

ICPMS Doherty Lecture 1

Mass Spectrometry

This material provides some background on how to measure isotope abundances by means of mass spectrometry. Mass spectrometers create and separate ionized atoms and molecules based on their electric charge and atomic mass, and have been in use since their invention by A.J. Dempster in 1918, and later modifications made by Alfred O. Nier (1940). Mass spectrometers consist of at least three components - an ion source (G, in Figure 1), a mass analyzer (A, in Figure 1), and an ion detector (E, in figure 1). In order to achieve long free pathways for the ions on their way from the ion source to the detector, high vacuum ($<10^{-7}$ torr) is required.

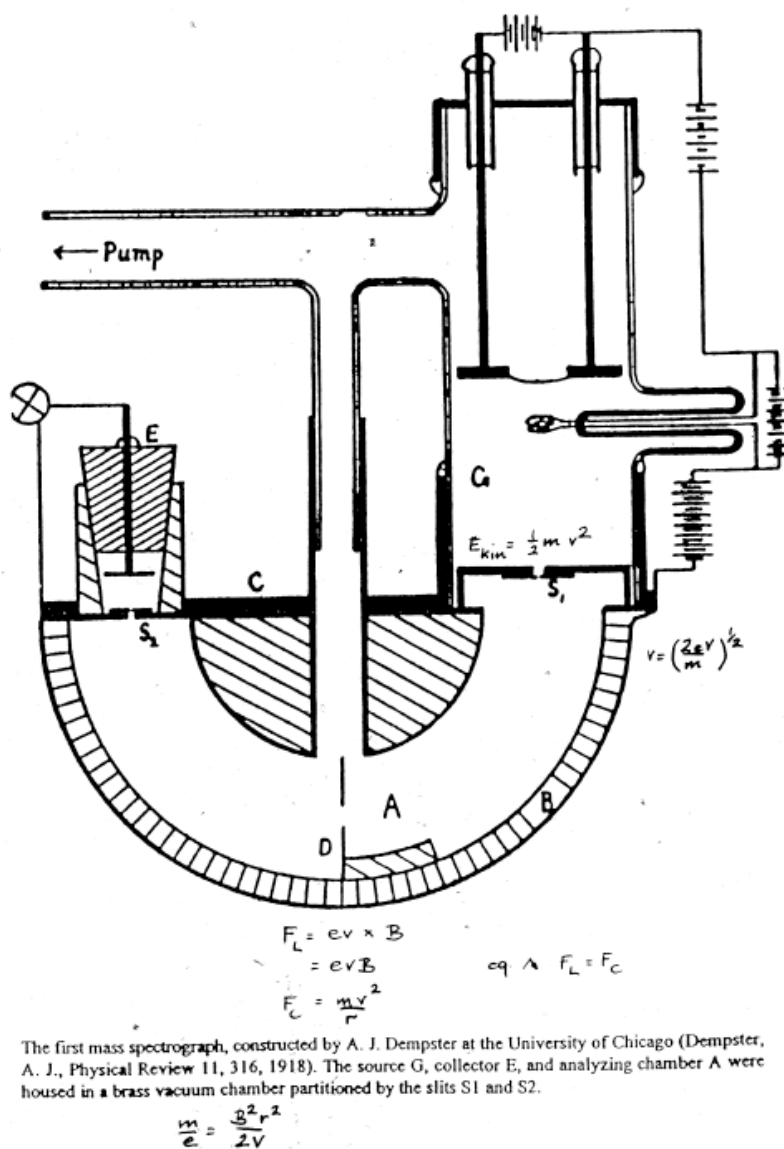


Figure 1: A. J. Dempster's mass spectrograph

IONIZATION (ION SOURCE)

Various methods are used to ionize elements/molecules of interest. They are all based on providing sufficient energy to overcome the first (and sometime also the second) binding energy of the most loosely bound electron (in the case of positive ions), or by forming negatively charged atoms or molecules by providing electrons.

