CHAPTER ONE

Isotopes and radioactivity

1.1 Reminders about the atomic nucleus

In the model first developed by **Niels Bohr** and **Ernest Rutherford** and extended by **Arnold Sommerfeld**, the atom is composed of two entities: a central nucleus, containing most of the mass, and an array of orbiting electrons.[1] The nucleus carries a positive charge of $+Ze$, which is balanced by the electron cloud's negative charge of $-Ze$. The number of protons, Z, is matched in an electrically neutral atom by the number of electrons. Each of these particles carries a negative electric charge e.

As a rough description, the nucleus of any element is made up of two types of particle, neutrons and protons. A neutron is slightly heavier than a proton with a mass of $m_{\mathrm{n}} = 1.674\,95 \cdot 10^{-27}$ kg compared with $m_{\mathrm{p}} = 1.672\,65 \cdot 10^{-27}$ kg for the proton. While of similar masses, then, the two particles differ above all in their charges. The proton has a positive charge $(+e)$ while the neutron is electrically neutral. The number of protons (Z) is the **atomic number**. The sum $A = N + Z$ of the number of neutrons (N) plus the number of protons (Z) gives the **mass number**. This provides a measure of the mass of the nuclide in question if we take as our unit the approximate mass of the neutron or proton. **Thomson** (1914) and **Aston** (1919) showed that, for a given atomic number Z, that is, for a given position in Mendeleyev's periodic table, there are atoms with different mass numbers A, and therefore nuclei which differ in the number of neutrons they contain (see Plate 1). Such nuclides are known as the **isotopes** of an element.

Thus there is one form of hydrogen whose nucleus is composed of just a single proton and another form of hydrogen (deuterium) whose nucleus comprises both a proton and a neutron; these are the two stable isotopes of hydrogen. Most elements have several naturally occurring isotopes. However, some, including sodium (Na), aluminum (Al), manganese (Mn), and niobium (Nb), have just one natural, stable isotope.

The existence of isotopes has given rise to a special form of notation for nuclides. The symbol of the element – H, He, Li, etc. – is completed by the atomic number and the mass number – ${}^{1}_{1}\mathrm{H}$, ${}^{2}_{1}\mathrm{H}$, ${}^{6}_{3}\mathrm{Li}$, ${}^{7}_{3}\mathrm{Li}$, etc. This notation leaves the right-hand side of the symbol free for chemical notations used for molecular or crystalline compounds such as ${}^{2}_{1}\mathrm{H}_2\ {}^{16}_{8}\mathrm{O}_2$. The notation at the lower left can be omitted as it duplicates the letter symbol of the chemical element.

---

[1] For the basic concepts of modern physics the exact references of original papers by prominent figures (Einstein, Fermi, etc.) are not cited. Readers should consult a standard textbook, for example Leighton (1959) or Beiser (1973).

Cambridge University Press
978-0-521-86228-8 - Isotope Geology
Claude J. Allegre
Excerpt
More information

The discovery of isotopes led immediately to that of **isobars**. These are atoms with the same mass numbers but with slightly different numbers of protons. The isobars rubidium $^{87}_{37}\mathrm{Rb}$ and strontium $^{87}_{38}\mathrm{Sr}$ or alternatively rhenium $^{187}_{75}\mathrm{Re}$ and osmium $^{187}_{76}\mathrm{Os}$ do not belong in the same slots in the periodic table and so are chemically distinct. It is important to know of isobars because, unless they are separated chemically beforehand, they "interfere" with one another when isotope abundances are measured with a mass spectrometer.

