Commun. Mass Spectrom. 25 (24) (2011) 3713–3722.
- [241] J.N. Bostic, S.J. Palafox, M.E. Rottmueller, A.H. Jahren, Effect of baking and fermentation on the stable carbon and nitrogen isotope ratios of grain-based food, Rapid Commun. Mass Spectrom. 29 (10) (2015) 937–947.
- [242] R. Fernandes, J. Meadows, A. Dreves, M.-J. Nadeau, P. Grootes, A preliminary study on the influence of cooking on the C and N isotopic composition of multiple organic fractions of fish (mackerel and haddock), J. Archaeol. Sci. 50 (2014) 153–159.
- [243] B. Doering, Measuring the potential influence of cooking on the carbon and nitrogen isotopic composition of spawning Chinook salmon, J. Archaeological Sci. Rep. 12 (2017) 491–498.
- [244] J. Zhou, B. Guo, Y. Wei, G. Zhang, S. Wei, Y. Ma, The effect of different cooking processes on stable C, N, and H isotopic compositions of beef, Food Chem. 182 (2015) 23–26.
- [245] A. Royer, V. Daux, F. Fourel, C. Lecuyer, Carbon, nitrogen and oxygen isotope fractionation during food cooking: implications for the interpretation of the fossil human record, Am. J. Phys. Anthropol. 163 (4) (2017) 759–771.
- [246] H. Willer, J. Lernoud, The world of organic agriculture. Statistics and emerging trends 2016., Research Institute of Organic Agriculture (FiBL), Frick, and IFOAM – Organics International, Bonn, 2016.
- [247] J. Molkentin, A. Giesemann, Follow-up of stable isotope analysis of organic versus conventional milk, Anal. Bioanal. Chem. 398 (3) (2010) 1493–1500.
- [248] J. Molkentin, Applicability of organic milk indicators to the authentication of processed products, Food Chem. 137 (1–4) (2013) 25–30.
- [249] I.M. Chung, I. Park, J.Y. Yoon, Y.S. Yang, S.H. Kim, Determination of organic milk authenticity using carbon and nitrogen natural isotopes, Food Chem. 160 (2014) 214–218.
- [250] S. Kaffarnik, M. Schröder, K. Lehnert, T. Baars, W. Vetter, 8¹³C values and phytanic acid diastereomer ratios: combined evaluation of two markers suggested for authentication of organic milk and dairy products, Eur. Food Res. Technol. 238 (5) (2014) 819–827.
- [251] S. Erich, S. Schill, E. Annweiler, H.U. Waiblinger, T. Kuballa, D.W. Lachenmeier, Y.B. Monakhova, Combined chemometric analysis of ¹H NMR, ¹³C NMR and stable isotope data to differentiate organic and conventional milk, Food Chem. 188 (2015) 1–7.
- [252] K.M. Rogers, Stable isotopes as a tool to differentiate eggs laid by caged, barn, free range, and organic hens, J. Agric. Food. Chem. 57 (10) (2009) 4236–4242.
- [253] J. Molkentin, I. Lehmann, U. Östermeyer, H. Rehbein, Traceability of organic fish authenticating the production origin of salmonids by chemical and isotopic analyses, Food Control 53 (2015) 55–66.
- [254] Y. Zhao, S. Yang, D. Wang, Stable carbon and nitrogen isotopes as a potential tool to differentiate pork from organic and conventional systems, J. Sci. Food Agric. 96 (11) (2016) 3950–3955.
- [255] C.T. Inácio, P.M. Chalk, A.M.T. Magalhães, Principles and Limitations of Stable Isotopes in Differentiating Organic and Conventional Foodstuffs: 1. Plant Products, Crit. Rev. Food Sci. Nutr. 55 (9) (2015) 1206–1218.
- [256] C.T. Inácio, P.M. Chalk, Principles and limitations of stable isotopes in

differentiating organic and conventional foodstuffs: 2. Animal products, Crit. Rev. Food Sci. Nutr. 57 (1) (2017) 181–196.

