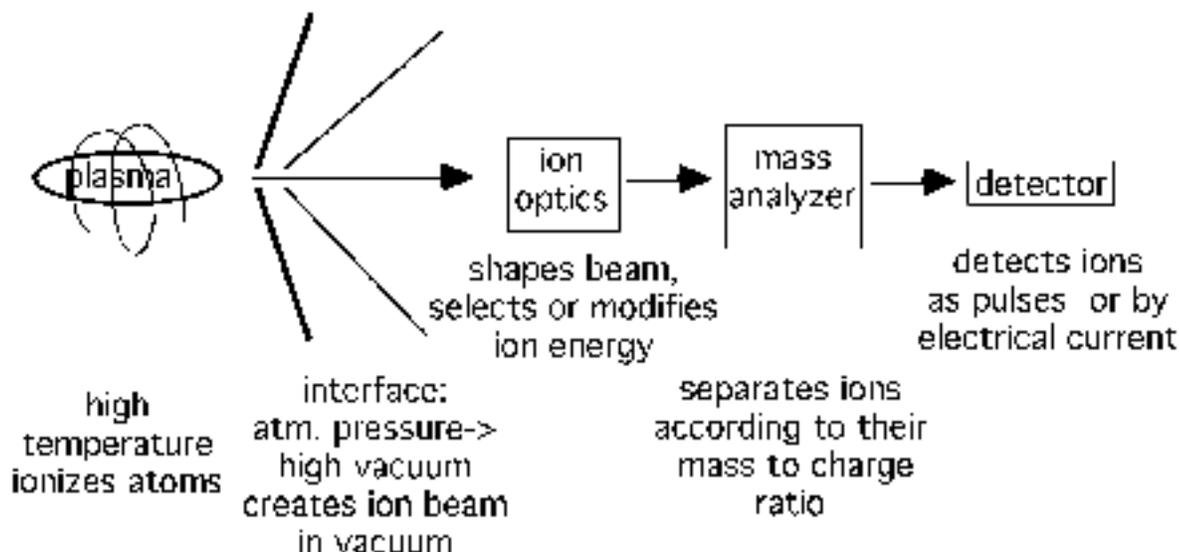


Inductively Coupled Plasma: Emission and Mass Spectrometry

I. Overview of ICPMS technology

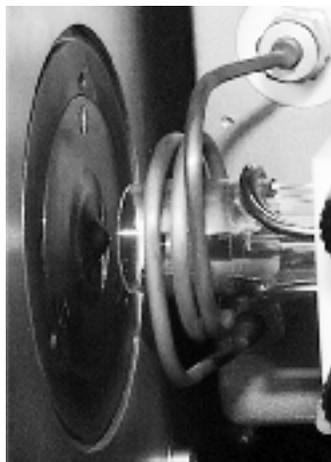
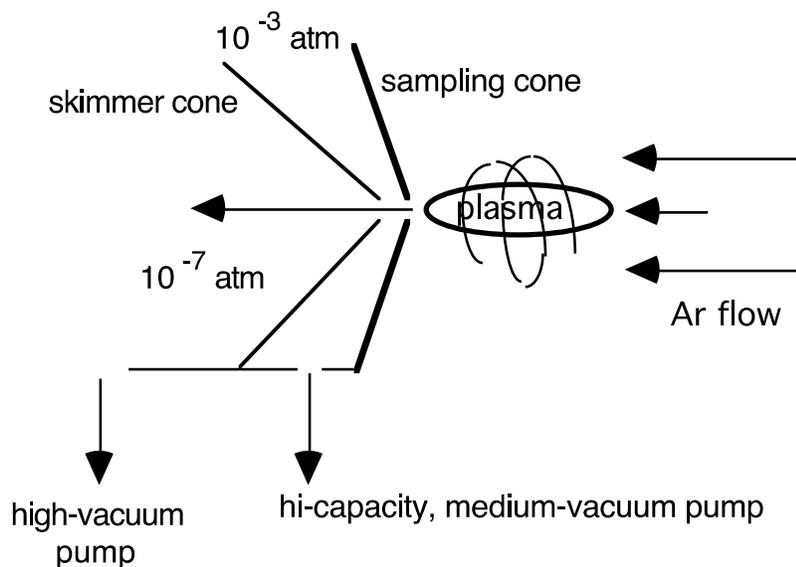