1.2 The mass spectrometer

Just as there would be no crystallography without x-rays nor astronomy without telescopes, so there would be no isotope geology without the invention of the mass spectrometer. This was the major contribution of **Thomson** (1914) and **Aston** (1918). Aston won the 1922 Nobel Prize for chemistry for developing this instrument and for the discoveries it enabled him to make.[2] Subsequent improvements were made by **Bainbridge** and **Jordan** (1936), **Nier** (1940), and **Inghram** and **Chupka** (1953). Major improvements have been made using advances in electronics and computing. A decisive step was taken by **Arriens** and **Compston** (1968) and **Wasserburg** *et al*. (1969) in connection with Moon exploration with the development of automated machines. More recent commercial machines have improved quality, performance, and reliability tenfold!

1.2.1 The principle of the mass spectrometer

The principle is straightforward enough. Atoms of the chemical element whose isotopic composition is to be measured are ionized in a vacuum chamber. The ions produced are then accelerated by using a potential difference of 3–20 kV. This produces a stream of ions, and so an electric current, which is passed through a magnetic field. The magnetic field exerts a force perpendicular to the "ionic current" and so bends the beam of ions. The lighter ions are deflected more than the heavier ones and so the ions can be sorted according to their masses. The relative abundance of each isotope can be measured from the relative values of the electron currents produced by each stream of ions separated out in this way.

Let us put this mathematically. Suppose atoms of the element in question have been ionized. The ion acceleration phase is:

$$eV = \frac{1}{2} mv^2$$

where eV is the electrical energy, $\frac{1}{2}mv^2$ is the kinetic energy, e is the ion's charge, v its speed, m its mass, and V the potential difference. It can be deduced that:

$$v = \left(\frac{2eV}{m}\right)^{\frac{1}{2}}.$$

---

[2] The other inventor of the mass spectrometer, J. J. Thomson, had already been awarded the 1906 Nobel Prize for physics for his discovery of the electron.

3 The mass spectrometer

Magnetic deflection is given by equating the magnetic force Bev to centripetal acceleration (v^2/R) multiplied by mass m, where B is the magnetic field and R the radius of curvature of the deflected path:

$$Bev = m\left(\frac{v^2}{R}\right).$$

It can be deduced that:

$$v = \frac{BeR}{m}.$$

Making the two values of v equal, which is tantamount to removing speed from the equation, gives:

$$\frac{m}{e} = \frac{B^2R^2}{2V}.$$

Therefore R is proportional to $\sqrt{m}$, for an ion of a given charge. Allowing for electron charge, elemental mass,[3] and differences in units, we can write:

$$m = \frac{B^2R^2}{20\,721\;V} \times 10^{12}$$

in which B is in teslas, m in atomic mass units, R in meters, and V in volts.

Exercise

A mass spectrometer has a radius of 0.3 m and an acceleration voltage of 10 000 V. The magnetic field is adjusted to the various masses to be measured. Calculate the atomic mass corresponding to a field of 0.5 T.

Answer

Just apply the formula with suitable units:

$$m = \frac{(0.5)^2 \times (0.3)^2}{20\,721 \times (10^4)} \times 10^{12} = 108.58.$$

Exercise

If hydrogen ions (mass number = 1) are accelerated with a voltage of 10 kV, at what speed are they emitted from the source?

Answer

Just apply the formula $v = (2eV/m)^{\frac{1}{2}}$. The electron charge is $1.60219 \cdot 10^{-19}$ coulombs and the atomic mass unit is $1.660\,540\,2 \cdot 10^{-27}$ kg.

$$v = \sqrt{1.9272 \cdot 10^{12}} = 1388\ \mathrm{km\,s^{-1}}$$

---

[3] Atomic mass unit: $m = 1.660\,540\,2 \cdot 10^{-27}$ kg, electron charge: $e = 1.602\,19 \cdot 10^{-19}$ C, therefore $e/m = 0.964 \cdot 10^8\ \mathrm{C\,kg^{-1}}$ (C = coulomb).

Cambridge University Press
978-0-521-86228-8 - Isotope Geology
Claude J. Allegre
Excerpt
More information

which is about 5 million km per hour. That is fast, admittedly, but still well below the speed of light, which is close to 1 billion km per hour! Heavy ions travel more slowly. For example ions of $m = 100$ would move at just a tenth of the hydrogen speed.

