Chapter 9
Isotopic Analysis Techniques Applied to Forensics: New Frontiers of Isotope Geochemistry

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Abstract The isotope composition of chemical elements is an invaluable investigation tool widely used in Earth Sciences. Rocks, waters and gases acquire specific radiogenic (e.g., $^{87}Sr/^{86}Sr$) and stable (e.g., $\delta^{18}O$) isotope ratios due to geological processes such as magmas' genesis and evolution, past climatic changes, mixing among distinct reservoirs. The power of these tracers bears in the particular isotope signature any geological material acquires due to both its history and specific processes undergone. Isotope approaches have recently been applied to track air, soil and water pollutants, to identify the provenance of archaeological artifacts, and to reconstruct diet and migration paths of past animals and humans. In this framework, isotope tracers can be efficiently coupled to more traditional investigation techniques to solve forensic issues, including linking a suspect to a crime scene, identifying crime victims and the guilty of an environmental crime, tracking the provenance of drugs, identifying explosives. In this chapter, laboratory techniques for the preparation of variable materials aimed at their isotope analysis are illustrated. Examples of application of isotope analysis techniques are described for a variety of forensic problems.

Keywords Radiogenic and stable isotope ratios · Isotope ratios in forensic investigations · Samples preparation techniques · Isotopic ratios determinations

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Most chemical elements include two or more isotopes, i.e., atoms with a specific *atomic number* Z (number of protons in the nucleus), but with a different *mass number* A (sum of protons and neutrons in the nucleus). Therefore, isotopes of the same chemical element are distinguished by their number of neutrons. There are two categories of isotopes: stable and radioactive. Isotopes subject to radioactive decay spontaneously transform over time by emitting high-energy particles to form other isotopes, which can in turn be stable or radioactive. On the other hand, isotopes that do not decay are stable, even over geological timescales; some of them can also be produced by the decay of radioactive isotopes, either directly or as intermediate or final terms of a decay series. These are then called *radiogenic*.

Radiogenic isotope geochemistry uses the isotope ratios of natural elements either to perform absolute dating of samples of geological material (rocks and minerals) or as a tracer of geological processes. The isotope ratios of these elements vary because of their more or less long permanence in the Earth' mantle or crust. During this time, the abundance of the radiogenic isotopes increases due to the radioactive decay of their parent isotopes. For example, ^{87}Sr increases over time due to radioactive decay of ^{87}Rb. *Stable isotope geochemistry* uses the fractionation existing between isotopes of a chemical element generally with a low atomic number, such as hydrogen, carbon, nitrogen, oxygen, and sulfur (light elements). Isotope fractionation is the enrichment, resulting from various natural processes, of a lighter isotope of a given element with respect to a heavier one, or vice versa. Therefore, *isotope geochemistry* offers efficient tools to investigate many geological processes, including variations in climatic conditions in marine and oceanic environments; assimilation of crustal rocks by a crystallizing magma; mixing between distinct magmas; mixing between waters from different sources; mixing of different clast types in sedimentation basins. For all these purposes, the isotope composition of the elements of interest is reported as ratio between the abundance of two isotopes of the same element, since these ratios are determined using specific analytical tools (Sect. 9.3). In the case of heavy elements such as Sr, Nd and Pb, the $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$ and $^{206}Pb/^{204}Pb$ ratios are used, where the radiogenic isotope, placed in the numerator, is related to a stable and non-radiogenic isotope of the same element placed in the denominator (White 2015, and references therein). In the case of light elements such as B, C, N and O, the so-called δ notation is used, in which the measured values of the isotope ratios are normalized to those of a standard, for example $\delta^{11}B$, $\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$ (White 2015, and references therein).

9.1   Sample Preparation

When facing a crime scene, investigators might need characterizing a great variety of both inorganic and organic materials. Moreover, other contexts besides crime scenes may offer additional investigation materials. More specifically, inorganic materials of interest may include soil, sand, clay, rock/mineral fragments, and parts from building constructions such as mortar, plaster, bricks, concrete, all derived

from natural raw materials. On the other side, organic materials of interest span among human or animal remains such as hair, bones, teeth, as well as food, beverages, plants including those cultivated for obtaining drugs such as *Cannabis* for marijuana, *Papaver somniferum* for opium, and *Erythroxylum coca* for cocaine.

Depending on the chemical nature and physical state of the find under investigation, and on the type of element(s) to be analyzed for its isotope composition, a specific preparation procedure suitable for the measurement must be followed. Furthermore, isotope analysis may be carried out either on simple compounds containing large amounts of the element of interest, or on chemically complex matrices where the element of interest is dispersed into trace amounts. This is important because there are some analytical techniques capable of analyzing a single element in a complex matrix, and others needing this element to be isolated from its matrix through specific separation techniques. The latter allow obtaining a single element in an ionic form in either aqueous or acid solution, an easily solubilized simple compound (a salt) of the element of interest, or a gaseous element or compound.

The element of interest may be in many cases a trace metal such as Sr or Pb dispersed in a solid. In these cases, sample preparation must be carried out in a *clean room* laboratory (Fig. 9.1), to minimize any possible contamination of the sample from external sources such as air, dust or water.

For isotope analysis, an ISO 6 class (i.e., <10,200 particles per m^3 with ≥0.3 μm diameter) clean room is desirable. The filtered air is introduced into the clean room with an overpressure of a few pascals and then extracted to the outside to assure an exchange of at least 50 air volumes per hour. As a further precaution aimed at minimizing sample contamination, the employed laboratory glassware is made up of either Teflon (PTFE, *Polytetrafluoroethylene*) or PFA (*Perfluoroalkoxy alkanes*) due to their chemical resistance and anti-stick properties. High-purity chemical reagents of *Suprapur®* and/or *Ultrapure* grades, diluted with Milli-Q® deionized water (18.2 MΩ cm^{-1} resistivity) are utilized for glassware cleaning, sample dissolution and the other chemical processes described in the following section. The latter procedures require using strongly corrosive and toxic reagents and must be carried out under a laminar flow hood (Fig. 9.1), capable of extracting and reducing their fumes.

9.1.1   Preparation Techniques for Inorganic Samples

Inorganic samples (*rocks*, *minerals*, *amorphous material*) of interest for forensic investigations are extremely variable in chemical composition. In several cases, they are constituted of variable amounts of minerals, namely natural solid substances where the constituent atoms are ordered in a tridimensional crystal lattice. Most minerals on Earth are silicates and carbonates, whereas other species such as oxides, phosphates, sulfides, and pure metals are less common.

Inorganic samples can be treated as a whole or might need to be subdivided into their constituting phases, including various minerals and amorphous fraction. The element of interest can occur in one or more of the separated phases. The separated
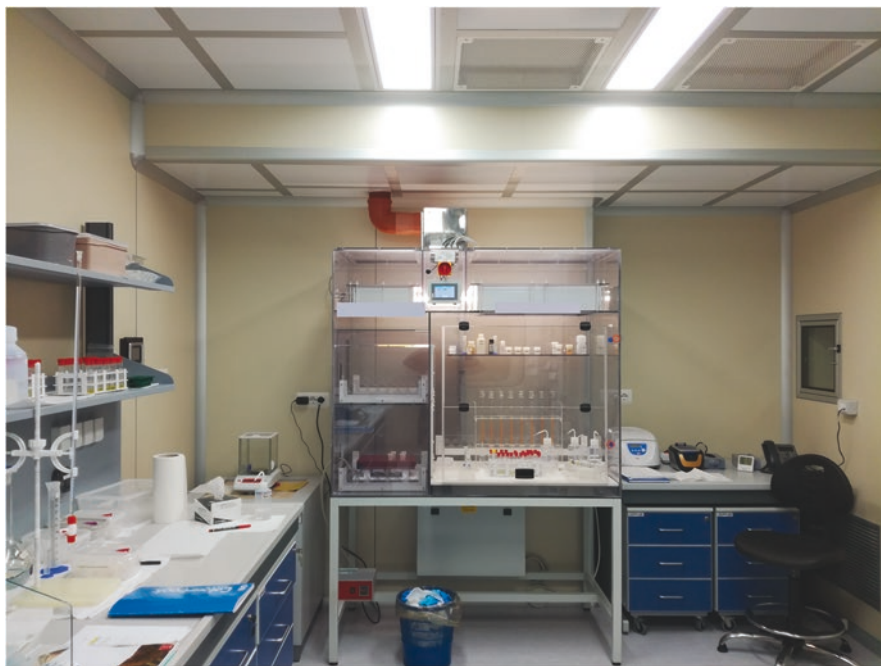
Fig. 9.1 ISO 6 class clean room. Notice the High Efficiency Particulate Air (HEPA) filters on the ceiling from which clean air enters the room and, in the background, a Perspex laminar flow hood equipped with two HEPA filters located on top, to achieve ISO 5 class. (Source: Clean Room, Department of Earth, Environmental and Resources Sciences (DiSTAR), University Federico II, Naples, Italy. Photo by M. D'Antonio)

fraction(s) of the sample will have a certain grain-size; the latter should be on the order of a few tens of microns for the sample to be efficiently treated during the following chemical procedures. Should the grain-size be too large, it can be reduced to the desired value by means of suitable pulverization techniques and devices, such as planetary ball mills.

9.1.1.1   Extraction with a Solvent

Based on the type of compound and its solubility, a variety of solvents can be used including simple water, diluted acid solutions of HCl, HNO_3, CH_3COOH, and organic solvents like CH_2Cl_2. One useful application is the extraction of a protein from food (Sect. 9.1.2.5). If the element of interest represents the main component of a simple, soluble compound such as a chloride or sulfide, it can be easily extracted using a suitable solvent. However, extraction with a solvent has a limited applicability because isotope analysis is carried out on mostly insoluble inorganic materials. Such

compounds are complex matrices where the element of interest does not form its own mineral but is dispersed in trace amounts. Therefore, the sample must be solubilized through dissolution with a mineral acid, as described in the following section.

9.1.1.2   Dissolution with Mineral Acids

A trace element of interest can be extracted from complex matrices utilizing various techniques depending on the chemical nature and physical state of the sample. A typical dissolution procedure of a solid inorganic sample, using *Suprapur®* grade reagents, includes several steps:

- Weighing 50–100 mg of the powdered sample in a PTFE crucible using a high-precision analytical balance (Fig. 9.2a).
- Leaching: based on the alteration state of the sample it may be useful to pre-treat the powder with 1–2 mL of a diluted HF or HCl, at either room or higher temperature, for few minutes to tens of minutes. The acid solution is then removed using a pipette with a sterilized tip, and the procedure repeated once or more times. At the end, the powder is rinsed several times with 1–2 mL of Milli-Q® water, every time removed with a pipette. This procedure can effectively remove secondary carbonates, chlorides and/or undesired silicate glass, that may contain significant amounts of trace elements that might interfere with the measured isotope ratio.
- First acid dissolution, finalized to the disaggregation of chemical bonds in most silicates: it is achieved by adding a mixture of 40 vol.% HF (the only mineral acid capable of dissolving silicates) and 14 M HNO_3 (5:1), for a total of 1.5 mL per 50 mg of powder, closing tightly the vial and leaving it on a hot plate (Fig. 9.2b) at a temperature of ~120 °C for a time variable from 12 h to 4–5 days, depending on the type of sample. At the end, the vial is left open on the hot plate under a laminar flow hood until complete evaporation is achieved (generally 3–4 h). The resulting solid will be made up of very reactive fluoride compounds.
- Second acid dissolution, aimed at transforming these fluorides into nitrates: 0.5 mL of 14 M HNO_3 are added to the sample in the vial, and left open on hot plate under a laminar flow hood until complete dryness. The resulting nitrates are almost completely soluble in diluted acid solutions. However, for isolating the element of interest for the isotope analysis, chlorides are the preferred chemical form (see Sect. 9.1.3).
- Third acid dissolution, to transform the nitrates back into chlorides: 2 mL of 6 M HCl are added to the sample in the vial and left open on the hot plate under laminar flow hood for the time required to reach complete evaporation.