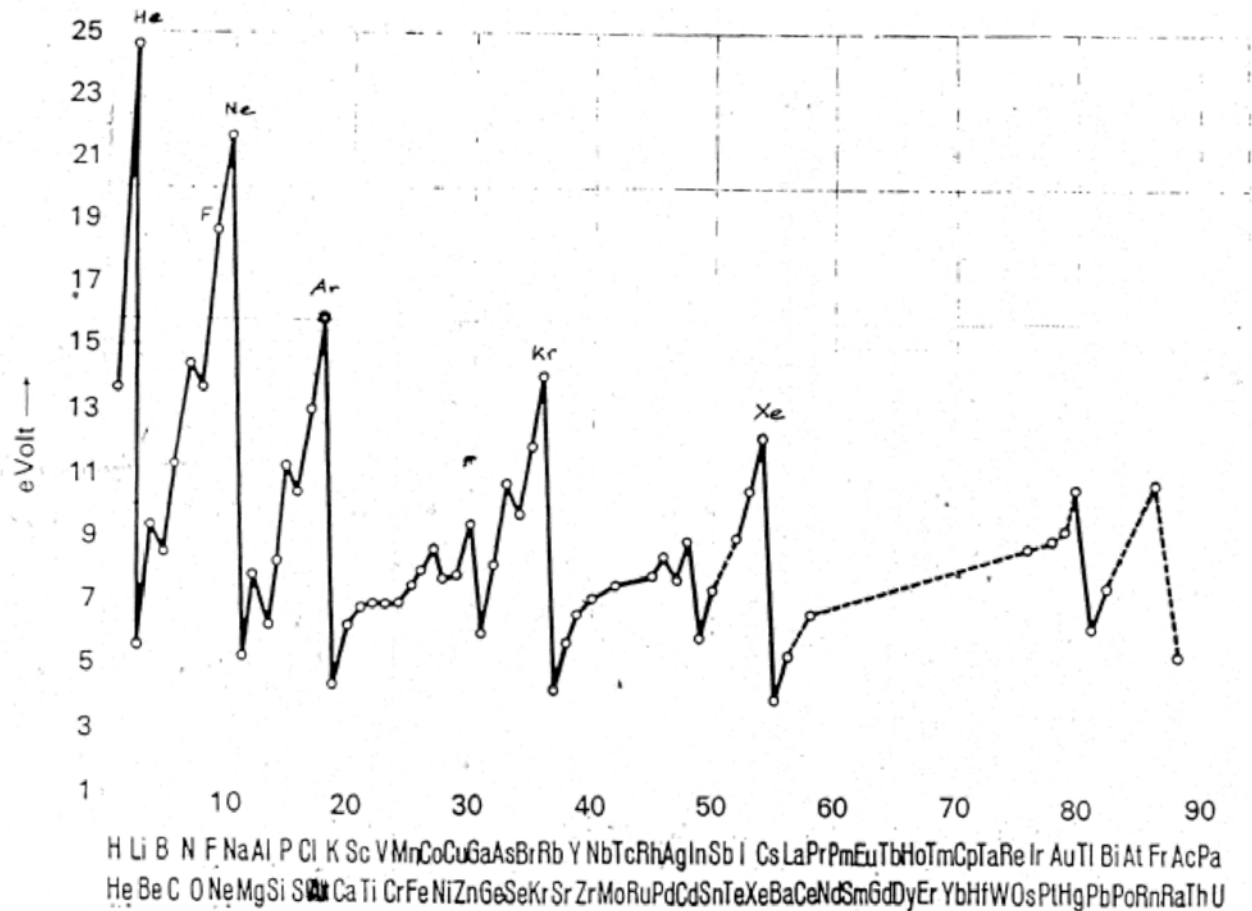


Figure 2: 1st ionization potentials

This is achieved by:

- 1) bombarding a solid or gas with electrons (electron bombardment, electron spray), or positive or negative ions (ion sputtering, as in an ion microprobe or in accelerator mass spectrometers),
- 2) heating a solid (thermal ionization), or
- 3) vaporizing and ionizing liquids, aerosols, or solids in a plasma (inductively coupled plasma) or with a laser (laser ionization).