1.2.2 The components of a mass spectrometer

The principal components of a mass spectrometer are the source, the magnet, and the collector and measurement systems, all of which are maintained under vacuum.

The source

The source has three functions:

- To generate ions from atoms. The ions may be positive or negative.
- To accelerate the ion by potential differences created by plates at different potentials (from ground to 20 KeV, and in accelerator mass spectrometers to several MeV).
- To shape the beam, through calibrated slits in the high-voltage plates. The beam from the source slit is usually rectangular.

The magnet

The magnet has two functions. It deviates the ions and this deflection separates them by mass. At the same time it treats the various components of the ion beam or a single mass as an optical instrument would. It handles both colors (masses) and also beam geometry. One of its properties is to focus each ion beam for each mass on the collector. The characteristics of focusing vary with the shape of the magnet and the shape of the pole face, which may be curved in various ways (Figure 1.1 and Plates 2 and 3). A further recent improvement, using computer simulation, has been to focus the beam not only in the x and y directions but in the z direction too. In modern solid-source mass spectrometers, the angular dispersion of ions is fully corrected and almost all the ions leaving the source end up in the collectors which are arranged in a focal plane.

The collectors

The collectors collect and integrate the ion charges so generating an electric current. The collector may be a Faraday bucket, which collects the charges and converts them into a current that is conducted along a wire to an electrical resistor. By measuring the potential difference across the resistor terminals, the current can be calculated from Ohm's law, $V = IR$. The advantage is that it is easy to amplify a potential difference electronically. It is convenient to work with voltages of about 1 V. As the currents to be measured range from 10^{-11} to 10^{-9} A, by Ohm's law, the resistors commonly used range from 10^{11} to 10^{9} Ω. This conversion may be made for small ion fluxes of **electron multipliers** or **ion counters**.[4] In all cases the results are obtained by collecting the ion charges and measuring them. Just ahead of the collector system is a slit that isolates the ion beam. This is explained below.

---

[4] Each ion pulse is either counted (ion counter) or multiplied by a technical trick of the trade to give a measurable current (electron multiplier).

Cambridge University Press
978-0-521-86228-8 - Isotope Geology
Claude J. Allegre
Excerpt
More information