The described procedure may vary depending on specific characteristics of the sample and on its chemical response to the different types of acid solutions employed. Adaptations may include (i) adding 30% H_2O_2 to the powder to remove organic matter; (ii) putting the closed vials with the mixture acid + sample in an
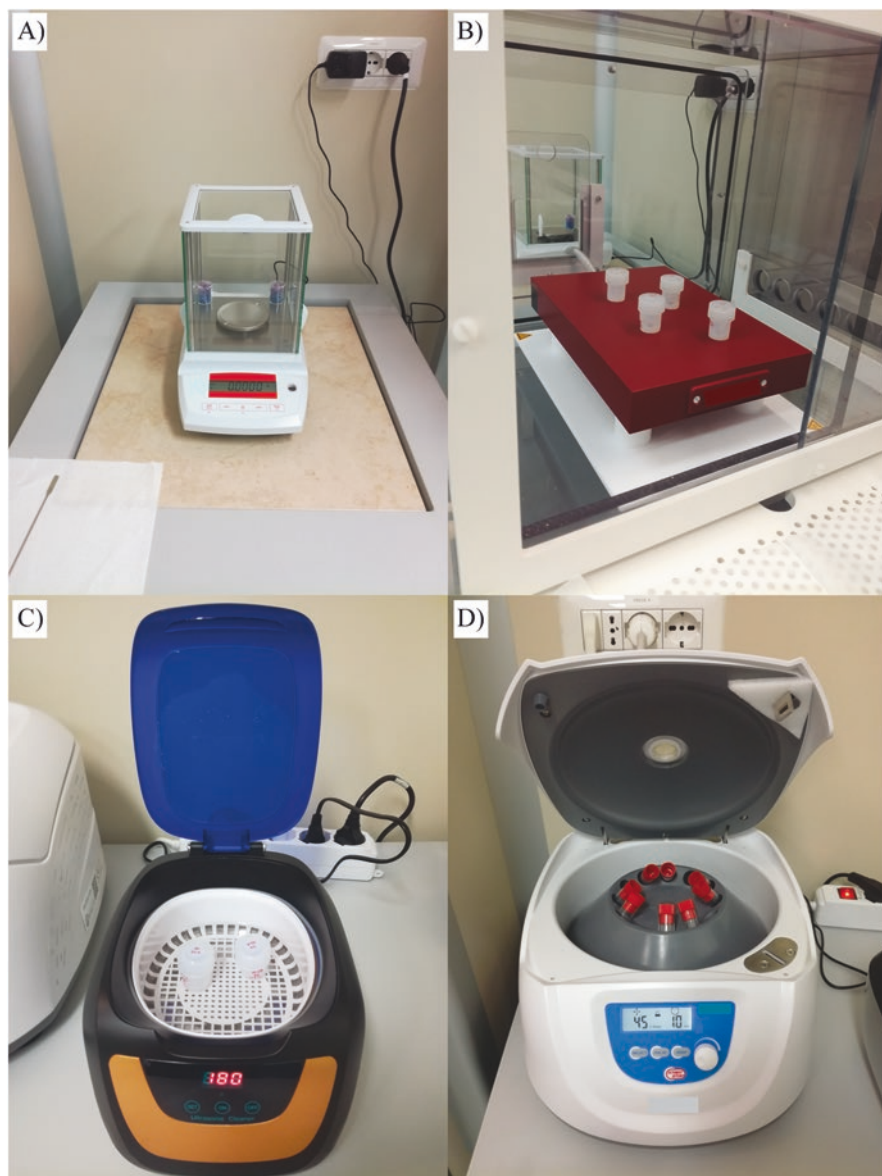
Fig. 9.2 Equipment commonly employed for sample preparation in a clean room. (**a**) high-precision analytical balance placed on an antivibration table; (**b**) PFA-coated, acid-resistant hot plate, with Savillex® vials on top for sample digestion; (**c**) ultrasonic bath; (**d**) centrifuge. (Source: Clean Room, DiSTAR, University Federico II, Naples, Italy. Photos by M. D'Antonio)

ultrasonic bath (Fig. 9.2c) for 5–10 min at the initial step of the acid dissolution to facilitate fragments' disaggregation; (iii) varying the residence time of the mixtures on the hot plate before opening the vials.

At the end of the acid dissolution, the chloride residue is generally fully soluble. It is then retaken with 1–2 mL of 2.5 M HCl, transferred into a pre-cleaned centrifuge tube, and centrifuged at 5000 rpm for 10 min (Fig. 9.2d). This latter procedure aims at separating possible insoluble matter that would have accumulated at the bottom of the tube, as samples may include a variable amount of accessory mineral phases that are poorly sensitive to the described acid dissolution (e.g., metal oxides, magnetite). The supernatant solution is ready to undergo chromatographic separation (Sect. 9.1.3); it contains virtually all the chemical elements of the original sample, except for silicon, which bonded with the anion F^- during the first dissolution and escaped from the solution as SiF_6 upon evaporation. Further details on the described procedures are provided by Arienzo et al. (2013).

9.1.1.3 Fusion with a Flux

When the matrix includes a significant amount of insoluble mineral phases, melting the sample at high temperature and then quenching it to obtain an easily soluble glass bead may be required. The laboratory should be thus equipped with the following: a muffle reaching temperatures of at least 1000 °C; crucibles made of noble metals or metal alloys (e.g., Pt, Pt-Ir, Au-Pd); some *fluxes*, namely low-melting compounds (e.g., anhydrous sodium carbonate, Na_2CO_3; sodium or potassium hydroxides; lithium metaborate – boric acid, $LiBO_2$), to be added to the powdered sample to lower its melting point. Complete fusion shall be achieved within 30–60 min; once cooled down, the glass bead will easily dissolve in diluted nitric acid solutions. *Contamination* of the sample by the flux itself, which adds significant amounts of chemical elements such as lithium, boron and especially alkalis plus a variety of trace elements may happen and heavily affect the result of the isotope measurement.

9.1.2 Preparation Techniques for Organic Samples

9.1.2.1 Teeth and Bones

Human or animal teeth and bones found on a crime scene must be cleaned in an ultrasonic bath (Fig. 9.2c) for several minutes with a suitable solution, such as methanol and chloroform (CH_4O:$CHCl_3$ = 2:1; Meier-Augenstein and Fraser 2008), or deionized water and hydrogen peroxide (H_2O:H_2O_2 = 3:1; Arienzo et al. 2020). A small piece of the tooth enamel or bone, both mostly made of hydroxyapatite, can be cut with a dental drill equipped with a diamond-coated saw (Fig. 9.3). The organic fragment is then washed again in the ultrasonic bath, followed by dissolution (like that described in Sect. 9.1.1.2), though simplified because teeth and bones dissolve in nitric and hydrochloric acids with no need for hydrofluoric acid (Arienzo

Fig. 9.3 Cutting of a tooth using a dental drill equipped with a diamond-coated saw. (Source: Radiogenic Isotope Laboratory, National Institute of Geophysics and Volcanology, Section of Naples Osservatorio Vesuviano, Naples, Italy (Photo by M. D'Antonio))

et al. 2020). Hydroxyapatite can be extracted through a buffer solution of 0.75 M ammonium hydroxide (NH_4OH) and silver nitrate ($AgNO_3$). Further details may be found in Meier-Augenstein (2010).

9.1.2.2 Hair

Made of keratin, a fibrous protein, hair must be treated with specific procedures. Among metals, Sr and Pb isotope ratios of hair from mummies and modern humans have been widely used as tracers for anthropological investigations (e.g., Font et al. 2012; Lugli et al. 2018) (see Discussion). The procedure includes several steps, using Milli-Q® water to remove surface dust and dirt, and Ultrapure grade reagents for dissolving 50–100 mg of hair cut in small pieces. Both archaeological and modern hair samples are immersed in a 2:1 chloroform:methanol solution ultrasonicated for 10 min, followed by rinsing with Milli-Q® water. The whole step is repeated three times. Then, a leaching procedure is carried out with cold 2 M HNO_3 for 30 min, repeated 2–3 times, followed by rinsing with Milli-Q® water. The dissolution is achieved by: (1) adding 2 mL of *aqua regia* (14 M HNO_3:8 M HCl = 3:1) in a PFA vial kept closed on hot plate at 110 °C for 24 h, followed by opening for complete evaporation; (2) adding 1 mL of 14 M HNO_3 at 110 °C for 24 h, followed by opening for evaporation; (3) removing organic matter adding alternated 100 μL aliquots of H_2O_2 and 14 M HNO_3 leaving the vial open on hot plate at 105 °C for evaporation. The residue is taken up in 3 mL of 3 M HNO_3. The obtained solution is ready for chromatographic separation (Sect. 9.1.3.1).

9.1.2.3 Soil

Soil being produced by the degradation of rocks exposed to the surface (bed-rock) is made up of an inorganic fraction, including variable amounts of minerals and non-crystalline material, and an organic fraction. The amount of soil needed for

determining the isotope ratio of a metal such as Pb, Cr, etc. is in the order of a few grams to tens of grams, significantly higher than for rock samples. This comes because, rather than their metal content in the bulk soil, it is important to analyze their labile, or "bioavailable" content. This corresponds to the metal content mostly retained at the soil's surface in its inorganic fragments and that is released in a diluted acid solution and thus available to the plants and other organisms. Any polluting metal added to a soil, for example either as deposited aerosols or wastewater, will also adsorb on the soil fragments surface. Once the amount of soil is weighed in a suitable beaker, there are many ways to extract its bioavailable fraction. One is leaving the sample immersed in 100 mL of 1 M ammonium acetate ($C_2H_3O_2NH_4$) overnight, slowly agitating the solution for the entire period. The solution is then filtered through a 0.45 μm filter, acidified with concentrated HNO_3 and left on a hot plate until complete dryness. The final residue is retaken in ~20 mL of 2.5 M HCl and, after being centrifuged for 10 min at 5000 rpm, is ready for chromatographic separation (Sects. 9.2.3 and 9.3). A different procedure can be adopted to extract bioavailable strontium from soil samples (Mercurio et al. 2014): adding a 1 M ammonium nitrate (NH_4NO_3) solution to 20 g of 2 mm size sieved soil, and agitating the solution for 2 h at 50 rpm, followed by filtration and acidification with a HNO_3:H_2O 1:1 solution.

9.1.2.4 Plants

Leaves can be crumbled in a mortar with a pestle and dissolved in methanol (Galimov et al. 2005) and analyzed (Sect. 9.2.3). The preparation of plant samples for analyzing the isotope ratios of their heavy metals is more complex because the organic fraction must be removed to isolate the element(s) of interest. According to Petrini et al. (2015), 2 mL of must can be left drying slowly at 70 °C; the residue is dissolved in 0.2 mL of concentrated Ultrapure HNO_3 for 2 h until the solution becomes clear. After dilution in 13 mL of Milli-Q® water, the solution is ready to be analyzed by ICP-MS techniques (Sect. 9.2.1). For analysis by TIMS (Sect. 9.2.2), a high temperature mineralization process (*thermal ashing*) is required to pre-concentrate trace elements. The procedure starts with drying 5 g of sample, pre-treated as previously described for ICP-MS, in a Nickel crucible at 60 °C; then, the sample is calcinated at temperature increasing up to 700 °C for 1 h in a muffle. The residual powder is dissolved in 2.5 M Ultrapure HCl, and the resulting solution is ready for separating the element of interest through liquid chromatography (Sect. 9.1.3.1). Mercurio et al. (2014) carried out the dissolution of branches, leaves, grapes and wine by acid leaching (HNO_3:H_2O_2 6:1 solution) in a microwave oven. The residue was then acidified with a HNO_3:H_2O 1:1 solution and kept at 4 °C before separating Sr by liquid chromatography (Sect. 9.1.3.1).