MASS/CHARGE SEPARATION (MASS ANALYZER)

An ion of mass m and charge e (1.602×10^{-19} C) acquires energy E in an electric field of potential difference of V volts. The ion energy can be expressed as

$$E = e V$$

The kinetic energy is

$$E_{\text{kin}} = \frac{1}{2} m v^2$$

v being the velocity of the ion. Ideally, all ions emerging from the ion source have the same energy (we will see later that this is an idealization), but because they have different masses m , the velocity v varies depending on their mass according to

$$v = (2eV / m)^{1/2}$$

After being focused into a rectangular ion beam by a series of “lenses”, the ions enter the magnetic separator, where a magnetic field B (measured in Tesla, T, Vs m^{-2}) acts upon them. The interaction of ions moving in a magnetic field is described by the Lorentz force F_L , according to

$$F_L = ev \times B \quad (F_L, v, \text{ and } B \text{ are vectors})$$

If ions enter the magnetic field perpendicular to the magnetic field lines, the equation can be simplified to

$$F_L = evB$$

The Lorentz force acts perpendicular to the direction the ion is traveling and the magnetic field lines. It thus accelerates the ions without changing their velocity (remember the **left hand rule**: thumb points in the direction of the magnetic field lines from N to S, index finger indicates the direction of the ions and the middle finger, bent 90° , indicates the direction of the Lorentz force). The ions follow a circular trajectory as long as the magnetic field acts upon them. The radius of the circular trajectory can be calculated with the above equations, because the Lorentz force has to be equal, but opposite, to the Centrifugal force F_C

$$F_C = mv^2 / r$$

In equilibrium ($F_L = F_C$)

$$evB = mv^2 / r$$

Thus,

$$r = mv / eB$$

Substituting the unknown velocity v using the equation above leads to

$$m / e = B^2 r^2 / 2V$$

If B is measured in 10^{-4} Tesla (=1 Gauss, old, non-SI unit), r in centimeter, m in dalton (or atomic mass units, amu), V in volts and e in units of electric charge the equation becomes

$$m / e = 4.825 * 10^{-5} B^2 r^2 / V$$

This equation can be modified to calculate the radius of an electromagnet necessary to focus single charged ions of an isotope of mass m, accelerated by a potential of V, into an ion detector. It is important to note that mass spectrometers deflect ions in a magnetic field according to their mass to charge ratio. Doubly charged ions therefore appear in the mass spectrum at 1/2 mass. It is also important to note that the radius is proportional to the square root of the mass. Heavier ions are thus bent less in a magnetic field.

Electrostatic Analyzer (ESA)

In thermal ionization the spread in ion energy is small (<1 eV), so that energy focussing is not necessary. However, plasma sources are so energetic that the spread of ion energies is much larger (15-20 eV) and energy focussing becomes an important component of the analyzer. These analyzers are constructed of curved electrostatic plates with opposite charges. The radius of the curvature must be defined by equating the electrostatic force (E) with the centrifugal force (F_C , see above)

$$r = mv^2 / E$$

The radius is thus directly proportional to the kinetic energy of the ions. Only ions of a particular kinetic energy can pass through the analyzer with radius r. All other ions are diverted and collide with the walls.

Quadrupole Analyzer

Quadrupole analyzers utilize a field generated by four parallel electrodes that ideally are hyperbolically shaped, but for practical reasons usually are cylindrical. Two opposite electrodes are electrically connected (Figure 3a). The applied voltage consists of a d.c. voltage, U, and a superimposed r.f. voltage, V. The governing equation is

$$\text{Total voltage} = U + V \cos \omega t$$

Ions injected into such a quadrupole field parallel to the z-axis (parallel to the electrodes, i.e., no field: $d^2z / dt^2 = 0$) are forced on oscillatory trajectories. The Mathieu' differential equations define the trajectories for ions in the x and y direction according to

$$d^2x / dt^2 + (a + 2q \cos \omega t) x = 0$$

and

$$d^2y / dt^2 - (a + 2q \cos \omega t) y = 0$$

with

$$a = 8 eU / m r_0^2 \omega^2$$

and

$$q = 4 eV / m r_0^2 \omega^2$$

(m = mass of ion [amu or dalton]; $2 r_0$ = distance between electrodes; ω = circular frequency; e = charge).