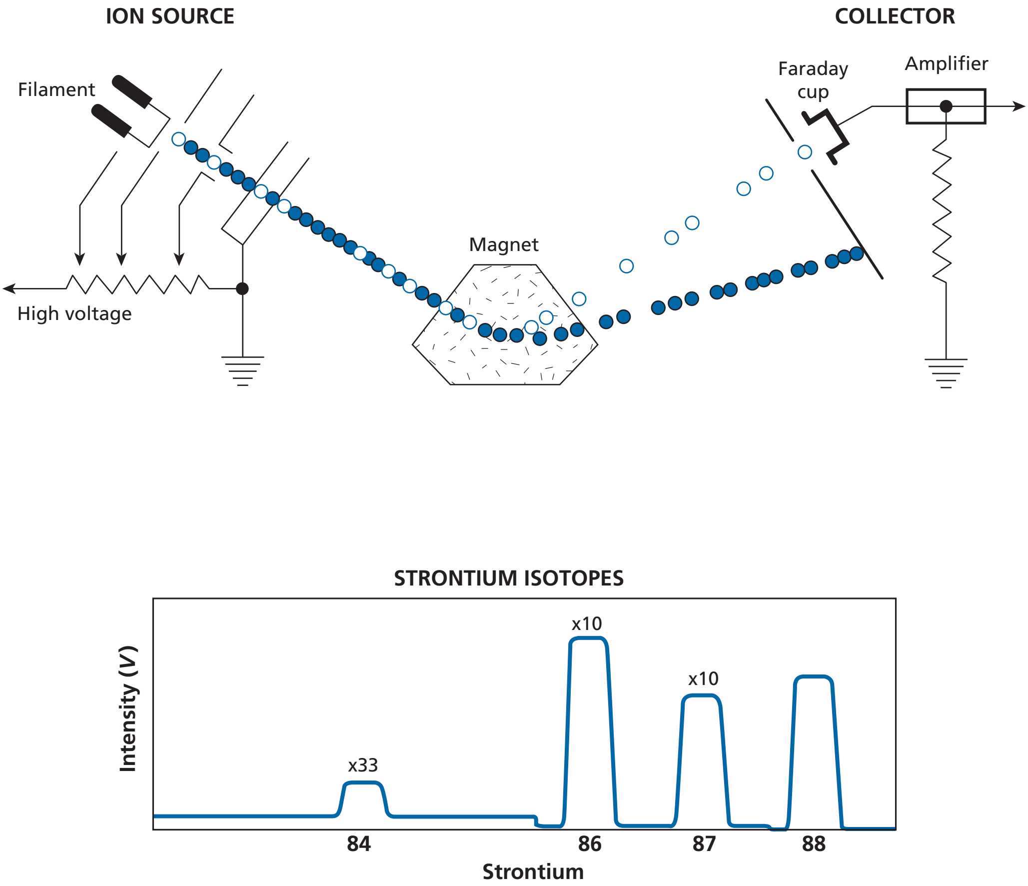

Figure 1.1 A thermal-ionization mass spectrometer. Top: in the center is the electromagnet whose field is perpendicular to the figure and directed downwards (through the page). By Fleming's rules, the force is directed upwards (towards the top of the page) since the stream of ions is coming from the left. An array of Faraday cups may be used for multicollection, that is, for simultaneous measurement of the current produced by each isotope. One important feature has been omitted: the whole arrangement is held in a vacuum of 10^{-7}–10^{-9} mm Hg.[5] Bottom: the mass spectrum of strontium.

The vacuum

A fourth important component is the vacuum. Ions can travel from the source to the collector only if they are in a vacuum. Otherwise they will lose their charge by collision with air molecules and return to the atom state. The whole system is built, then, in a tube where a vacuum can be maintained. In general, a vacuum of 10^{-7} millibars is produced near the source and another vacuum of 10^{-9} millibars or better near the collector. Even so, some air

---

[5] The SI unit of pressure is the pascal (Pa) but for a time it was measured by the height expressed in centimeters (cm) of a column of mercury in reference to Torricelli's experiment. This unit has been used ever since for measuring extreme vacuums. "Standard" atmospheric pressure of 10^5 Pa corresponds to 76 cm of mercury.

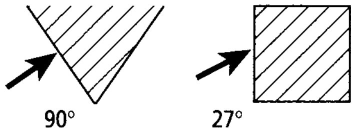

Figure 1.2 (a) Incident beam in the focal plane. (b) Magnet focalization. The beam from the source has a certain aperture. The trajectories of some ions that are not strictly perpendicular to the source are refocused by the magnetic field. The refocusing surface for the various masses at the collector end is curved if the magnet faces are plane, but may be plane if a curved magnet face is used. The figure shows schematically how the magnet separates three isotopes in both configurations.

molecules remain inside the mass spectrometer and collide with the beams, partially disrupting their initial rectangular section.

All of these components contribute to the quality of the data obtained. Mass spectrometer quality is characterized by a number of features.

Efficiency

This is given by the ratio

$$\frac{\text{Number of ions collected}}{\text{Number of atoms in source}} = E$$

$$\text{Number of ions} = \text{intensity} \times \text{duration} \times \frac{6.24 \times 10^{18}}{Z \leftarrow \text{ion charge}}$$

$$\text{Number of atoms} = \frac{\text{mass}}{\text{atomic mass}} \times \text{Avogadro's number.}$$

Efficiency varies with atomic mass.

Ionization efficiency of the source (I) and transmission efficiency of the total ion optics (T):

$$I \times T = E$$

The value of T is variable: 1% for ICP-MS, 25% for ion probes.