Leaves and inflorescences were treated by West et al. (2009b) as follows: an aliquot of the dried sample is crumbled in a mortar with a pestle; the coarse fraction is then eliminated with a 250 μm opening stainless-steel sieve. The finest part is thermally ashed by increasing temperature every 2 h to 80, 200 and 600 °C. The

dissolution of the obtained powder is accomplished using concentrated HNO_3 in a PTFE vial on hot plate, until complete evaporation. 30% H_2O_2 is finally added at 80 °C to remove organic matter residues. The dried sample is retaken in a 3.5 M HNO_3 solution that can be utilized for separating the element(s) of interest through liquid chromatography techniques (Sect. 9.1.3.1).

9.1.2.5   Food

Various types of food can be isotopically analyzed for both light and heavy atomic number elements. The sample preparation strictly depends on the type of material and the specific analytical technique to be utilized. $\delta^{18}O$ and δD can be measured directly on water extracted from frozen meat. For the oxygen isotopes, water is equilibrated with a reference sample of known $\delta^{18}O$. For hydrogen isotopes, water goes through *pyrolysis*, i.e., combustion in absence of oxygen, and then reduction in a hot furnace containing chromium at 1075 °C, allowing the release of hydrogen. Isotope analysis can also be carried out on protein extracted from food dry residues obtained with dichloromethane (CH_2Cl_2) in a *Soxhlet extractor*, successively homogenized in a vibrating ball mill. A weighed amount of the protein placed in a tin capsule undergoes pyrolysis in a furnace filled with tungsten and cobalt oxides at 590 °C. The released CO_2 and NO_x are then separated by gas chromatographic techniques for determining their $\delta^{13}C$ and $\delta^{15}N$ (Boner and Förstel 2004).

The isotope composition of light elements, e.g., H, C, N, O, can be measured on casein and/or glycerin extracted from 4 g of frozen and dried cheese by means of petroleum ether (pure or mixed with ethylic ether in 2:1 ratio) in a *Soxhlet* device, (e.g., Pillonel et al. 2005; Camin et al. 2012). The extracted protein is then homogenized and centrifuged to separate ether, cleaned twice with deionized water, and centrifuged again. The residue is lyophilized and kept at room temperature. An aliquot is combusted or pyrolyzed, if analyzed by gaseous source mass spectrometry techniques (IRMS; Sect. 9.3.3). If ICP-MS techniques (Sect. 9.3.1) are used, 0.65 g of the sample are weighed in a quartz crucible and placed in a microwave oven with 4 mL of 14 M HNO_3 and 2 mL of H_2O_2, both of *Suprapur*® grade.

For rice samples, the preparation is similar to that of cheese. If the isotope analysis is made by ICP-MS techniques (Sect. 9.2.1), the sample is digested with concentrated HNO_3 in a microwave oven. For IRMS techniques (Sect. 9.2.3), the sample is dried, pulverized, and homogenized. Then, a 0.5–2 mg aliquot is weighed in a tin or silver capsule and subjected to pyrolysis (Kelly et al. 2002; Suzuki et al. 2008).

Liu et al. (2014) analyzed Sr and B isotopes in unroasted coffee beans from the main production zones worldwide. Beans were first dried and frozen, then 5 g were pulverized, from which 50 mg were dissolved in a $HNO_3 – H_2O_2$ solution in a PTFE vial left for 2 h on hot plate at 120 °C. The obtained solution, diluted in Milli-Q® water, was in part utilized for determining the trace element content by ICP-MS (Sect. 9.2.1), and in part subject to chromatography to separate Sr and B (Sect. 9.1.3), before analysis by TIMS (Sect. 9.2.2).

9.1.2.6   Beverages

Wine is one of the key beverages isotopically investigated with the purpose of authenticating its terroir and identifying adulterations. $\delta^{13}C$ can be determined on: (i) ethanol isolated by distillation; (ii) sugars isolated by lyophilization after precipitation of other components with $Ca(OH)_2$; (iii) organic acids isolated by liquid chromatography (e.g., Rossmann et al. 1996; Weber et al. 1997). Combustion of its sugars allows the release of a gaseous compound from which CO_2 is separated and purified (Sect. 9.1.2.7).

$\delta^{18}O$ is determined on the water extracted from wine through complex distillation procedures carried out under vacuum, followed by freezing in liquid nitrogen (-195.8 °C) and re-heating (West et al. 2007). Similar procedures can be applied to beer, whisky, champagne, and even on carbonated non-alcoholic beverages for determining $\delta^{13}C$ (Meier-Augenstein 2010, and quoted references).

Strontium isotope ratios in wine has recently developed as one frontier application in food isotope geochemistry (Saar de Almeida et al. 2022). Marchionni et al. (2016) determined $^{87}Sr/^{86}Sr$ on 5–10 mL of wine, must and grape juice left to dry at 90 °C. Residues were digested with 3 mL of high-purity 30% H_2O_2 leaving the vial closed for 1 day at 40 °C, then opening it until complete evaporation at 90 °C. A second dissolution step was achieved with 2 mL of high-purity concentrated HNO_3, left closed for 1 day at 150 °C and then opened to evaporation. The residue was taken up in 1 mL of 3 M HNO_3 from which Sr was separated by chromatography (Sect. 9.1.3). Similar preparation techniques to those described for the analysis of must and grape in Sect. 9.1.2.4 were also used (Mercurio et al. 2014; Petrini et al. 2015).

For Sr isotopes in olive oil by TIMS (Sect. 9.2.2), Medini et al. (2015) proposed a specific protocol. Up to 100 g of oil is dissolved in an Ultrapure 7 M $HNO_3:H_2O_2$ 7:1 solution; the residue is calcinated in a quartz crucible left for 2 h in a muffle at 650 °C; the residue is taken up in 2 M HNO_3; lastly, Sr purification is carried out by chromatography (Sect. 9.1.3.1).

9.1.2.7   Extraction of a Gas from a Solid

Light elements' (H, C, N, O, S) stable isotopes must be analyzed under gaseous form (Sect. 9.2.3). However, the element(s) of interest is (are) often hosted in a solid compound, either organic or inorganic, requiring specific protocols for extraction as a gas. In most cases, the material to be analyzed is animal or vegetal tissue fragments that can be solubilized through various techniques as described in the previous sections. For inorganic solid materials, conversion is carried out through one or more of the following techniques: isotope exchange, acid dissolution, oxidation, reduction, combustion, under vacuum pyrolysis, fluorination combined with laser ablation. One reason for combining more than one technique is that the gas of interest can be a component of a gaseous solution, from which it needs to be isolated. To this purpose, ad-hoc extraction/purification lines (Fig. 9.4) are available,

Fig. 9.4 An example of gas extraction and purification line. (Source: Geowissenschaftliches Zentrum, Abteilung Geochemie, Georg-August-Universität, Göttingen, Germany. Photo courtesy by R.S. Iovine)

assembling several cold and hot "traps" connected by metal hairline tubes and valves, and including a vacuum pumps system and a gas-chromatographer (Sect. 9.1.3.2). Cold traps are held at $-195.8\ °C$ by liquid nitrogen to capture condensable gases (e.g., H_2O, CO_2, SO_2), whereas non-condensable gases (e.g., O_2, N_2, noble gases) are either pumped out by the vacuum system, if undesired, or let go further to enter the gas chromatographer. Hot traps, held at high temperature, are designed to either oxidize or reduce gaseous species. At the end of the extraction/purification line, a gas chromatographer separates the gaseous species of interest that will be analyzed individually, as described in Sect. 9.2.3.

9.1.3   Chromatographic Separation Techniques

Chromatographic separation is needed when the chemical element of interest must be isolated from the hosting matrix prior to its isotope analysis. Chromatography is based on the different affinities that chemical elements have when they interact with certain materials. A chromatography device is composed of (i) a *stationary phase* capable of selectively trap and then sequentially release chemical elements, and (ii)
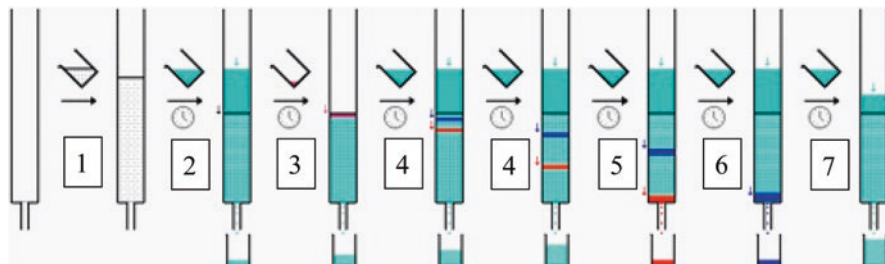
Fig. 9.5 Sketch of chromatographic columns illustrating the sequence of steps to separate compounds (or single ionized elements) from a complex matrix. (1) ion exchange resin (stationary phase); (2) conditioning of the resin with a fixed molarity acid solution; (3) loading of the sample (mobile phase) containing two different compounds (red and blue); (4) discarding of the eluates, during which the two compounds are physically separated by the resin; (5) collection of the eluate containing the red compound; (6) collection of the eluate containing the blue compound; (7) cleaning and reconditioning of the resin for a future use. (Source: Wikipedia, modified, https://en.wikipedia.org/wiki/Chromatography#/media/File:Column_chromatography_sequence.png)

a *mobile phase* containing the element of interest within its matrix. The stationary phase can be placed in a column (Fig. 9.5), on paper, etc. Depending on the physical state of the mobile phase, either liquid or gaseous phase chromatography can be employed.

9.1.3.1   Liquid Phase Chromatographic Separation

To analyze metals such as alkalis and alkaline earths including Sr, Rare Earth Elements (REE) including Nd, heavy metals such as Cr, Pb, etc., liquid phase ion-exchange chromatography is employed on already liquid samples or samples solubilized with one of the techniques described in Sects. 9.1.1 and 9.1.2. Figure 9.6 illustrates chromatographic columns employed to separate Sr and REE from both inorganic and organic samples. Such columns are made of hot-molded 22 cm high cylindric quartz tubes with inner diameter of ~0.5 cm. The total volume of the column is ~20 mL including the top cylinder reservoir. The stationary phase is made up of a cation exchange resin bed (AG 50 W X-8, 200–400 mesh, BioRad®), held by a 20 μm porous filter (*Teflon frit*) at the bottom. The *column volume, CV*, i.e., the effective volume of resin, is usually 2 mL. For samples whose concentration of the element of interest is low, microcolumns (Fig. 9.6b) with a reduced column volume (100–200 μL) can be used to achieve an efficient separation, with the advantage of reducing the reagents to be used and, hence the total *blank* of the analysis. The column is loaded with usually 0.5 mL of the solubilized sample for CV = 2 mL. Since the AG 50 W X-8 resin is conditioned in 2.5 M HCl for an efficient separation of alkalis and alkaline earth metals, the sample solution must have the same form at the end of the preparation procedure (see Sects. 9.1.1 and 9.1.2).