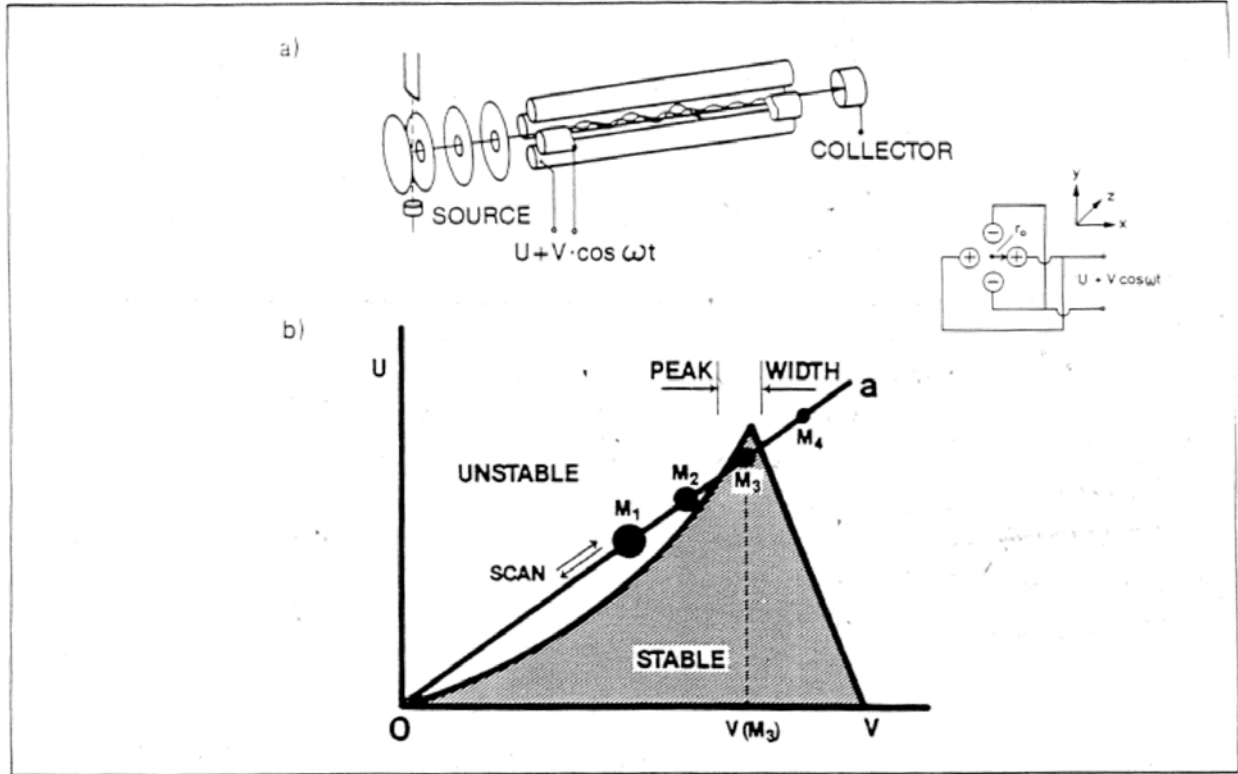


Fig. 11. (a) Schematic of quadrupole analyzer. An rf voltage, V , with a superimposed d.c. voltage, U , is applied to the rods. The injected ions oscillate in the resulting quadrupole field [1, 2, 16-18]. (b) The oscillations are stable only when the equation $m = 2.83 eV / \omega r_0^2$ is fulfilled (mass = m , charge = e , circular frequency = ω , field radius = r_0). Ions having unstable oscillations are filtered out. According to the above equation, scanning of the masses can be performed by sweeping the rf voltage, V . The superimposed d.c. voltage, U , is also swept, while the ratio U/V is kept constant (slope $O-a$). The ions "threaded" on the line $O-a$ are then moving through the stable part of the stability diagram ($m_1 > m_2 > m_3 > m_4$).