The values of I have been greatly improved but vary with the nature of the element and the ionization process. The range is 5‱ to 100% (ICP-MS)!

Power of resolution

The question is, what is the smallest difference in mass that can be separated and then measured using a mass spectrometer? A formal definition is:

Cambridge University Press
978-0-521-86228-8 - Isotope Geology
Claude J. Allegre
Excerpt
More information

$$\text{resolving power } RP = \frac{M_1}{\Delta M}$$

where M_1 is the mass. ΔM is defined as $M_2 = M_1 + \Delta M$, where M_2 is the closest mass to M_1 that does not overlap by more than 50% in the collector.

We can also define a resolving power at 1%.

The distance Δx between two beams in the focal plane is written:

$$\Delta x = K\frac{\Delta m}{m}.$$

Depending on the angle of the incident beam to the magnet, $K = R$ for an angle of incidence of $90°$; $K = 2R$ for an angle of $27°$.

From the formula above:

$$RP = C\frac{R}{\Delta x},$$

R being the radius of curvature and Δx the distance between two beams of M and $M + \Delta M$.

This is just to show that when one wants to separate two masses more efficiently, the radius has to be increased and then the voltage adjusted accordingly. Suppose we want to separate ^{87}Rb and ^{87}Sr by the difference in mass of neutrons and protons alone. A "monster" mass spectrometer would be required. However, interferences between two masses can be avoided when separating isotopes of an element from contaminating molecules. (Methane $^{12}CH_4$ has the same mass as ^{16}O and benzene C_6H_6 interferes at mass 78 with krypton.)

Abundance sensitivity

Another important characteristic is the Δx distance (in millimeters) between the beams. We have to come back to the slits in the collectors. The problem is easy enough to understand. At first, the beam is rectangular. Collisions with residual air molecules means that, when it reaches the collector slit, the beam is wider and trapezoid-shaped with long tails. Collector slits are open so that they can receive one mass but no contribution from the adjacent mass. When the abundances of two adjacent isotopes are very different, the tail of the more abundant isotope forms background noise for the less abundant one. Measuring the less abundant isotope involves reconstructing the tail of the more abundant one mathematically. This is possible only if the tail is not too big. Narrowing the collector slit brings about a rapid decline in sensitivity.

Abundance sensitivity is the measurement of the contribution of the tail of one isotope to the signal of the neighboring isotope. It is given as a signal/noise ratio multiplied by the mass ratios. Special instruments have been developed for measuring abundance sensitivity in extreme cases, such as measuring ^{14}C close to the massively more abundant ^{12}C. Abundance sensitivity is related to resolving power but also to the quality of the ion optics.

Cambridge University Press
978-0-521-86228-8 - Isotope Geology
Claude J. Allegre
Excerpt
More information

Exercise

The isotopic composition of the element rubidium (Rb) is measured, giving a current $i = 10^{-11}$ A for the mass of ^{87}Rb. How many ions per second is that? If the measurement lasts 1 hour how much Rb has been used if the ionization yield is 1%?

Answer

The intensity of an electrical current is defined by $i = dq/dt$, where dq is the quantity of electrical charge and dt the unit of time. Electrical current is therefore the quantity of electrical charge flowing per unit time. The ampere, the unit of electrical current, is defined as being 1 coulomb per second, the coulomb being the unit of electrical charge. The charge of an electron is $-1.6 \cdot 10^{-19}$ coulombs. The positive charge is identical but with the opposite sign. An intensity of 10^{-11} amps therefore corresponds to 10^{-11} coulombs per second / $1.6 \cdot 10^{-19}$ coulombs $= 62.5 \cdot 10^{6}$ ions per second.