Each column needs to be pre-calibrated to establish the correct volume of eluent to use before passing the volume of eluent containing Sr. A careful calibration of
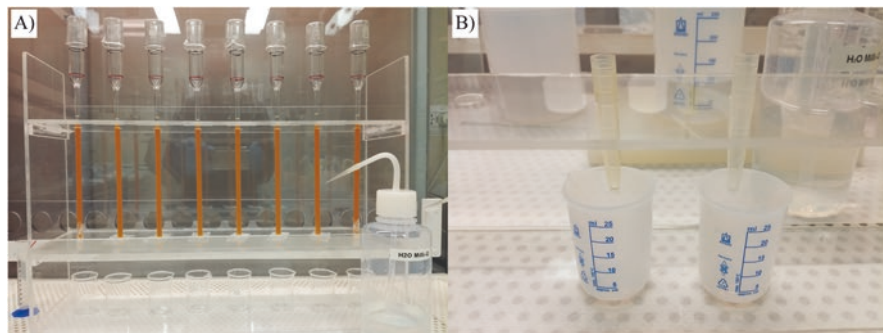
Fig. 9.6 (**a**) Chromatographic columns filled with cation exchange resin (see text for details), used to separate Sr and REE from both inorganic and organic samples. (**b**) Microcolumns built from 1 mL sterile pipette tips to be filled with Sr-Spec® cation exchange resin, used to separate Sr and Pb for samples with low concentrations of these elements. (Source: Clean Room, DiSTAR, University Federico II, Naples, Italy. Photo by M. D'Antonio)

each column will prevent collecting Rb, a metal showing affinity with Sr, that isobarically interfere with Sr during analysis (see Sect. 9.2). The eluate containing Sr, collected in a PTFE vial, is then left to evaporate on hot plate under laminar flow hood until complete dryness.

After the collection of Sr, from the same sample aliquot it is possible to separate the light Rare Earth Elements (LREE) all together, including neodymium for determining its isotope ratio. The eluent must be stronger than the one used for collecting Sr, usually 6 M HCl, and the right volumes to be discarded and collected with the LREE must be established with a calibration as well. The eluate containing the LREE, after evaporated to complete dryness, will be introduced in chromatographic columns filled with LN Spec® resin for separating Nd. All Sr and Nd dry fractions are nitrified with a few droplets of 14 M HNO_3, before loading onto a metal filament that will be introduced into the mass spectrometer (Sect. 9.2.2.1).

After purification, the resin can be regenerated through cleaning with several CVs of 6 M HCl, rinsing with 1.5 CVs of Milli-Q® water, and finally reconditioning with a few CVs of 2.5 M HCl.

9.1.3.2 Gas Phase Chromatographic Separation

The separation of light elements, such as H, C, N, O, S from a gaseous mixture is achieved through *gas-chromatography* (GC). The typical scheme of a *gas-chromatographer* (Fig. 9.7) includes: an injection system for the gas sample (1 in Fig. 9.7a) that uses an inert carrier gas such as Helium or Argon (2); a small, temperature-controlled oven (3 in Fig. 9.7a, b) hosting a thin chromatographic column of variable length, from a few dm (*packed column*; Fig. 9.7c) to a few tens of meters (*capillary column*; Fig. 9.7d). In the column, the various gaseous species of the sample interact differently with the stationary phase, made of a *zeolite* or
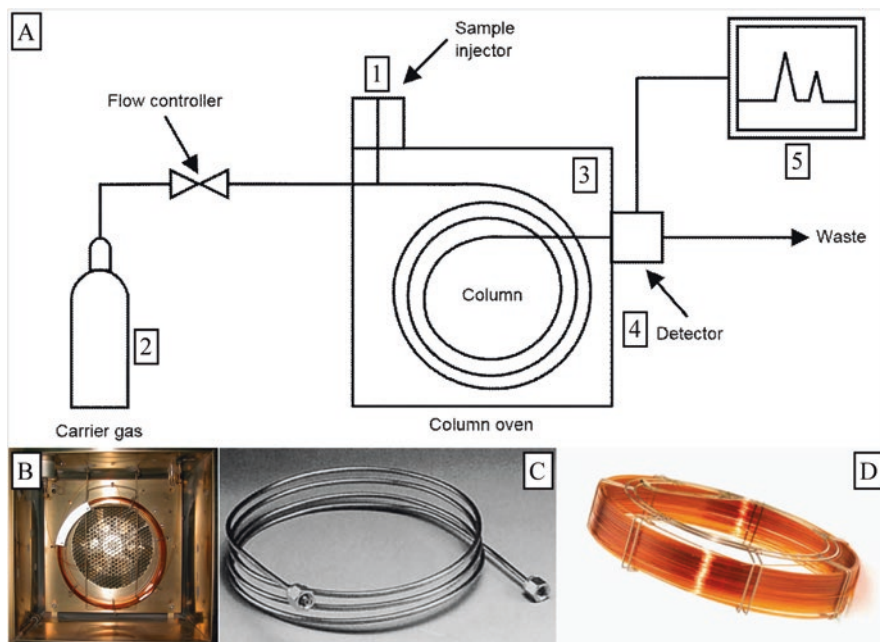
Fig. 9.7 Scheme of a gas-chromatographer. (**a**) instrument parts: (1) sample injector; (2) reference (carrier) gas reservoir; (3) oven hosting the chromatographic column; (4) detector; (5) schematic chromatogram; (**b**) inner part of the oven; (**c**) packed chromatographic column; (**d**) capillary chromatographic column. (Source: Wikipedia, modified)

polystyrene adhering by a few tens of μm on the inner walls of the column, and are separated before they reach the detector (4 in Fig. 9.7a). The detector is either an ionizing flame or a thermal conductivity device or a reduction photometer. Lastly, the signals out of the detector are converted into a chromatogram (5 in Fig. 9.7a) where each gas is distinguished by a gaussian-shaped peak, whose area is proportional to its amount in the mixture. Quantitative measurements are possible by means of calibration curves obtained by analyzing reference samples with known composition (standards). The gas-chromatographer is interfaced with the gas source mass spectrometer (Sect. 9.2.3).

9.2 Instrumentation

Mass spectrometry is the main analytical technique for determining the isotope ratios of elements. It separates charged particles (i.e., ions) based on their mass or, more correctly, based on their mass/charge ratio. Therefore, it allows both distinguishing isotopes of a single element and calculating ratios between their abundances (isotope ratios). Samples of all physical states of matter can be analyzed but

must be treated to be introduced as a solid, liquid or gas in the differently designed spectrometers, summarized below. For the isotope ratios of heavy elements (Pb, Sr, REE), either inductively coupled plasma-mass spectrometry (ICP-MS), in which the sample is analyzed as a liquid, or thermal ionization mass spectrometry (TIMS), as a solid, exist. For both techniques, the sample is transformed, by high temperature heating, into free atoms and, partially, into positive or negative ions. Isotope ratio mass spectrometry (IRMS) is used for light elements (H, C, N, O, S), where samples are introduced as a gas, obtained from a gas, solid or liquid sample through appropriate preparation (Sect. 9.1). Alpha (α) and gamma (γ) spectrometry are specifically used for measuring the radioactivity of unstable isotopes.

9.2.1 Inductively Coupled Plasma-Mass Spectrometry

9.2.1.1 Principles and Instrumentation

ICP-MS combines mass spectrometry with an inductively coupled plasma source and consists of (Fig. 9.8): a sample injection system, an ion source, called ICP torch, where ions are generated and then extracted; a mass analyzer; an ion detection apparatus; a data acquisition and processing system (computer). The sample is a liquid
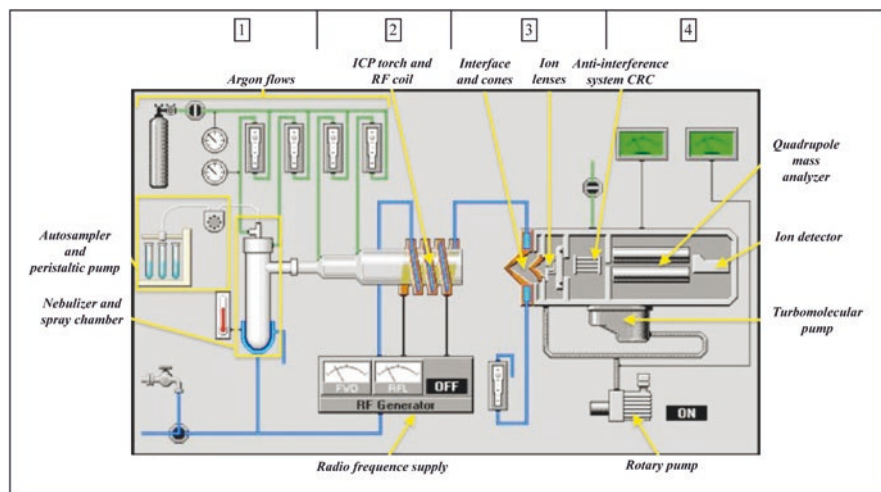

Fig. 9.8 Schematic of an inductively coupled plasma-mass spectrometer. Instrument parts: (1) sample gas injection system; (2) ICP torch; (3) interface between plasma and mass spectrometer, including a *sampling cone* and a *skimmer cone*; (4) mass spectrometer consisting of a *quadrupole mass analyzer* and an *ion detector*. (Source: The University of Texas at Austin, Department of Geological Sciences, Jackson School of Geosciences, TX, U.S.A., http://www.jsg.utexas.edu/icp-ms/icp-ms/, modified)

solution that may even be a complex matrix, such as that resulting from the dissolution techniques described in Sect. 9.1.

The liquid sample is aspirated through a peristaltic pump and introduced into a nebulizer, which converts it into an aerosol. The nebulizer rarely produces a uniform aerosol consisting of droplets of the same size. To prevent the largest droplets from reaching the plasma, a spray chamber is placed between the nebulizer and the ICP torch. The gas carrying the aerosol enters the chamber where it undergoes a change of direction. The largest drops are eliminated by being blocked along the walls of the spray chamber and are drained off, whereas the smallest ones reach the plasma.

The ICP torch consists of three concentric quartz tubes inside which argon circulates. The plasma is obtained with an inductively coupled radiofrequency generator (Fig. 9.8). A water-cooled copper coil, powered by a radio frequency (RF) generator, creates an intense magnetic field wrapping the ICP torch. The ionization of argon gas is triggered by a spark produced by a Tesla coil, and the resulting cations (Ar^+) and electrons are accelerated by the magnetic field produced by radio frequencies. Collisions between charged particles and argon atoms generate a plasma, an ionized gas stable at very high temperatures. The sample entering the plasma is rapidly volatilized at 6000–10,000 kelvins, and most of its compounds are dissociated into their constituent elements, partially ionized. These ions produced at atmospheric pressure are extracted from the plasma thanks to the high vacuum of the mass spectrometer. The interface between the plasma source and the mass spectrometer consists of two opened nickel cones, the *sampling cone* and the *skimmer cone*, which allow ions to pass, deflecting most of the molecules and atoms in the neutral state. Ions focusing after the skimmer cone is obtained through electrostatic lenses. A *photon stop* placed along the direction of the beam, prevents light reaching the ion detector reducing the background signal. The ion beam is deflected around the photon stop and moves towards the mass analyzer. The most common mass analyzer is a mass filter called *quadrupole*. It allows only ions having a certain mass/charge ratio to reach the detector, by varying potentials applied to two opposite pairs of metal cylinders. The resolution of the quadrupole is sufficient to separate masses of elements showing adjacent peaks. The ability to count the ions individually and the low background signal give the instrument a good sensitivity. Indeed, ICP-MS allows quantifying a great variety of chemical elements, including trace elements, either sequentially or simultaneously. More sophisticated than quadrupoles, multi-collector ICP-MS are equipped with Faraday Cups and/or secondary ion multipliers (SEM), corresponding to those installed on TIMS spectrometers (Sect. 9.2.2). They allow determining the isotope ratios of many chemical elements from complex liquid matrices.

9.2.1.2 Measurement Procedures

The analytical sensitivity of mass spectrometers varies as a function of (i) isobaric interferences caused by the superposition of the peak(s) of the target element with those generated by other chemical species with similar masses, and/or (ii) effects

resulting from the matrix composition. The ability to investigate all mass signals during a series of scans can be used to do a purely qualitative analysis of the sample. The spectrum can be visually examined to check for the analyte presence or absence.