- II. Inductively coupled plasma: ~1 liter per minute of Ar gas flows through a copper coil (~3-5 turns, ~1" diameter, cooled by internal water flow) connected to a 1-2 kilowatt radiofrequency generator. The slower central Ar flow is sheathed by a stronger outer flow (~10 liters/min). The slower-moving Ar gas becomes inductively coupled to the radiofrequency energy (the moving electrons and nuclei are ripped apart in opposite directions by the magnetic field resulting in the formation of a plasma (a "gas" of electrons and positively charged argon ions). This plasma has a very high temperature - dependent on conditions and sometimes hard to define by conventional measures - but it is on the order of 5,000-10,000 degrees Kelvin. The plasma emits an intense light rich in ultra-violet that cannot be viewed without special eye protection (e.g. welding hood).
- A. This plasma is capable of ionizing almost all elements with high efficiency - most elements are >90% ionized although a few unusually stable atoms with higher ionization potentials (e.g. Zn, Cd) are somewhat less efficiently ionized. The samples must be injected into the plasma as a gas, mist or very fine particles ($\leq \sim 10 \mu\text{m}$).
- B. As the ions jump back to their ground state, they emit photons of characteristic wavelengths. Observation of these photons through a spectrophotometer is the basis of ICP-OES: inductively coupled plasma optical emission spectroscopy. This method is less prone (but not immune) to interferences than lower-temperature flame emission methods, and the high degree of ionization leads to many photons per given number of atoms - hence it is a relatively sensitive method (depending on the element, detection limits typically fall somewhere between flame AAS and graphite furnace AAS (certain new ICP-OES instruments view a larger portion of the plasma and claim near-GFAAS detection limits, but this benefit comes with increased

interferences as cooler portions of the plasma are viewed). Certain elements (usually the more refractory elements) are analyzed much more easily by ICP-OES than the other methods, and multi-element analysis is easy by multiple detectors or wavelength scanning.

III. Quadrupole ICPMS: Inductively coupled plasma mass spectrometry.

A. In the late 1970's, Gray and Date in Britain and Houk in the U.S. conceived of using the ICP as an ion source for mass spectrometry. The principle problem is in transferring ions at atmospheric pressure (necessary to maintain a sufficient atom density for efficient sample ionization) into a mass spectrometer that must operate at low pressure. They solved this problem by using a dual-"pinhole" inlet system with massive vacuum pumps to allow some of the sample to go into the high vacuum at greatly reduced pressure. They used a quadrupole mass spectrometer (which is more tolerant of higher pressures than magnetic sector instruments, and has the additional benefit of allowing for millisecond scans over 0-250 amu).



The beam is then further focused and accelerated by slits and electrostatic optics.

One problem is of secondary discharges between the plasma and the (grounded) sampling cone. Various strategies are used to minimize these, including capacitive balancing of the RF generator.

Plasma shield: a grounded metallic strip that is sometimes placed between the RF load coils and the torch; it appears that this minimizes the “energy spread” of the ions in the plasma.

B. Plasma “torch”



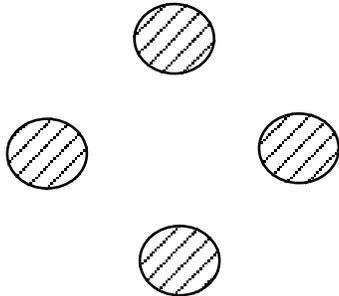
1. Gases flow into concentric quartz cylinders. The “cool gas” (or sheath) is flowing so fast that insignificant coupling occurs between it and the RF magnetic field. The intermediate and nebulizer gases move more slowly, couple with the RF magnetic field, and heat up to form the plasma.
2. At some point in the plasma, the sample is optimally ionized; this is the point at which you want the plasma to impinge upon the sample cone.