If this intensity is maintained for 1 hour: $6.25 \cdot 10^{7} \times 3600 = 2.2464 \cdot 10^{11}$ ions of ^{87}Rb^{+}. As the ionization is 1%, this corresponds to $2.2464 \cdot 10^{13}$ atoms of 87^{Rb} placed on the emitter filament. As ^{85}Rb/^{87}Rb $= 2.5933$, Rb$_{\text{total}}$ (in atoms) $=$ ^{87}Rb (in atoms) $(1 + 2.5933)$.

So a total number of $8.0719 \cdot 10^{13}$ atoms of Rb is placed on the filament. As the atomic mass of Rb is 85.468 g, the total weight of Rb is 11 ng.

Exercise

How much rock is needed to determine the isotopic composition of Rb by measuring a sample for 20 minutes at 10^{-11} A if its concentration in Rb is 10 ppm (parts per million)?

Answer

If 11 ng of Rb are needed for 1 hour, for 20 minutes we need $(11 \times 20)/60 = 3.66$ ng, that is $3.66 \cdot 10^{-9}/10^{-5} = 0.36$ mg of rock or mineral.

It can be seen, then, that mass spectrometry is a very sensitive technique.

1.2.3 Various developments in mass spectrometers

Mass spectrometers have come a long way since the first instruments developed by J. J. Thomson and F. Aston. To give some idea of the advances made, when Al Nier was measuring lead isotopes as a postdoctoral fellow at Harvard in 1939 (more about this later), he used a galvanometer projecting a beam of light onto the wall and measured the peak with a ruler! Nowadays everything takes the form of a computer output.

Ionization

The first technique was to use the element to be measured as a gaseous compound. When bombarded by electrons, atoms of the gas lose electrons and so become ionized (Nier, 1935, 1938, 1939). Later came the thermal-ionization technique (TIMS) (Inghram and Chupka, 1953). In the so-called solid-source mass spectrometer, a salt of the element is deposited on a metal filament (Ta, W, Pt). The filament is heated by the Joule effect of an increasing electric current. At a certain temperature, the element ionizes (generally as positive ions [Sr, Rb, Sm, Nd, U, Pb] but also as negative ions [Os]). Ionization became a fundamental characteristic of mass spectrometry.

Cambridge University Press
978-0-521-86228-8 - Isotope Geology
Claude J. Allegre
Excerpt
More information

Nowadays, as an alternative, plasma is used for optimal ionization in instruments named ICP-MS.

Ion optics

Substantial effort has been put into optics combining various geometries and assemblies. **Bainbridge** and **Jordan** (1936) used a magnetic field to turn the beam through 180°. **Mattauch** and **Herzog** (1934) combined electric and magnetic fields to separate ions and focus beams. Magnet shapes were modified to improve transmission efficiency.

Computerized numerical simulation has allowed tremendous advances in ion optics design. All of the techniques used tended to maximize ionization and transmission, to increase resolution power and abundance sensitivity, and to minimize the high voltage requirement and the size of the magnet, which are both big factors in cost. However, when the ionization process created a wide dispersion in ion energies, more sophisticated ion optics were required to refocus the ion beam in a narrow band on the collectors. So ICP-MS, ion probe, and AMS instruments have become large and more expensive.

Collectors are another important issue. Early mass spectrometers had a single collector. By scanning the magnetic field, the ion beam passed in sequence through the collector and a spectrum of ion abundance was recorded (Figure 1.1). Nowadays most mass spectrometers use simultaneous ion collection with an array of collectors side by side, each collector corresponding to a distinct mass. This seems an obvious technique to use as it eliminates fluctuations between the recordings of one mass (peak) to another. However, it is technically extremely difficult to achieve, both mechanically, accurately installing several collectors in a small space, and electronically, controlling drifting of the electronic circuits with time. These problems have now been virtually eradicated. It is worth noting that, unlike in most areas of science, all advances since 1980 have been made by industrial engineers rather than by academic scientists. However, because of electronic "noise" and electrical instabilities, all isotopic measurements are statistical. On each run, thousands of spectra are recorded and statistically processed. Only since microcomputers have been available have such techniques become feasible.