Since many instruments give a sensitivity vs. mass plot, it is possible to build a curve that gives information on the ionization degree and the isotope abundance. This response curve can be used to calibrate the instrument and to provide semi-quantitative data when indicative analyte concentration values only are required. The most common and widespread calibration method involves the use of standards, usually three plus a blank. In this case, numerous standard solutions are prepared that cover a wide range of concentrations. Least squares regression methods are then used to build calibration curves for each element. To avoid signal fluctuations due to the instrument sensitivity decrease between one series of measurements and the next, two different approaches are used: correction of the instrumental drift and internal standardization. The range and combination of elements that can be determined by ICP-MS are very large. The instrument provides the possibility for the simultaneous determination of many chemical elements including trace elements. Some volatile trace elements, such as Hg and As, may be lost during the preparation of the solution, so their determination is impossible. This means that a successful analysis depends mostly on a survey to be carried out on the matrix in advance. Indeed, before a quantitative analysis, the sample should be qualitatively known to identify its major and trace elements, and evaluate possible interferences, especially related to acid dissolution. The final dilution of the sample should only be done after it has been decided whether or not to include certain elements in the survey.

9.2.2 Thermal Ionization Mass Spectrometry – Solid Source Mass Spectrometers

9.2.2.1 Principles and Instrumentation

TIMS can separate charged particles (positive or negative ions) through the combined use of an electric field and a magnetic field. According to the original scheme proposed by the physicist Alfred Nier in 1940, it consists of (Fig. 9.9): an ion source; a magnetic analyzer crossed by a flight tube along which ions move; a detection apparatus (collector array in Fig. 9.9b); an acquisition system, i.e., a PC. In order not to disturb the ion motion by collisions with other particles, the whole system is kept under high vacuum through: an oil bath rotary pump and a liquid nitrogen cryogenic pump for pre-vacuum, that reach pressures of up to 10^{-3} mbar; a turbo-molecular pump and two ion pumps for reaching higher vacuum, up to 10^{-9} mbar. The ion source of *solid source* mass spectrometers consists of a vacuum chamber ($P \leq 10^{-7}$ mbar) hosting a turret containing several samples that are analyzed individually (Fig. 9.9). The solid sample is retaken with a micro-drop of diluted acid solution and loaded onto a previously outgassed pure metal (Re, W, Ta) filament
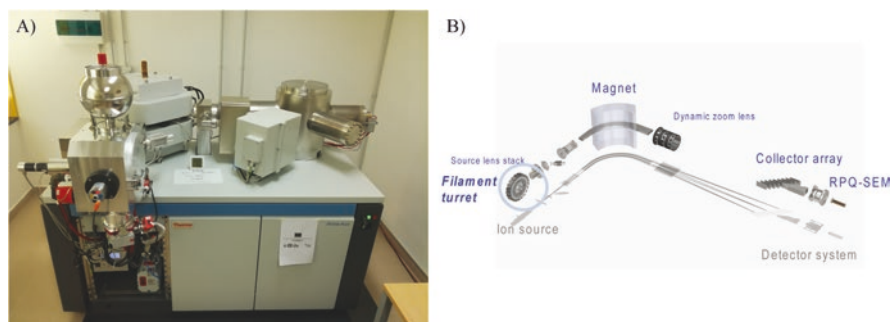
Fig. 9.9 (**a**) Triton Plus® thermal ionization mass spectrometer. (Source: Mass Spectrometry Laboratory, DiSTAR, University of Naples, Italy). (**b**) Technical scheme of the Triton Plus®. (Source: Permission by Thermo-Fisher Scientific, April 2018)
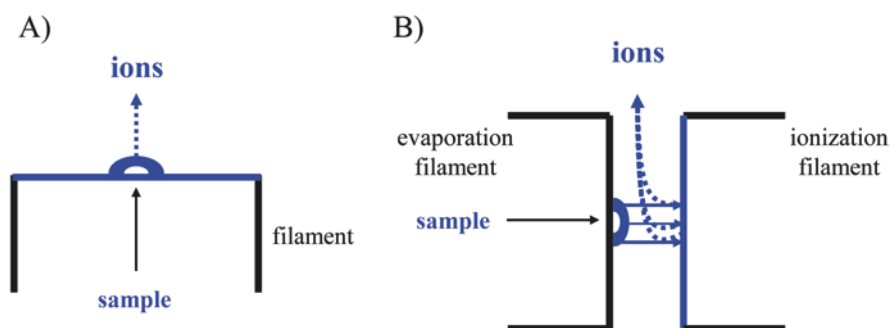

Fig. 9.10 Schematic of (**a**) single filament configuration, and (**b**) double filament configuration. (Source: M. D'Antonio)

(Fig. 9.10), welded on a steel support. In the source, the filament is heated at high temperature by an electric current and emits electrons by *thermionic emission*. The thermionic emission is such that only a part of the atoms to be analyzed is ionized. Elements with ionization energies lower than the *work function* of the filament (a parameter related to type of metal of the filament) will produce many ions at low temperatures, whereas elements with higher ionization energies will require a high filament temperature which causes a rapid loss of the sample. This can be avoided with the use of two (or three) filament systems (Fig. 9.10b), where only one of them, called evaporation filament, is loaded with the sample. The ionization filament is brought to high temperatures (~1700 °C), whereas the evaporation filament is heated at lower temperatures (~1100 °C).

The ions produced by thermo-ionization are accelerated to high voltage (10 kV) in the analyzer tube, held at high vacuum (10^{-9} mbar), and focused through a system of electrostatic lenses, to form a high-energy ion beam entering the flight tube of the magnetic analyzer (Fig. 9.9b). The flight tube forms an arc, with a radius of curvature r, that passes through a magnetic field of intensity B generated by an external

electromagnet with variable intensity. The ions of the beam are charged particles q with mass m and velocity v. Their kinetic energy due to the voltage V acceleration is $E = \frac{1}{2}mv^2 = qV$. It comes that $v^2 = 2qV/m$. In the magnetic field of intensity B and perpendicular to the beam trajectory, ions will be deviated by the Lorentz force $(F = qvB)$ following a curvilinear trajectory of radius r, resulting from the balance between the aforementioned force and the centripetal force mv^2/r. Combining the previously determined equations of forces' equilibrium and of ion velocity gives: $2qV/m = B^2q^2r^2/m^2$. Expressing the ratio m/q as a function of the intensity of the magnetic field B, the acceleration voltage V and the radius of curvature r, yields: $m/q = B^2r^2/2\ V$, so that the magnetic field can separate ions with different mass/charge ratios.

To unambiguously identify the isotopes being analyzed, the magnetic field needs to be calibrated to assign a known value of B to each m/q ratio value, specific to a given isotope. The mass spectrometer must be able to distinguish ion beams with similar but still distinct m/q ratios, i.e., ions that differ by a single atomic mass unit (amu) and send them separately to the detectors. The detection apparatus consists of one or more ion collectors (Fig. 9.9b) which convert charged particles into an electrical signal. Each collector is connected to an amplifier, which renders the signal processable. The most common collectors are Faraday Cups, carbon-coated metal boxes. The ion beam enters the Faraday Cup through a slit, hits a positively charged electrode, which creates a current flow from the ground through a strong resistance (10^{-11} ohm or less). The potential difference ($V = RI$) across the resistance represents the signal that will be subsequently amplified and processed to give the isotope ratio of interest, being proportional to the charge deposited by the ion beam on the electrode. Another detection device, used for ion beams of low intensity, is the secondary ion multiplier (Secondary Electron Multiplier), generally coupled to a quadrupole mass filter (Retarding Potential Quadrupole). The last part of the TIMS spectrometer is the acquisition system, consisting of one or two computers that manage most of its functions (only some are performed manually, such as introducing the samples into the source and liquid nitrogen into the cryogenic pump) and the software for processing the acquired data.

9.2.2.2 Measurement Procedures

The isotope ratios measurement procedure involves several steps: the right ionization temperature of the filament is reached by heating it by supplying current at increasing amperage; the value of magnetic field suitable for the measurement of a given isotope ratio is selected and the ion beam is focused; then the spatial configuration of the Faraday Cups suitable for detecting the various ion beams of the element to be analyzed is chosen and the automatic calculation procedure of the isotope ratios starts. Measurements can be carried out in static or dynamic mode: the former uses several collectors at the same time to measure various isotopes of a given element while keeping the magnetic field constant, whereas the latter involves the use of one or more collectors at a time where selected isotopes of the element are

measured by varying the magnetic field. The calculation of the isotope ratios of a given element requires appropriate corrections for the baseline (background signal or background noise), isobaric interferences and within-run mass fractionation. The baseline results of both ions diffused by the ionized sample and the electronic noise of the detection system, whereas the isobaric interferences are due to isotopes of other elements with the same mass number as the one of interest. The correction is made by monitoring an interference-free isotope. For example, ^{87}Rb interferes isobarically with ^{87}Sr. To correct this interference, ^{85}Rb can be used as it is not isobaric with any Sr isotope. The correction is made as: $^{87}Sr_{corr} = {}^{87}Sr_{meas} - ({}^{87}Rb/{}^{85}Rb)$ $^{85}Rb_{meas}$, where $^{87}Rb/^{85}Rb$ is the average natural isotope ratio of rubidium. Mass fractionation is observed when the sample is held at high temperatures for long times causing the thermal ionization of lower mass isotopes, which over time leads to their depletion in the sample, compared to higher mass isotopes. To correct this effect in the case of strontium, it is necessary to consider that one of the isotopes of interest, ^{87}Sr, is radiogenic and variable in nature. Therefore, it is necessary to normalize the $^{87}Sr/^{86}Sr$ ratio using a stable and non-radiogenic isotope, usually ^{86}Sr, to a value assumed for a ratio between non-radiogenic isotopes that does not vary in nature (e.g., $^{86}Sr/^{88}Sr = 0.1194$), considering that it is known how much the fractionation degree changes with mass difference. An exponential correction law has been shown to well describe the mass fractionation of strontium and other elements. Current TIMS spectrometers provide automatic corrections for both within-run mass fractionation and isobaric interferences during measurement of the element of interest, reaching accuracies of 10^{-6} (e.g., Avanzinelli et al. 2005; Arienzo et al. 2013).

9.2.3 Thermal Ionization Mass Spectrometry – Gas Source Mass Spectrometry

9.2.3.1 Principles and Instrumentation

IRMS presents a lower sensitivity but much higher resolution and precision compared to solid source mass spectrometry. Compared to the latter, IRMS mainly differ in the sample introduction system and the source, as well as in the mass analyzer, as the electromagnet generally generates a magnetic field of fixed intensity. The gas source mass spectrometer (Fig. 9.11) includes an ion source, a mass analyzer consisting of a flight tube and a magnetic sector, and ion detectors.