Figure 3: Quadrupole Analyzer

Solutions to these differential equations fall into two categories – stable and unstable trajectories. Given a certain setting for V and U , only ions with certain m/e values fulfill the requirements with respect to a and q for stable trajectories and pass through the quadrupole mass analyzer. All other ions are forced on unstable trajectories that will lead to collisions with the electrodes or the walls of the flight tube. This is best shown in a plot of U vs. V , i.e. the quadrupole stability diagram, that shows the region of stable and unstable trajectories. The linear trend ($O-a$) shown in Figure 3b depends on the ratio of U/V (more precisely a/q , i.e., $2U/V$). The mass resolution of a quadrupole filter can be set by changing the slope of this linear trend. A shallow slope (small a/q) corresponds to low mass resolution ($m/\Delta m$) whereas a steep trend that barely cuts across the apex of the stability field corresponds to high mass resolution. Mass resolution is nearly inversely related to the transmission, i.e. the ratio between the number of ions

detected at the end of the mass analyzer to number of ions injected. This is indicated by the “peak width” in Figure 3b. Compared to magnetic sector analyzers quadrupole analyzers have fairly poor mass resolution, but very good transmission. The electric field generated by the quadrupole analyzer can be changed very rapidly (milliseconds) over a wide mass range by changing the r.f. voltage and d.c. voltage while maintaining a constant slope (a/q). This is an advantage when less stable ion sources are used (e.g., Ar plasma).

ION DETECTION

The ions exiting the mass analyzer(s) are separated according to their mass to charge ratio, and can be detected with a suitable ion detector. Commonly used are Faraday detectors (cups) and secondary electron multipliers (SEM). Faraday cups measure the intensity of the ion beam, I , by converting the current intensity into a potential, U , by means of a resistance, R , according to

$$U = R I$$

Typical ion beam intensities are of the order 10^{-13} to 10^{-9} ampere (A), requiring a resistance of $\sim 10^{10}$ ohm to produce potentials of 1 mV to 10 V. Smaller ion beam intensities have to be amplified, and amplification is usually done by means of SEM. An SEM consists of a conversion dynode that converts the ion beam into an electron beam. These electrons are then accelerated across a potential gradient in a sequence of steps (i.e. dynodes), each step multiplying the incoming electrons by a certain factor (the “gain”). The resulting cascade of electrons leads to the required amplification of the incoming ion beam. With SEM individual ions (electrons) can be detected - an art called “ion counting”. These SEM come in two forms - discrete and continuous dynode electron multipliers. The former has discrete plates (dynodes) at set potentials to accelerate electrons, whereas the latter consists of a continuous channel (sometimes with a built-in conversion dynode) with a potential gradient from the entrance funnel to the back end.

The signal processing electronics of SEM are characterized by a fixed time constant (τ) that defines the time needed to process one signal. For modern electronics this time constant is on the order of tens of nanoseconds. During the processing of one signal new signals cannot be processed - the detector is busy. For obvious reasons this time constant is called “dead time”. As the ion beam intensities increase (i.e. ions entering the detector more and more frequently), fewer and fewer of the incoming ions can be processed relative to the number of incoming ions. Knowing the dead time allows to correct for the “sluggishness” of SEM electronics. Dead time becomes an important issue only at high count rates of, say, more than several hundred thousand counts per second (cps). For a detector with a fixed τ (a so-called “non-paralyzable” system) the true count rate (n) is related to the measured count rate (m) by

$$n = m / (1 - m \tau)$$

Determining τ is critical for accurate count rates and isotope ratios. I am attaching two methods to this script that can be used to determine τ . Both methods assume that the measured

ion beam intensities (and ratios) are not affected by instrumental fractionation. If they are, these effects have to be corrected for before the dead time is determined.