1.2.4 Preparatory chemistry and final accuracy

In most mass spectrometry techniques (except for ion probes) chemical separation is used before measurement to purify the element whose isotopic composition is under study. Since the elements to be measured are present as traces, they have to be separated from the major elements which would otherwise prevent any ionization as the major elements rather than the trace elements would give out their electrons. For example, an excess of K inhibits any Rb ionization. Chemical separation also prevents isobaric interference between, say, ^{87}Rb and ^{87}Sr or ^{187}Re and ^{187}Os.

Chemical separation can be done in gaseous form in purification lines, as for rare gases or for oxygen or hydrogen measurement, or in liquid solution for most elements. The basic technique in the latter case is the ion-exchange column as introduced by Aldrich *et al.* (1953). All these operations have to be performed in very clean conditions, otherwise sample contamination will ruin measurement. The greater the accuracy of mass spectrometry, the cleaner the chemistry required. The chemistry is carried out in a clean room with special equipment using specially prepared ultra-clean reagents, that are far cleaner than any commercial versions.

When judging measurement reliability, investigators have to state the level of their blanks. The blank is the amount of the target elements measured in a chemical process done without any sample. The blank has to be negligible or very small compared with the amount of material to be measured. So increases in accuracy are linked not only with the improvement of the mass spectrometer but also of the blanks.

Although this is not the place to give full technical details about conditions for preparing and measuring samples, as these can only be learned in the laboratory and not from textbooks, a few general remarks may be made.

Modern techniques allow isotope ratios to be measured with a degree of precision of 10^{-5} or 10^{-6} (a few ppm!) on samples weighing just a few nanograms (10^{-9} g) or even a few picograms (10^{-12} g). For example, if a rock contains 10 ppm of strontium, its isotope composition can be measured on 10^{-9} g with a degree of precision of 30 ppm. Therefore just 10^{-4} g, that is, 0.1 mg would be needed to make the measurement. This method can be used for studying precious rocks, such as samples of moon rock or meteorites, or minor or rare minerals, that is, minerals that are difficult to separate and concentrate. What do such levels of precision mean? They mean we can readily tell apart two isotope ratios of strontium, say 0.702 21 and 0.702 23, that is, to within 0.000 03, even where low concentrations are involved. To achieve such precision the measurement must be "internally calibrated." When measuring the abundance ratio (A_1/A_2) of two isotopes, the electrical current ratio (I_1/I_2) detected is slightly different from (A_1/A_2). The difference is engendered by the measurement itself. This is termed **mass discrimination**.[6] Either of two methods is used for calibrating measurements.

The first is the internal standard method. If the element has three or more isotopes one particular ratio is chosen as the reference ratio and correction is made for mass discrimination. So if the abundances are A_1, A_2, A_3, we take $(A_1/A_3) = R$. The measurement (I_1/I_2) is written $R(1 + \delta\Delta m)$, where Δm is the difference in mass between A_1 and A_3. The fractionation coefficient δ is calculated and then applied to the measurement of the ratio (A_1/A_2).[7]

The second method is to measure a standard sample periodically and to express the values measured in terms of that standard.

The extraordinary precision the mass spectrometer can achieve must not be jeopardized by accidental contamination when preparing samples. To this end ultra-clean preparatory chemistry is developed using ultra-pure chemical reagents in clean rooms (Plate 3 bottom).

1.2.5 Ionization techniques and the corresponding spectrometers

Four major ionization techniques are used depending on the characteristics of the various chemical elements (ionization potential).

Thermal-ionization mass spectrometry (TIMS)

The element to be analyzed is first purified chemically (especially to separate any isobars) and deposited on a refractory filament. Heating the filament in a vacuum by the Joule effect

---

[6] Such discrimination depends on the type of mass spectrometer used. It decreases with mass for any given type.

[7] In high-precision mass spectrometry an exponential law rather than a linear one is used to correct mass fractionation.