- [257] S.D. Kelly, A.S. Bateman, Comparison of mineral concentrations in commercially grown organic and conventional crops – Tomatoes (*Lycopersicon esculentum*) and lettuces (*Lactuca sativa*), Food Chem. 119 (2) (2010) 738–745.
- [258] K.H. Laursen, A. Mihailova, S.D. Kelly, V.N. Epov, S. Berail, J.K. Schjoerring, O.F. Donard, E.H. Larsen, N. Pedentchouk, A.D. Marca-Bell, U. Halekoh, J.E. Olesen, S. Husted, Is it really organic? - Multi-isotopic analysis as a tool to discriminate between organic and conventional plants, Food Chem. 141 (3) (2013) 2812–2820.
- [259] M. Paolini, L. Ziller, K.H. Laursen, S. Husted, F. Camin, Compound-Specific δ^{15} N and δ^{13} C Analyses of Amino Acids for Potential Discrimination between Organically and Conventionally Grown Wheat, J. Agric. Food. Chem. 63 (25) (2015) 5841–5850.
- [260] M. Hohmann, Y. Monakhova, S. Erich, N. Christoph, H. Wachter, U. Holzgrabe, Differentiation of organically and conventionally grown tomatoes by chemometric analysis of combined data from proton nuclear magnetic resonance and mid-infrared spectroscopy and stable isotope analysis, J. Agric. Food. Chem. 63 (43) (2015) 9666–9675.
- [261] A. Mihailova, N. Pedentchouk, S.D. Kelly, Stable isotope analysis of plant-derived nitrate - novel method for discrimination between organically and conventionally grown vegetables, Food Chem. 154 (2014) 238–245.
- [262] N. Christoph, A. Hermann, H. Wachter, 25 Years authentication of wine with stable isotope analysis in the European Union – Review and outlook, BIO Web of Conferences 5 (2015) 02020.
- [263] H. Chen, B.H. Shen, S.J. Zhang, P. Xiang, X.Y. Zhuo, M. Shen, Alcohol consumption or contamination: a preliminary study on the determination of the ethanol origin by stable carbon isotope analysis, Forensic Sci. Int. 289 (2018) 374–380.
- [264] H. Kawashima, The measurement of stable carbon isotope ratios of eight methamidophos samples, J. Forensic Sci. 60 (5) (2015) 1360–1364.
- [265] E. Ehtesham, F. Camin, L. Bontempo, R.D. Frew, Stable isotope measurements and modeling to verify the authenticity of dairy products, in: J.F. Carter, L.A. Chesson (Eds.), Food Forensics: Stable Isotopes as a Guide to Authenticity and Origin, CRC Press, Boca Raton, 2017, pp. 239–256.
- [266] B.Y. Song, S. Gwak, M. Jung, G. Nam, N.Y. Kim, Tracing the source of methomyl using stable isotope analysis, Rapid Commun. Mass Spectrom. 32 (3) (2018) 235–240.
- [267] G. Michalski, S. Earman, C. Dahman, R.L. Hershey, T. Mihevc, Multiple isotope forensics of nitrate in a wild horse poisoning incident, Forensic Sci. Int. 198 (1–3) (2010) 103–109.
- [268] H.W. Kreuzer, J. Horita, J.J. Moran, B.A. Tomkins, D.B. Janszen, A. Carman, Stable carbon and nitrogen isotope ratios of sodium and potassium cyanide as a forensic signature. J. Forensic Sci. 57 (1) (2012) 75–79.
- [269] I. Tea, I. Antheaume, B.L. Zhang, A test to identify cyanide origin by isotope ratio mass spectrometry for forensic investigation, Forensic Sci. Int. 217 (1–3) (2012) 168–173.