C. Quadrupole mass filters

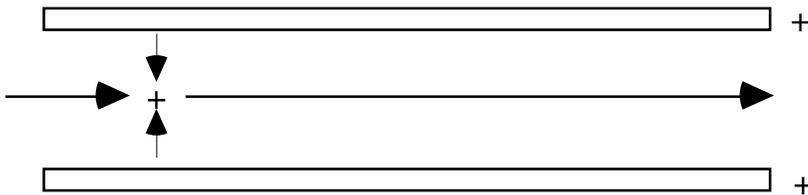
1. Unlike conventional magnetic-sector instruments, which in effect form a mass spectrum by viewing the magnetically-produced image of a slit (much as a prism or grating makes an optical spectrum of the image of a slit), quadrupole mass spectrometers are mass filters in that they do not form an image but rather simply

act as a filter which allows a certain range of masses to pass through. One pair of poles serves as a low-mass filter, the other serves as a high-mass filter.

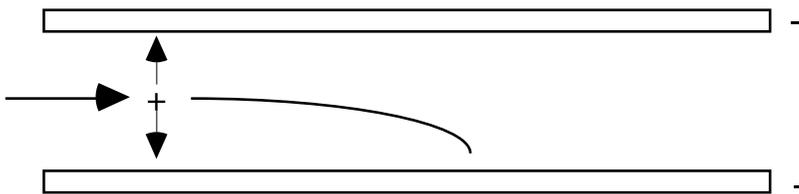
Quadrupole mass filter, end view:



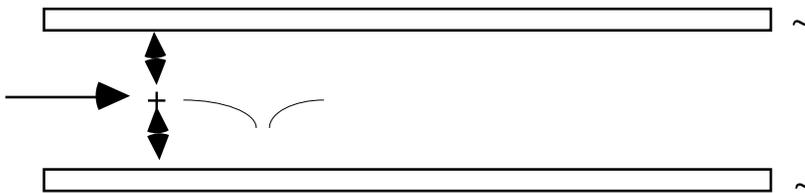
- Imagine a beam of positive ions traveling between two poles which are positively charged. If an ion has a trajectory which carries it away from the center, electric repulsion forces it back towards the center. Hence positively charged poles tend to have a focusing effect, keeping ions on beam.



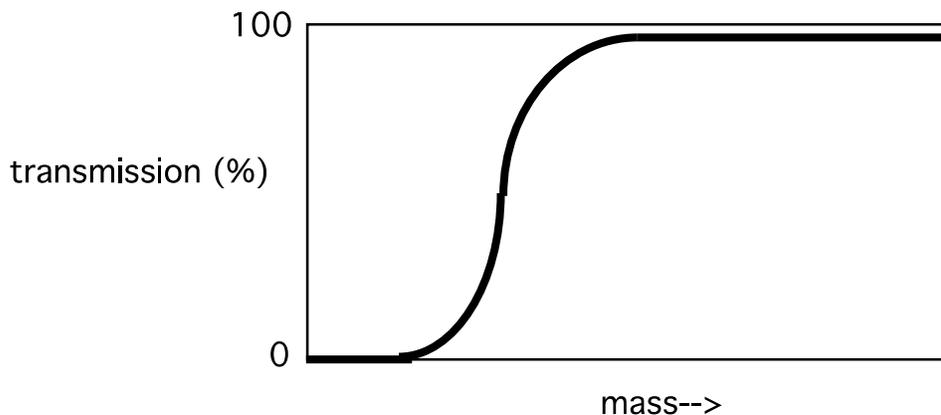
- Imagine a beam of positive ions traveling between two poles that are negatively charged. If an ion strays from the center, the electric attraction pulls it further away from the center until the ion hits a pole and is discharged. Hence negatively charged poles tend to have a defocusing effect, removing ions from the beam.



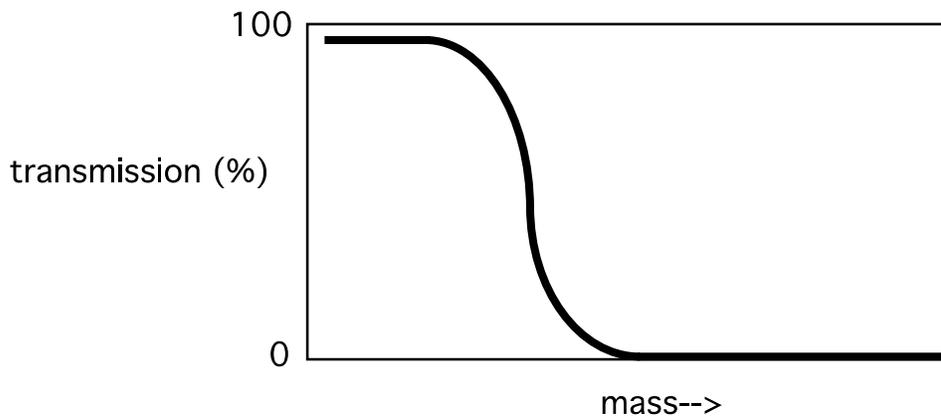
- Now image an alternating (AC) voltage on the poles. Depending on the voltage, frequency, and ionic mass, charge and velocity, the ions are alternately either defocused and focused:



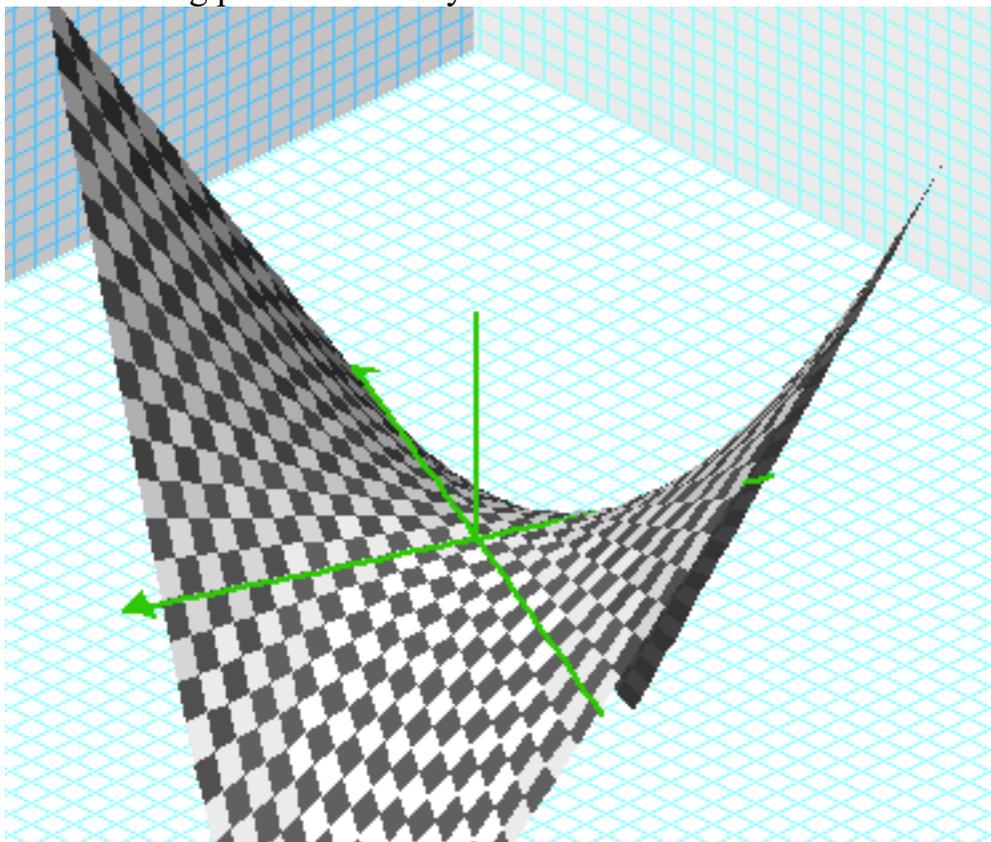
5. Suppose on one pair of rods an AC voltage is combined with a small positive bias. If the mass of the ion is large, or the frequency of the AC is high, then the ion will tend to feel the effect of the average (DC) field. If the mass of the ion is light, then it will experience rather large swings which bring it into contact with the electrodes. Hence a pair of rods with an alternating current will tend to serve as a high-pass filter, trapping the light ions and letting heavy ions through:

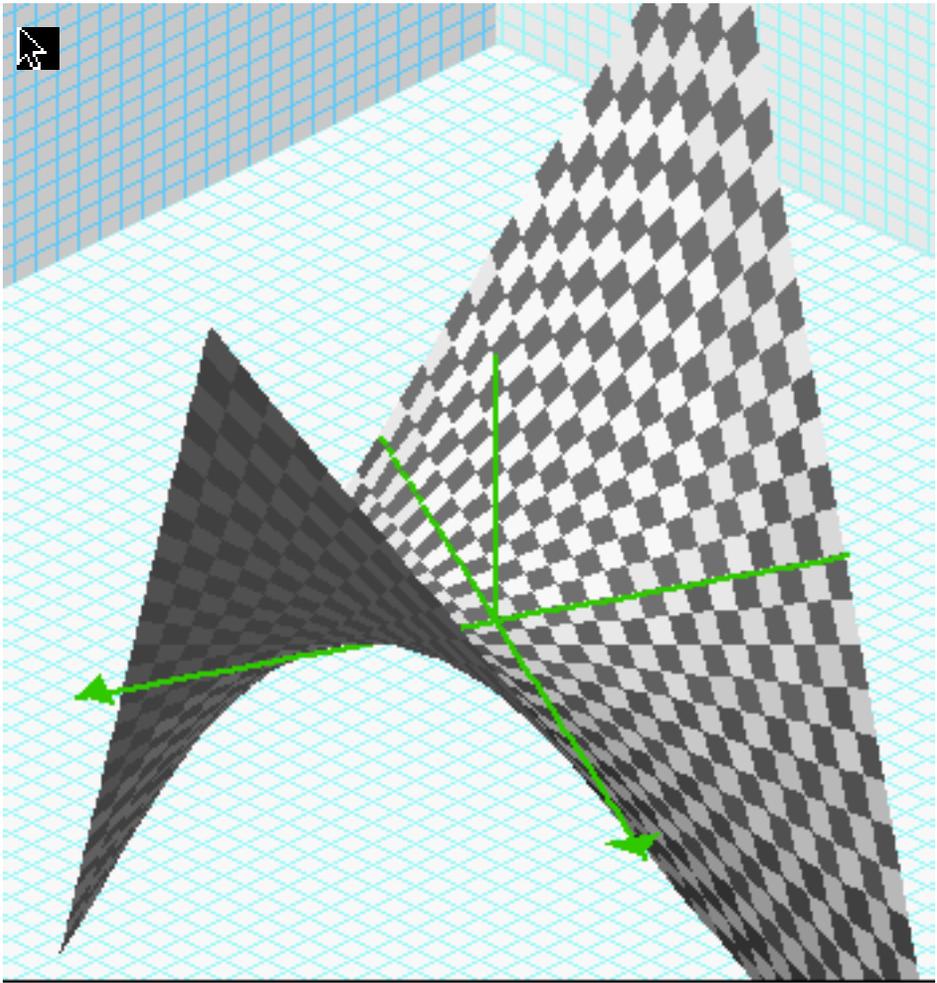


6. Suppose on the other pair of rods, an AC voltage is combined with a small negative bias. The heavy ions will tend to feel the effect of the average and be defocused and lost. The light ions will be restored to the beam by the positive phases of the AC field. Hence this pair of rods will act as a low-pass filter:



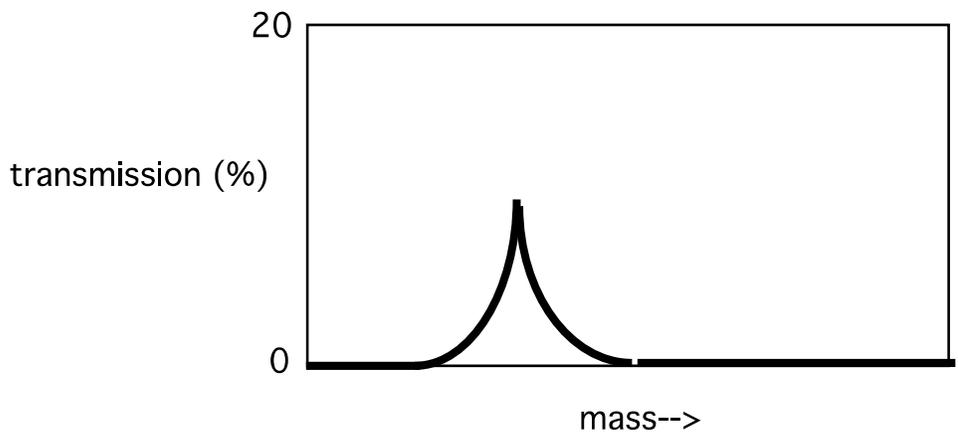
This works as if you had a ball traveling through space on a saddle surface with oscillating peaks and valleys :





“ion surfing”

7. The net result of both pairs of poles is to serve as a narrow-range filter.



8. Because the electrostatic field can be changed rapidly, the parameters of the DC and AC fields on the poles can be changed rapidly to alter the position of the

mass notch. Hence a quadrupole mass spectrometer can rapidly (~ 1 millisecond) scan the entire mass range (1-250 amu).