The instrument is kept under high vacuum (P = 10^{-8} mbar) to prevent collisions between ions and residual gas molecules. The source consists of a chamber into which the sample/reference gas is injected and ionized by an electron beam (energy between 50 and 100 keV). Electrons are produced by a filament heated at high temperature and follow a helical path within a magnetic field. The source also includes two electrodes, one with a positive potential (ion accelerator, Fig. 9.11), which accelerates the created ions towards the inlet slit of the flight tube, and the other with
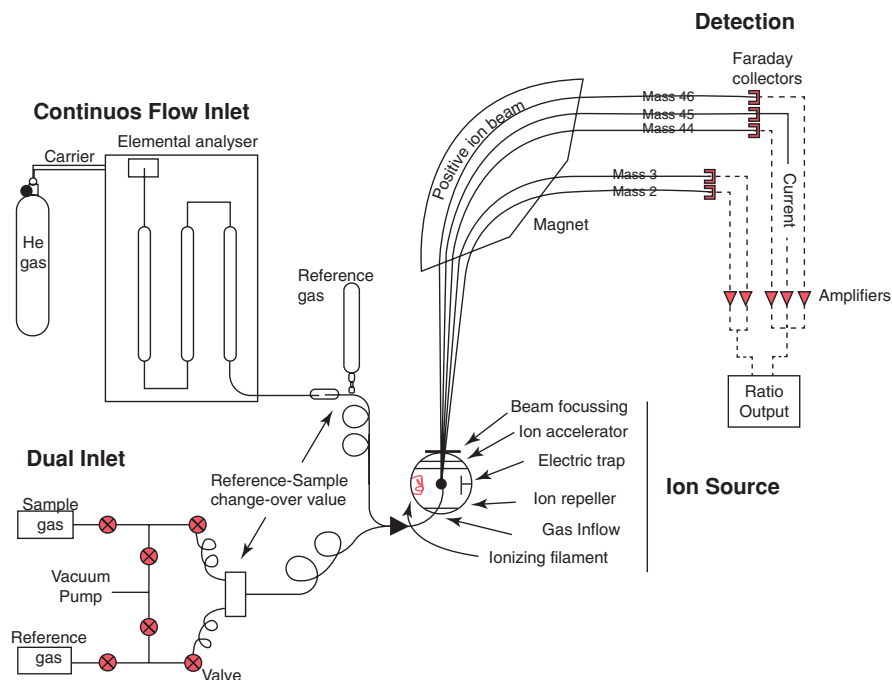
Fig. 9.11 Schematic of a gas-source mass spectrometer for the measurement of stable elements in gaseous form. (Source: Sustainability of semi–Arid Hydrology and Riparian Areas (Tucson, AZ, U.S.A.). http://web.sahra.arizona.edu/programs/isotopes/methods/gas.html)

a negative potential (electric trap, Fig. 9.11) that traps the ionizing electron beam. The beam of positive ions of the gas, repelled by a third positive potential electrode (ion repeller, Fig. 9.11), exits from the source, is focused through a series of electrostatic lenses of variable potentials, and finally enters the flight tube. There the ion beam crosses the magnetic field, which separates ions into distinct ion beams based on their mass/charge ratio, as described in Sect. 9.2.2.1. A series of fixed Faraday Cups arranged along an oblique focal plane to the incident ion beams, collect their respective charge and convert them into an electrical signal. Following amplification, this signal serves as the basis for calculating the isotope ratios of interest of the gas being measured. The isotope ratios determination of a light element involves the comparison with a standard of the same element of known isotope composition. The sample-standard comparison process is controlled by the gas injection system. The most used configurations are (Fig. 9.11): (1) double injection (Dual Inlet, DI-IRMS) and (2) continuous helium flow (Continuous Flow inlet, CF-IRMS). The DI-IRMS includes two tanks, one for the sample gas and one for the standard gas, connected by means of capillaries to a system of valves (changeover valve) which allows to alternately inject the sample and the reference gas into the source. Flow velocities for the two gases in the capillaries are equalized thanks to a variable volume system (metal bellows) that regulates the pressure, ensuring a non-turbulent flow, limiting

possible isotope fractionation. The continuous flow injection system uses helium as a carrier gas. The helium flow is maintained at 0.2 ml per minute and the background pressure in the instrument at ~10^{-5} mbar. In the Dual Inlet configuration, samples are prepared and purified (converted into an elementary gas or simple gaseous compound isolated from other unwanted gases) off-line by a vacuum line that may include compression pumps, concentrators, reaction furnaces and micro-distillation apparatuses (extraction/purification line; Sect. 9.1.2.7). In the continuous helium flow configuration, the sample preparation and purification line is interfaced with the mass spectrometer, making the analysis simpler and faster. The mass spectrometer may be coupled to peripherals such as liquid or gas-chromatographers, used for separating the liquid(s)/gas(es) of interest from the matrix (Sect. 9.1.3.2). The last part of the instrument is the acquisition system, consisting of a PC that controls most of the functions, including opening and closing valves, as well as processing the data.

9.2.3.2   Measurement Procedures

Gas mass spectrometers combine different techniques for introducing, separating and purifying the gaseous species of interest. Gas-chromatography (GC) is used for the separation of small gas quantities (down to a few micromoles) and is linked to a combustion system (C) to convert solid samples into gases that can be analyzed by the mass spectrometer. For example, C-GC-IRMS can measure C, N and S stable isotopes: samples disposed in tin capsules are placed in a furnace filled with oxygen and carried by helium, creating a flash combustion at high temperature (1800 °C). Catalyzed by the presence of oxygen, the combustion reaction converts samples into CO_2, NO_x, SO_x and H_2O. Therefore, this technique is referred as Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS). Following oxidation, gases pass through a reduction column containing copper heated to 650 °C, transforming formed nitrogen oxides into N_2. Gases are then separated by gas-chromatography before being split between a thermal conductivity detector that quantifies each gas produced, and the mass spectrometer. For the analysis of the C isotopic composition, the latter can be present in different forms (organic carbon, carbonates, CO_2-bearing fluid inclusions, etc.) even in the same sample, such as geological materials. In these cases, combustion at different temperature intervals (step-heating) is used by energizing the surface of the sample with a laser ablation system interfaced with the mass spectrometer, so that the various molecular components of carbon are released and measured separately. For DI-IRMS, samples are converted into a simple gas via either an off-line procedure and subsequently introduced into the mass spectrometer, or an interfaced laser ablation device as described above. Off-line sample preparation procedures require a longer time and larger samples (millimoles), with the risk of contamination and isotope fractionation during the processing steps. While DI-IRMS is generally more accurate when measuring isotope ratios of light elements, CF-IRMS offers advantages including: online sample preparation and purification; ability to analyze smaller samples; simultaneous analysis

of multiple gas species (N, C, S…); higher throughput; better cost/benefit ratio. The main drawback is a lower accuracy in the determined isotope ratio.

For all IRMS techniques, direct comparisons are made between the intensity ratios of the ionic beams of the sample gas and those of gases of known isotope ratios (either reference gas or certified standards) to determine the ‰ value of the δ parameter (Sect. 9.1). Data must eventually be corrected for the effects of instrumental drift and for the isobaric interferences through suitable factors that are adjusted for each gas being measured.

9.2.4   Alpha and Gamma Spectrometry

The alpha and gamma spectrometric techniques are used to quantify radioactive isotopes that emit alpha particles, i.e., an ^{4}He atom, or gamma photons, i.e., very short wavelength electromagnetic radiation. In both cases, their emission occurs at specific energy values (in MeV) characteristic of each isotope species, which therefore can be identified and, with particular techniques, quantitatively analyzed. Measurements can be carried out both on the field, through portable meters that measure radioactivity, but do not allow identifying isotopes, or in the laboratory using spectrometers that allow both identification and quantification of the radionuclides. The main part of these instruments is a detector sensitive to ionizing particles, constituted in its modern versions of a semiconductor crystal (e.g., silicon, Si or germanium, Ge).

9.3   Application of Isotope Forensics

Although isotope geochemistry was originally developed for research in geology after its discovery by Harold Urey in 1934, the evolution of its analytical techniques has allowed to vastly extend its application fields: from mining exploration to biogeochemical cycles, or the human impact on our environment. Since recently, isotope geochemistry has also demonstrated its added value when trying to tackle key forensics issues (e.g., Muccio and Jackson 2009; Matos and Jackson 2019): e.g., food adulteration, drugs, illicit pharmaceuticals, microbiology, doping, explosives, ammunitions. The application of isotope geochemistry to forensic investigations was historically limited to the study of stable isotope systematics. During the 90's, in the US where forensic science was born, C (δ^{13}C) and N (δ^{15}N) isotope compositions were first used to characterize seized drugs or adulterated wines. Building on these promising results, the US and UK created the "Forensic Isotope Ratio Mass Spectrometry Network" (FIRMS), a still active today scientific network regarded as the standard benchmark for stable isotope forensic practitioners. FIRMS aims at developing the scope of stable isotope techniques in forensic applications, with the ultimate goal of raising awareness of the relevance and importance of isotope

geochemistry in forensic science, crime detection and reduction. To further push the limits of the forensic isotope geochemistry it became necessary to characterize materials of inorganic nature containing, among others, heavy metals (e.g., fragments of soil, rocks, illegally transported radioactive material). This marked a step increase in the analysis of radiogenic isotopes, in combination or not with the then classical analysis of stable isotopes, opening new routes to forensic investigations.

In the following sections we are presenting a series of examples of application of isotope forensics, taken from the current literature.

9.3.1   Placement of a Suspect at the Crime Scene

At the scene of a crime numerous artifacts can be suitable for isotopically identifying their origin, by making comparisons with materials of known locations. This can then be used to place a suspect at the crime scene. For example, the origin of wood fragments can be inferred through the analysis of H, C, and O isotopes. Other examples include soil or rock fragments, found on the crime scene that can isotopically be related to precise locations. These isotope characteristics can then be compared to those measured in shoe soles, car or motorcycle tires, or from the home surroundings of suspected individuals. Farmer et al. (2007) used $\delta^{13}C$ and δD, in a case of an individual suspected of attempting to burn materials potentially related to a murder case. Characterizing safety matches seized at the suspect's house and those recovered from a crime scene, the authors showed that they were (isotopically) different, which was also confirmed by XRD and microscopy analysis.

9.3.2   Human Provenancing

The large scope of available literature detailing the effective application of isotope analysis techniques to the identification of unidentified human remains include examples such as the deaths related to the crossing of the Mexico-United States border, reported by Aggarwal et al. (2008), or the recent migration events from Africa and the Middle East to Europe, involving hundreds of victims each year.

The added value of stable or radiogenic isotope systematics resides in the fact that their study in human tissues allows determining the provenance of human beings or of their remains. A particular attention is made on human tissues that once formed will not, or slightly, be modified, such as the tooth enamel, hair or bones. Paraphrasing the old adage "we are what we eat", one can state that isotopically-speaking "we are what we eat plus or minus a few ‰" (DeNiro and Epstein 1976). In fact, isotope (^2H, ^{13}C, ^{15}N, ^{18}O or ^{34}S among others) abundances in the different human tissues reflect what the person ate and drunk during her/his recent life, also including her/his recent geographical mobility. To put it differently, diet and geolocation of a human being influence the isotope compositions of her/his tissues,