- [270] H.W. Kreuzer, J.B. West, J.R. Ehleringer, Forensic applications of light-element stable isotope ratios of *Ricinus communis* seeds and ricin preparations, J. Forensic Sci. 58 (Suppl 1) (2013) S43–S51.
- [271] J.J. Moran, C.G. Fraga, M.K. Nims, Stable-carbon isotope ratios for sourcing the nerve-agent precursor methylphosphonic dichloride and its products, Talanta 186 (2018) 678–683.
- [272] V. Causin, C. Marega, A. Marigo, R. Casamassima, G. Peluso, L. Ripani, Forensic differentiation of paper by X-ray diffraction and infrared spectroscopy, Forensic Sci. Int. 197 (1–3) (2010) 70–74.
- [273] T. Trejos, A. Flores, J.R. Almirall, Micro-spectrochemical analysis of document paper and gel inks by laser ablation inductively coupled plasma mass spectrometry and laser induced breakdown spectroscopy, Spectrochim. Acta, Pt. B: Atom. Spectrosc. 65 (11) (2010) 884–895.
- [274] C. Neumann, R. Ramotowski, T. Genessay, Forensic examination of ink by highperformance thin layer chromatography - The United States Secret Service Digital Ink Library, J. Chromatogr. A 1218 (19) (2011) 2793–2811.
- [275] C.E. Berger, D. Ramos, Objective paper structure comparison: assessing comparison algorithms, Forensic Sci. Int. 222 (1–3) (2012) 360–367.
- [276] J.A. Green, Reliability of paper brightness in authenticating documents, J. Forensic Sci. 57 (4) (2012) 1003–1007.
- [277] Review of the scientific approaches used during the FBI's investigation of the, anthrax letters, The National Academies Press, Washington, DC, 2001, p. 2011.
- [278] K. Jones, S. Benson, C. Roux, The forensic analysis of office paper using carbon isotope ratio mass spectrometry - Part 1: understanding the background population and homogeneity of paper for the comparison and discrimination of samples, Forensic Sci. Int. 231 (1–3) (2013) 354–363.

- [279] K. Jones, S. Benson, C. Roux, The forensic analysis of office paper using carbon isotope ratio mass spectrometry -part 2: method development, validation and sample handling, Forensic Sci. Int. 231 (1–3) (2013) 364–374.
- [280] K. Jones, S. Benson, C. Roux, The forensic analysis of office paper using carbon isotope ratio mass spectrometry. Part 3: characterizing the source materials and the effect of production and usage on the δ^{13} C values of paper, Forensic Sci. Int. 233 (1–3) (2013) 355–364.
- [281] K. Jones, S. Benson, C. Roux, The forensic analysis of office paper using oxygen isotope ratio mass spectrometry. Part 1: understanding the background population and homogeneity of paper for the comparison and discrimination of samples, Forensic Sci. Int. 262 (2016) 97–107.
- [282] K. Jones, S. Benson, C. Roux, The forensic analysis of office paper using oxygen Isotope Ratio Mass Spectrometry, part 2: characterising the source materials and the effect of production and usage on the δ^{18} O values of cellulose and paper, Forensic Sci. Int. 268 (2016) 151–158.
- [283] A. van Es, J. de Koeijer, G. van der Peijl, Discrimination of document paper by XRF, LA–ICP–MS and IRMS using multivariate statistical techniques, Sci. Justice 49 (2) (2009) 120–126.
- [284] A. Braz, M. Lopez-Lopez, C. Garcia-Ruiz, Raman spectroscopy for forensic analysis of inks in questioned documents, Forensic Sci. Int. 232 (1–3) (2013) 206–212.
- [285] A. Braz, M. Lopez-Lopez, C. Garcia-Ruiz, Studying the variability in the Raman signature of writing pen inks, Forensic Sci. Int. 245C (2014) 38–44.
- [286] C.K. Muro, K.C. Doty, J. Bueno, L. Halamkova, I.K. Lednev, Vibrational spectroscopy: recent developments to revolutionize forensic science, Anal. Chem. 87 (1) (2015) 306–327.