Dead Time Correction

Determination of the Dead Time correction factor

To determine right dead time value the following procedures are possible:

1. Determination of the isotope ratio $^{175}\text{Lu} / ^{176}\text{Lu}$.

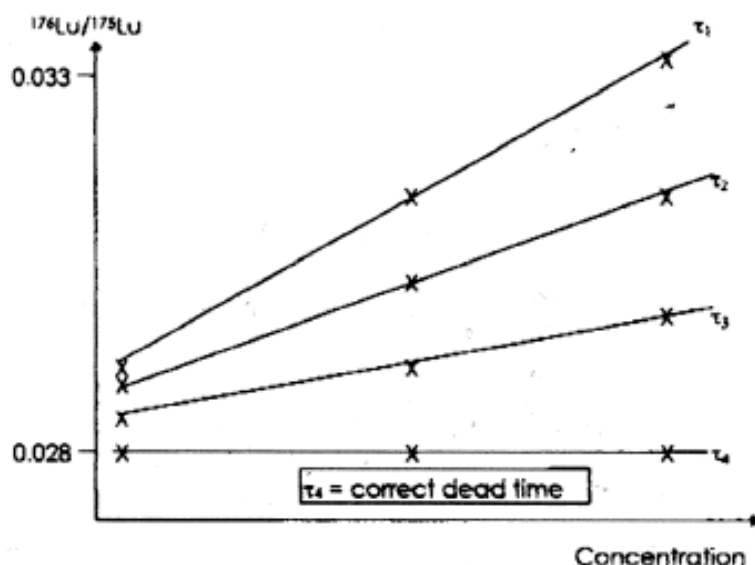
Prepare a Lu solution which results in a countrate of about $2 \cdot 10^6$ cps for ^{175}Lu , a second solution which results in a countrate of about 5000 cps for ^{176}Lu and another solution with a concentration between solution 1 and solution 2.

Create three methods for the several solution in a way that totally 10^6 ions per each of the isotopes will be collected at the multiplier (by changing the sample time e.g. if there are 5000 cps then use a sample time of 200 s).

Analyze a blank solution followed by each of the three concentrations of Lu. Use the appropriate parameter for each concentration.

With this procedure completed, it is evident that without a dead-time correction the ratio $176/175$ increases with the Lu concentration.

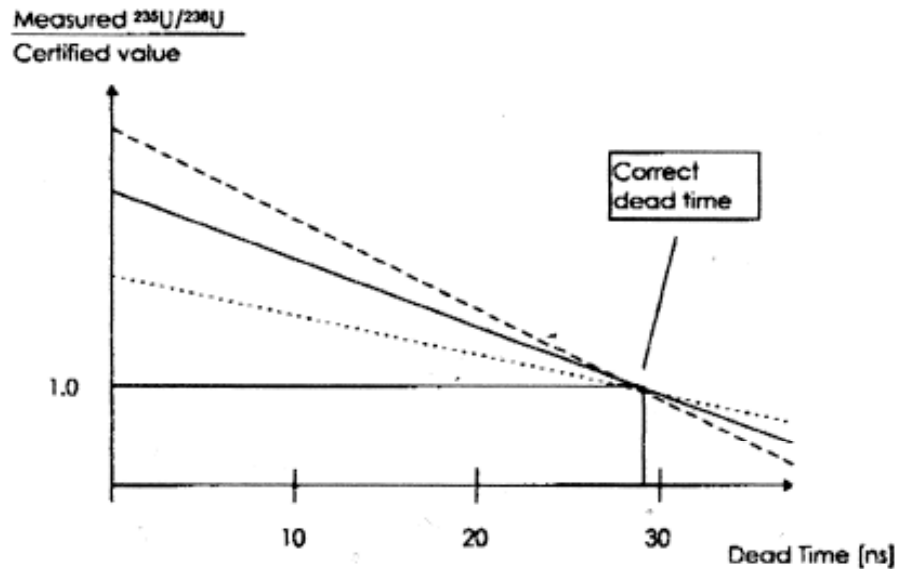
Correct the obtained intensities with several dead time values, calculate the resulting ratios and compare them for the different concentrations. At the right dead time value the isotope ratios are equal for all three concentrations.



Dead Time Correction

2. Determination of e.g. several uranium samples of various known isotopic composition

Use different uranium samples of various known isotopic composition and concentration and determine the intensities for ^{235}U and ^{238}U . Calculate for each of the sample the ratio applying several (e.g. three) different dead times and plot the calculated values/expected value against the dead time. At the intersection of the curves the corresponding dead time can be seen.