including hair, nails, teeth or bones. One of the basic principles on which the reconstruction of a person's geographical history is based is that food is the sole source for carbon and nitrogen in the human body. Similarly, the water we drink and take from cooked food is an important source of hydrogen in our body (~30%).
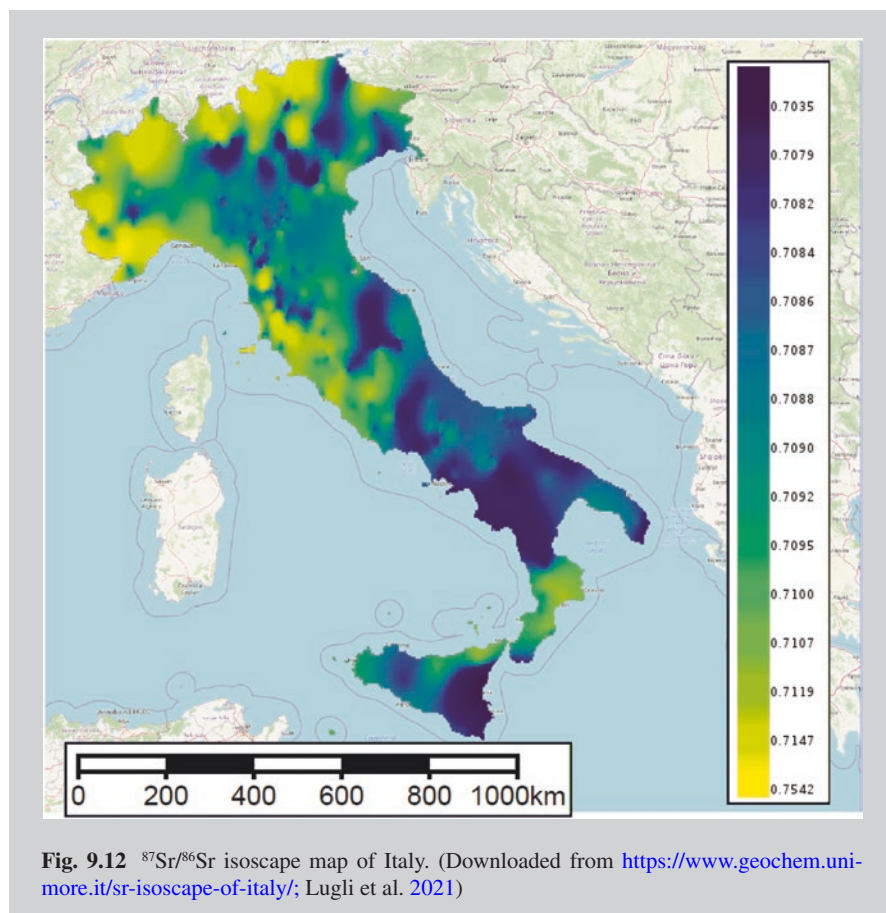
The mean annual $\delta^{13}C$ for terrestrial plants is determined by their photosynthetic pathway: C_3 and C_4 plants, and CAM (Crassulacean Acid Metabolism) plants. These different photosynthetic pathways reflect in their distinct $\delta^{13}C$ ranges: -33 to $-24‰$ for C_3 plants, -16 to $-10‰$ for the C_4 ones and -20 to $-10‰$ for the CAM ones (O'Leary 1988). The δD and $\delta^{18}O$ of drinking water is controlled by those of the meteoric recharge. It has to be noted that isotope compositions of rainwater are subject to seasonal variations originating from variations in its temperature and evaporation rate (Bowen 2008, 2010). Coupling isoscape maps of local/national/international precipitations with computational models it is thus possible to identify, or more precisely to exclude, areas of geographical provenance. Chesson and Berg (2021) provided an in-depth review of the selection of appropriate human tissues samples and gave guidance on the available options for the isotope analysis preparation, analysis and data handling.

Strontium Isotopes in Human Provenancing

Studies have shown that the strontium (Sr) isotope ratios measured in bones and/or teeth can successfully be used for the identification of human remains (e.g., Rauch et al. 2007). Living beings do not biologically use Sr but it is a key biomineral constituent of bones and teeth as it enters their mineral structure by substitution with calcium. Sr is thus taken up early in people's life and is fixed in bones and teeth, recording the average $^{87}Sr/^{86}Sr$ ratio of the "bedrock" of the locality where people were born and raised during the early stages of their life. Sr isotope ratios have carved their niche as proxies of dietary habits and migratory routes of ancient populations, in the certification of different food types and more generally in forensic sciences. Coelho et al. (2017) report a useful collection of literature works on these topics. To increase even more the identification power of Sr isotopes, it can be coupled to those of other heavy and light elements.

The Sr isotope approach required the creation of isotope base maps (also known as isoscapes, see Fig. 9.12; Bowen 2010) that allow a direct comparison of a given isotope parameter from a certain geographical area to that of a sample of water, hair, drug or plant grown in that area. This was synthetized by Bataille and Bowen (2012) and Chesson et al. (2012) who modeled $^{87}Sr/^{86}Sr$ in bedrocks by developing GIS-based models for Sr isotopes in rock and water that included the combined effects of lithology and time. However, given the variable bedrock of each area, the above methodology is not without some uncertainty, which can be reduced only by making detailed studies of a given area.

Fig. 9.12 $^{87}Sr/^{86}Sr$ isoscape map of Italy. (Downloaded from https://www.geochem.uni-more.it/sr-isoscape-of-italy/; Lugli et al. 2021)

9.3.3 Drugs

In 1997, C and N isotope compositions measured on cannabis samples seized from a truck were brought to the Australian Supreme Court of the Northern Territories as evidence in a drug trafficking trial: the case of Queen versus Thomas Ivan Brettschneider. The values were identical (at 95% confidence level) to those measured on samples seized from a suspect plantation. This constituted the first official use of isotope forensic techniques to solve a drug trafficking case. Tracking the geographical origin of different drug types, either natural (cannabis, marijuana, cocaine) or semisynthetic (amphetamine, methamphetamine, morphine, heroin) by means of C and N isotopes has been one of the most popular applications in forensic science in USA, Brazil and Asia since the 1990s. Interestingly, these forensic applications is that it is possible to infer the geographic location where the plants were

grown and whether the cultivation took place "indoor" or "outdoor". For example, as C and N isotope compositions in marijuana are very sensitive to climatic conditions and variations in latitude (Shibuya et al. 2007), it was possible to discriminate Brazilian marijuana grown in the arid regions of Bahia and Pernambuco ($\delta^{13}C = -26.28 \pm 1.55‰$ and $\delta^{15}N = 1.51 \pm 3.11‰$, respectively) from that grown in humid regions such as Mato Grosso do Sul and Para ($\delta^{13}C = -29.77 \pm 1.05‰$, and $\delta^{15}N = 5.89 \pm 1.73‰$, respectively). The combination of isotope systematics is extremely useful when trying to reconstruct the path of illicit drug trafficking. This approach can be implemented to other types of narcotics. Since the first study of Mas et al. (1995), $\delta^{13}C$ and $\delta^{15}N$ have been used to trace the origin of Ecstasy tablets (MDMA; 3,4-methylenedioxymethamphetamine). This pioneer study was followed by many others (Carter et al. 2002a, b, 2005; Palhol et al. 2003, 2004; Billault et al. 2007; Buchanan et al. 2008).

Like natural processes, illicit manufacturing processes, that use different chemical transformation techniques (e.g., the acetylation of morphine to create a heroin base that is then transformed into heroin hydrochloride) may be accompanied by significant isotope fractionations during the different processing steps. These can ultimately be used to discriminate between different origins of the same type of narcotic (Carter et al. 2005). They were first described by Desage et al. (1991) on heroin samples. Still, the authors reported a narrow range of $\delta^{13}C$ values, from $-31.5‰$ to $-33.5‰$ for samples covering a wide geographic area. Similarly, Casale et al. (2005) reported no C isotope fractionation during the conversion of cocaine base to cocaine HCl but a N isotope fractionation of 1‰. The authors also demonstrated that there was a kinetic carbon isotope fractionation of $-1.8‰$ during the acetylation of morphine to heroin that is depleting the end-product in ^{13}C. Acetylation is also accompanied by an isotope fractionation against ^{15}N. Building on this, Hurley et al. (2010) proposed to add the H isotope systematics. The authors developed stable isotope-based models incorporating $\delta^{13}C$ and δD to predict geographic origin and growth environment for marijuana trafficking in the USA. When tested, the model predictions were 60–67% reliable for the determination of the region of origin and 86% accurate for the cultivation environment.

Recently, studies have proposed Sr isotope ratios as another useful tool in forensic drug provenancing. Unlike light elements, $^{87}Sr/^{86}Sr$ ratios are not fractionated by natural processes. They are thus directly linked to the parent material. West et al. (2009a) first analyzed the $^{87}Sr/^{86}Sr$ ratios of marijuana samples grown in 79 counties across the US, trying to relate them to the isotope signal of the geology they were grown on. The authors concluded that there was some remaining unexplained variability in their dataset, though marijuana Sr isotope ratios do retain a primary geological signal based on the bedrock age. This means that the primary geological footprint, which differs in different geographical areas, leaves a recognizable trace in the Sr isotope ratios of plants. More recently, DeBord et al. (2017) published the first use of $^{87}Sr/^{86}Sr$ ratios for the geographic origin of 186 illicit heroin samples of known origin. The authors demonstrated that the technique showed 77–82% discrimination between South American and Mexican heroin.

9.3.4 Explosives

With the increasing threat of terrorism in our modern lives and the broad range of explosive devices available, sourcing explosives has become a growing interest for government sectors. The very first published isotope analysis of explosives dates back to 1975 (Nissembaum 1975), where the author discriminated 2,4,6-Trinitrotoluene (TNT) samples from different countries based on their $\delta^{13}C$, showing that the observed variations were linked to both the isotope composition of the starting materials and the country of origin. The manufacturer Thermo reported in 1995 that 3 samples of TNT explosives from different countries could be distinguished when coupling their $\delta^{13}C$ and $\delta^{15}N$, concluding that further research was needed to determine whether these resulted of different production sites, of substrate lots in the production process, or of post-production adulteration (Thermo 1995). After that, isotope geochemistry demonstrated its efficiency at discriminating other types of explosives: RDX or T4; plastic explosives, such as Semtex; TNT (e.g., Benson et al. 2009a, b, 2010; Widory et al. 2009; Brust et al. 2015; Bezemer et al. 2016). Reported values mostly include O and N isotopes but also, to a lesser extent, C and H ones. Phillips et al. (2002) showed that Pentaerythritol Tetranitrate (PETN) based explosives produced by the same manufacturer fall within a tight cluster of stable isotope compositions, distinguishable from others. Lott et al. (2002) tested whether isotopes were useful in determining the "point of origin" of explosives, specifically whether differences in production processes or substrates used in the manufacturing process might lead to difference in their corresponding isotope ratios. Historically, the UK Forensic Explosive Laboratory (FEL) is probably the first laboratory that included the isotope geochemistry of explosives in its research scope. Since, the technique has spread worldwide with new dedicated laboratories being implemented in Europe, the US, China and elsewhere.

Fractionation of Stable Isotopes for Discriminating Explosives
As most of the chemical procedures involved in the preparation of explosives do not proceed in a quantitative fashion and generate product yields that are generally <100%, isotope fractionations of light elements occur. Lock and Meier-Augenstein (2008) reported average fraction factors (α) of 1.0087 ± 0.0003 and of 0.9860 ± 0.0005 between hexamine (precursor) and its RDX product for $\delta^{13}C$ and $\delta^{15}N$, respectively. These distinct α values can then be used to characterize differently treated explosives. Benson et al. (2009a) discriminated the starting materials and/or manufacturing processes samples of TATP and PETN samples based on their C, N and O isotope compositions. These authors published a second article focusing more specifically on a multi-isotope approach (N, O and H isotopes) to discriminate lots of ammonium nitrate (AN), a common oxidizer used in improvised explosive mixtures (Benson et al. 2009b). They also compared pre- and post-blast samples and showed a N isotope fractionation, resulting in a ^{15}N enrichment of the

(continued)

post-blast samples that was explained as the likely result of both a kinetic isotope fractionation effect and also of the breakdown of the nitrate ion into nitrite. Going further, Brust et al. (2015) combined IRMS (Sect. 9.2.3.1) and ICP-MS (Sect. 9.2.1.1) to augment the discrimination power of this approach. The authors successfully discriminated between samples from different manufacturers and between different types of AN, combining their $\delta^{15}N$ and $\delta^{18}O$ to elements such as Mg, Ca, Fe and Sr. Measuring $\delta^{13}C$ and δD they concluded that the added value of these last two isotope systematics was negligible for differentiating the origin of AN. More recently, Can et al. (2021) reviewed the different isotope techniques that have been reported in the literature to isotopically characterize common explosives such as ammonium nitrate, black powder, TNT, pentaerythritol tetranitrate (PETN) and cyclotrimethylene trinitroamine (RDX).