- [287] L.A. Chesson, B.J. Tipple, J.E. Barnette, T.E. Cerling, J.R. Ehleringer, The potential for application of ink stable isotope analysis in questioned document examination, Sci. Justice 55 (1) (2015) 27–33.
- [288] Y. Suzuki, R. Kobe, R. Nakashita, A novel method to discriminate between natural and synthetic fibers by stable carbon, nitrogen, and oxygen isotope analyses, Chem. Lett. 41 (3) (2012) 242–243.
- [289] N.N. Daeid, W. Meier-Augenstein, H.F. Kemp, Investigating the provenance of undyed spun cotton fibre using multi-isotope profiles and chemometric analysis, Rapid Commun. Mass Spectrom. 25 (13) (2011) 1812–1816.
- [290] W. Meier-Augenstein, H.F. Kemp, E.R. Schenk, J.R. Almirall, Discrimination of unprocessed cotton on the basis of geographic origin using multi-element stable isotope signatures, Rapid Commun. Mass Spectrom. 28 (5) (2014) 545–552.
- [291] K. Jones, F. Koens, T. Simpson, Background survey of polyethylene in the Australian Capital Territory - a demonstration of variability in isotopic abundance values and their application to forensic casework, Sci. Justice 58 (4) (2018) 276–281.
- [292] F.A. Idoine, J.F. Carter, R. Sleeman, Bulk and compound-specific isotopic characterisation of illicit heroin and cling film, Rapid Commun. Mass Spectrom. 19 (22) (2005) 3207–3215.
- [293] J.F. Carter, R. Sleeman, J.C. Hill, F. Idoine, E.L. Titterton, Isotope ratio mass spectrometry as a tool for forensic investigation (examples from recent studies), Sci. Justice 45 (3) (2005) 141–149.
- [294] E. Taylor, J.F. Carter, J.C. Hill, C. Morton, N.N. Daeid, R. Sleeman, Stable isotope ratio mass spectrometry and physical comparison for the forensic examination of grip-seal plastic bags, Forensic Sci. Int. 177 (2–3) (2008) 214–220.
- [295] J.F. Carter, P.L. Grundy, J.C. Hill, N.C. Ronan, E.L. Titterton, R. Sleeman, Forensic isotope ratio mass spectrometry of packaging tapes, Analyst 129 (12) (2004) 1206–1210.
- [296] M. Horacek, J.S. Min, S. Heo, J. Park, W. Papesch, The application of isotope ratio mass spectrometry for discrimination and comparison of adhesive tapes, Rapid Commun. Mass Spectrom. 22 (11) (2008) 1763–1766.
- [297] K.W. McMahon, S.D. Newsome, Amino acid isotope analysis: A new frontier in studies of animal migration and foraging ecology, in: K.A. Hobson, L.I. Wassenaar (Eds.), Tracking Animal Migration with Stable Isotopes, Academic Press, 2019, pp. 173–190.
- [298] S. Khodjaniyazova, M. Nazari, K.P. Garrard, M.P.V. Matos, G.P. Jackson, D.C. Muddiman, Characterization of the spectral accuracy of an orbitrap mass analyzer using Isotope Ratio Mass Spectrometry, Anal. Chem. 90 (3) (2018) 1897–1906.
- [299] A.A. Baczynski, P.J. Polissar, D. Juchelka, J. Schwieters, A. Hilkert, R.E. Summons, K.H. Freeman, Picomolar-scale compound-specific isotope analyses, Rapid Commun. Mass Spectrom. 32 (9) (2018) 730–738.
- [300] B. Fry, J.F. Carter, K. Yamada, N. Yoshida, D. Juchelka, Position-specific ¹³C/¹²C analysis of amino acid carboxyl groups - automated flow-injection analysis based on reaction with ninhydrin, Rapid Commun. Mass Spectrom. 32 (12) (2018) 992–1000.