It is also important to realize that mass spectrometers are optimized to detect relative ion beam intensities, rather than absolute ion beam intensities. Mass spectrometers are thus optimized to measure ratios of ion beam intensities, or isotope ratios. This is done by varying either the magnetic field strength or the accelerating voltage back and forth between the proper setting for the isotopes of interest (single collector mode). Alternatively, the detector consists of multiple ion detectors (multi-collector mode) capable of measuring multiple ion beams at the same time. The advantage of multi-collector mass spectrometers is that temporal variations in the ion beam intensity do not influence the analytical results.

Measurement uncertainties

All measurements are afflicted with uncertainties. For large number of events, binomial distributions asymptotically approach Gaussian (or normal) distributions. The spread in events (here numerical values of isotope ratios, count rates or ion beam intensities) is equal to $\sqrt{N}$. According to Gaussian statistics about 2/3 of the results lie within the range $N \pm \sqrt{N}$ (one standard deviation), about 95% lie within the range $N \pm 2\sqrt{N}$ (two standard deviations), and ~99% lie within the range $N \pm 3\sqrt{N}$. The fractional uncertainty is thus $\sqrt{N}/N$, or $1/\sqrt{N}$. If you measure twice as long you get twice as many events

$$N^* = 2N$$

the fractional uncertainty is $\sqrt{(2N)}/2N = 1/\sqrt{(2N)}$

i.e. $\sqrt{1/2} * 1/\sqrt{N}$

reducing the fractional uncertainty only by ~30%. The fractional uncertainty improves only as the square root of time (or ion beam intensity). If you attempt to improve the uncertainty by a factor of two, you need to measure four times as long.

In order to evaluate if uncertainties associated with small ion beam intensities significantly affect the measured ratios it is often helpful to assume that all uncertainties are associated with uncertainties in the smallest ion beam (least abundant isotope). By assuming an arbitrary uncertainty in the measurement of this ion beam you can plot an “error trend” on plots of isotope ratio versus another isotope ratio (same isotope in the denominator, i.e. $m_2 = m_4$, if m_1 and m_3 are isotopes in the numerator). This trend is often distinct from a “instrumental fractionation trend” and helps to assess what process dominates the uncertainty of your analysis.

Instrumental fractionation

Unfortunately, mass spectrometers are not free of artifacts and corrections are required. For the purpose of this lecture let us assume that fractionation depends only on the mass difference of the ions of interest.

In thermal ionization mass spectrometers (TIMS) the main mass fractionation happens during the process of evaporation and ionization from the metal band (the filament) on which the sample was deposited on. Heavier atoms/molecules have a slightly lower vapor pressure than light atoms/molecules, because lighter free particles have slightly higher velocities for a given kinetic energy.

$$E_{\text{kin}} = 1/2 mv^2$$

In addition, an assemblage of atom/molecules tends to self-adjust to a distribution of energy states with minimal energy. Intermolecular forces can be described by a quantum-mechanical energy “well”, whose zero point energy is mass dependent, being lower for heavier masses. Both features lead to preferential evaporation of the light masses. This means that at the start of

the analysis the light isotopes are preferentially detected. If the given reservoir is small, the remaining number of light isotopes constantly decreases. The ratio of light to heavy isotopes therefore tends to be higher than the starting ratio at the beginning of the analysis, then approaches the starting ratio and later becomes smaller than the starting ratio.

In ICP-MS analysis, reservoir effects are not important because the reservoir (solution) is usually large compared to the fraction that enters the mass spectrometer. However, all ions have to pass through a series of small openings (cones) into the mass spectrometer (they are traveling from ambient pressure to the high vacuum inside the mass spectrometer), resulting in significant space charge effects (the accumulation of positively charged ions in a small volume). Ions with smaller masses are more affected by such space charge effects, leading to a preferential transmission of heavier ions into the mass spectrometer. Instrumental fractionation in ICP mass spectrometers is thus opposite to fractionation in TIMS.