Howa et al. (2016) proposed a new method for separating components of plastic explosives based on their solubility: binder, oil, explosive, and insoluble. These fractions produced isotope compositions of individual compounds, such as RDX and HMX for the explosive fraction, and Sudan I and N-phenyl-2-naphthaleneamine for the oil fraction. The authors show that adding the isotope characteristics of non-explosive materials (e.g., binder) allowed discriminating between chemically and isotopically indistinguishable C-4 samples if only raw material or the RDX component were analyzed. Two-ways radio transmitter are generally employed to initiate improvised explosive devices (IEDs). Combining the δD and $\delta^{13}C$ analysis of five sampling points taken in commercially supplied radios Quirk et al. (2009) found that it provided a pattern that was characteristic of a given radio. Those same radios were then subjected to detonation and analyzed similarly. The authors concluded that when 3 or more post-blast fragments were recovered it was isotopically possible to associate these with the undamaged radio with a high degree of certainty.

Environmental contaminations due to the presence of nitroaromatic compounds (NACs) are a common problem at military training installations, abandoned production facilities or munition disposal sites (e.g., Kalderis et al. 2011). As NACs are present in different phases and may undergo competing degradation pathways, assessing their fate is challenging but can be achieved by a compound-specific multi-isotope approach (C, N and H isotopes; Wijker et al. 2013).

9.3.5 Radioactive Materials

The isotope analysis of heavy elements is also used in investigations of radioactive material trafficking and is usually referred as nuclear forensics. This is a relatively young discipline, with a steady increase in the scientific publications within the last two decades (Burk 2005; Aggarwal 2016). Radioactive materials (e.g., actinides)

emit radiations that can be harmful to human health, even at extremely low levels (i.e., microgram amounts). The main objective of nuclear forensic and investigations is to find out the origin of interdicted, stolen, or lost material to eliminate its accessibility to illicit traffickers. Nuclear fuel generally consists of uranium enriched in its ^{235}U and plutonium, but other radioactive elements can be used in so-called radiological dispersal device (RDD). RDDs consist of a non-fissile radioactive material, that cannot explode through a nuclear reaction but could ignite if metallic, that is treated to make it very volatile. A RDD is defined as a weapon designed to disperse radioactive material, consisting either of nuclear power plant or hospital waste, over an area using either conventional explosives, of even modest power, or more covert dispersion methods to contaminate objects and people (Hanson 2008). The recognition of low-level radioactive weapons as part of the class of atomic weapons could lead to the inclusion of depleted uranium weapons in this category (Ahn and Seo 2021).

In these cases, isotope analysis can be used to identify the nature and origin of radioactive material or weapons based on them, and to monitor their illicit trafficking (Wallenius et al. 2006; Mayer et al. 2007; Fahey et al. 2010; Kristo and Tumey 2013). To prevent the fabrication of eventual dirty bombs, radioactive materials need to be precisely and rapidly identified. The Geiger-Muller counter (GM counter) is usually the most conventional radiation detector used. However, it cannot distinguish the different radiation types. Secondary-Ion Mass Spectroscopy (SIMS), TIMS, alfa and gamma spectrometry (Sects. 9.2.2 and 9.2.4) are used for isotope analysis, but they will take longer for obtaining results. In 2018, Beals et al. showed that the study of fission products' properties helps eliminate ambiguity in identifying low-yield nuclear detonation in its early stages, by allowing to discriminate three categories of explosive devices: (i) RDD, (ii) a failed nuclear device where nuclear material is scattered by conventional devices and (iii) a nuclear device that scatters nuclear material producing a very low-yield from nuclear fission. More recently, Kim et al. (2019) evoked the feasibility for laser-induced breakdown spectroscopy (LIBS) to identify radioactive materials in dirty bomb terror scenes.

9.3.6 Environmental Forensics

Environmental forensics has emerged as a discipline directed towards determining parties liable for causing spills of contaminants into the environment. It has thus become important to be able to determine the source(s) of these contaminants as well as to characterize their transportation and potential degradation history. Isotope geochemistry has widely demonstrated its added value as one of the most refined and promising techniques in this sense. As early as in 1947, J.H. Sterner evoked the possibility to use tracer isotopes in industrial toxicology (Sterner 1947). The author then predicted that the use of radioactive and stable isotopes was "likely to extend" in the following decades, which seems to have been correct, but also concluded that "the radioactive isotopes have advantages over the stable isotopes", which should be open to debate in the present section. Environmental forensics cover a broad range

of contaminants, which complexifies the use of a single technique to track their respective sources and fate in the environment. It is thus usually necessary to use a variety of analytical techniques to resolve this issue. Bulk and compound-specific isotope ratio analysis of light and heavy isotope systematics have been vastly documented as well as advances and remaining challenges when applied to environmental contamination (Elsner and Imfeld 2016).

Schmidt et al. (2004) published a review of the isotope analysis of organic contaminants that included the identification and quantification of biodegradation processes and corresponding isotope fractionations on a range of environmental matrices. The contamination of soils, aquifers and groundwater bodies is an important issue that has relied a lot on isotope geochemistry to identify particular emission sources. Many different isotope systematics have been employed, including N and O isotopes in nitrates (e.g., Chen et al. 2020; Peters et al. 2018), C isotopes in tracking the provenance of hydrocarbons and related refinery products and wastes (e.g., Wang et al. 2018; Humez et al. 2019; Liu et al. 2021). Air pollution issues have been tackled by the study of atmospheric gases and aerosols (e.g., Xiao et al. 2020) but also through the indirect study of bioindicators (e.g., Kousehlar and Widom 2020; Soba et al. 2021).

Heavy metal isotope systematics have also been investigated and showed that they can help identify sources of contamination, and even more to characterize the extent of environmental contamination when combined with multi-element screening (e.g., Pontér et al. 2016). Non-conventional isotope systematics may as well provide key information about environmental contamination. For example, Tieman et al. (2020) employed barium isotopes to track the source of dissolved solids in produced water from the unconventional Marcellus Shale Gas Play, and Li et al. (2021) used the mercury isotope signature of residential coal combustion to discuss its impact on air quality in rural areas in China. This can be achieved as most contaminants of anthropogenic origin display an isotope profile that significantly differs from that of their corresponding natural sources.

9.3.7   Food Adulteration

The certification of food products, their authenticity and origins has become a growing priority amongst consumers and producers. Counterfeited products do not meet safety standards, leading to various levels of health risks for consumers. A number of European food products are now protected with specific geographical origin (Protected Designation of Origin; PDO) and production (Protected Geographical Indications; PGI) labels. The European Union adopted the regulation No. 1169/2011 that requires the provision of food information to consumers by identifying the origin of a food as being either its country of origin or its place of provenance (e.g., Monahan et al. 2018). This arose the need for developing authentication techniques to prevent the mislabeling of PDO and PGI foods. As early as in 2003, stable isotope analysis was already performed on a regular basis in Europe and the USA to authenticate wines, certain liqueurs, olive oil and other vegetable oils, natural flavors, and honey (Ogrinc et al. 2003).

The foundation of the isotope approach relies on the fact that during their growth, plants absorb bioavailable elements that are present in the soil. These inherited elements can provide information about the geological substratum on which plants grew and can transfer this information to the food and beverages that are produced from them (e.g., Vinciguerra et al. 2016). This soil-plant connection reflects in the isotope ratios of their respective constituting elements, creating "isotope fingerprints" that can be used to trace their origin (e.g., Allen et al. 1994; Asfaha et al. 2011; Zhao and Zhao 2020). Historically, light isotopes were majorly analyzed, but recent studies demonstrated the added value of heavier isotope systematics, such as Sr isotopes, as effective tracers of the "bedrock" on which, for example, olive trees and grapevines grow, opening new perspectives in the field of viticulture (e.g., Mercurio et al. 2014; Guibourdenche et al. 2020). Several factors can contribute to the final isotope ratios measured in animal-based foods. For example, the $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ of animal tissues are highly influenced by its diet, usually consisting of different plant species for herbivorous animals such as cattle and sheep (e.g., Camin et al. 2017). For $\delta^{18}O$ and δD, isotope compositions in animals' tissues are driven by drinking water and food (e.g., Hobson and Koehler 2015). GIS driven isotope maps and isotope footprints were thus developed for food products including beer, honey, cereal crops, cheese, fruit juices, tea, coffee, olive oil, peppers, soft fruit, tiger prawns, crab, rice, tomato-based products, vinegar, wine and asparagus (e.g., Cabanero et al. 2006; West et al. 2007; Flores et al. 2013; Zhao et al. 2013; Carter et al. 2015; Stevenson et al. 2015; Zhao et al. 2016; Chen et al. 2016; Luo et al. 2016, 2019; Chiocchini et al. 2016; Camin et al. 2017; Perini et al. 2018; Gopi et al. 2019; Richter et al. 2019). Isotope comparison of these with pre-defined isoscapes allows demonstrating the provenance and thus authenticity of food products (e.g., Danezis et al. 2016).

Following the increasing demand for centralized and certified data in the domain of isotopes for food science, Eftimov et al. (2019) recently proposed an ISO-FOOD ontology to link and harmonize the existing different knowledge repositories. As stated by the authors, "such an ontology will help stable isotope scientists, data managers, educators and trainers as well as producers, control agencies and policy makers to more easily answer questions concerning quality of measurements in food commodities, the main stable isotope characteristics of food of plant and animal origin, geographical location, and authenticity".

Isotope Geochemistry in Doping
Doping represents one of the major issues in sports, mostly through the use of synthetic steroids. Before 1982, xenobiotic steroids were the only class of steroids that had been banned. Following the prohibition of testosterone administration by the International Olympic Committee and subsequently by the World Anti-Doping Agency (WADA 2022), the need for the implementation of new tools to maximize the detection of synthetic steroid doping

violations arose. Historically, molecular spectrometry techniques, such as GC-MS, were the reference methods to detect and quantify the administration of synthetic steroids (Thevis et al. 2020). This steroid profile, based on the analysis of several urinary steroids that are generated by the athlete's endocrine system, serves as a screening method for urine samples entering the laboratory and allows eliminating those of nonsuspicious nature. For those of suspicious nature, isotope geochemistry revealed its added value by characterizing the origin and metabolic pathways undergone by metabolites in biological fluids (e.g., Montes de Oca Porto et al. 2020; Iannella et al. 2021). Southan et al. (1990), using the example of gonadal and pharmaceutical testosterone, first demonstrated that the distribution of C stable isotopes was distinguishable between endogenous and exogenous (i.e., synthetic) metabolites.

Studies demonstrated that the administration of steroids, particularly testosterone, resulted in a ^{13}C depletion in the corresponding steroid diol metabolites: $\delta^{13}C$ values are shifting from their endogenous values towards exogenous isotope compositions (e.g., Shackleton et al. 1997; Aguilera et al. 1999). Cawley and Flenker (2008) thus proposed a two-stage protocol to ensure a precise and reliable certification of steroid abuse in urine samples.

A preliminary screening based on the measurement of the $\delta^{13}C$ of androsterone and etiocholanolone, the terminal androgen metabolites that are excreted in urinary concentrations, helped to identify suspicious samples with C isotope compositions that would fall outside of the reference intervals such as those reported by Ueki and Okano (1999) and de la Torre et al. (2001) for endogenous steroid metabolites ($-25 < \delta^{13}C < -15\text{‰}$) and commercially available steroids ($-36 < \delta^{13}C < -26\text{‰}$).

For samples classified as suspicious, the authors recommend that the doping action is confirmed by a second $\delta^{13}C$ analysis on the aab- and bab-diols (i.e., steroid diol metabolites) and/or testosterone.

While most of the literature available is focusing on the use of C isotopes, recent studies have turned their attention to other isotope systematics such as H isotopes (e.g., Piper et al. 2009; Putz et al. 2020).

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