9. In order to maximize time spent on ions of interest, this analyzer can be operated in “peak jumping” mode where you rapidly change the m/e value from one element to the next. You have to wait a short time (fractions of a millisecond) for the mass to “settle”, take a quick measurement, then move to the next element with little time lost measuring between peaks.
 10. Mass resolution on a quadrupole mass spectrometer is a little bit better than 1 amu. Because the system acts as a filter rather than an imaging device, the peaks are not flat-topped. Quadrupole mass spectrometers also do not have constant transmission across the mass range; sensitivity can vary by as much as 1% per amu at high masses.
- D. Detection: the usual detection device is the electron multiplier (or a variant referred to as a discrete dynode), which is similar to a photomultiplier except that the photosensitive surface is not required; instead, the electron cascade is stimulated by an impinging ion. This may be operated in pulse mode (counting of pulses due to single ion impacts) or in analog mode (measurement of steady current resulting from multiple impacts). Some instruments use a “Daly” detector, which uses a high negative voltage (~30kV) to impact the ions onto a metal knob, releasing a few electrons that are then accelerated away to impact onto a scintillating crystal, with the light pulses counted by a photomultiplier outside of the vacuum system. This detector has the advantage that the detector is not degraded by the impacts, so it has a long and trouble-free life and a relatively stable efficiency (~95%). Both types of detectors can only tolerate a maximum of $\sim 10^6$ cps, so they usually have circuits that “trip out” when count rates exceed that maximum.
- E. Dissolved solids limitation: if a high concentration of dissolved solids is in the sample, the nebulizer will form salts at the tip and clog; in general, dissolved solids must be <0.1% for most nebulizers. Even at ~0.1%, the dissolved solids will condense on the sampling and skimmer cones, eventually plugging up the interface, so only limited runs are possible at ~0.1% dissolved solids.
- F. Ion transmission in an ICPMS: from the sublime to the ridiculous:

$$\text{cps} = [\text{Concentration of atoms}] * f_{\text{liquid flow}} * f_{\text{nebulized}} * f_{\text{ionized}} * f_{\text{interface}} * f_{\text{transmitted}}$$

1. A typical ICPMS nebulizer delivers only about 1% of the sample as a fine spray to the plasma. Other sample introduction devices can be more efficient – microconcentric nebulizers (~10%), desolvating nebulizers (~50%), electrothermal vaporization (~50%)(i.e., graphite furnace as a source of atoms) laser ablation (~50%), hydride generation (~100%).
2. Once the atoms are delivered to the plasma, most of them are ionized. Some elements (e.g. Zn, Cd) are less efficiently ionized. For some elements 1-30% can be further lost to double ionization (e.g. Ba⁺⁺) or oxides (e.g. CeO⁺, UO⁺)

3. Typically about 0.1-10% of the ions in the plasma pass through the skimmer cone and 10-90% of these ions become part of the ion beam (depends on configuration).
5. The quadrupole mass spectrometer itself has a transmission efficiency on the order of 10% of the ions which enter it.
6. The electron multiplier counts (almost) every atom that exits the quadrupole.
7. Overall, therefore, in a quadrupole ICPMS system using a conventional concentric glass nebulizer system, about only 1 out of every 1-10 million atoms in the sample arrives at the detector! The principle points of improvement are in sample introduction (with little further progress possible, perhaps a factor of 3 at most from the most efficient sources) and ion transmission in the interface (possibly orders of magnitude). During the past 10 years, maximum transmission has been improved by a factor of 100.
8. The detection limit is partially determined by the background count rate: the count rate observed when you are parked on a mass with no isotopes or polyatomics, or at half-mass next to low-count rate peaks when the resolution is sufficient. Because the quadrupole has a linear flight path, photons coming in from the plasma, or generated within the ion beam by electrons dropping to ground state, are counted as if they are ions – but they are not selected against by the QMS. This background can be minimized to some extent by bending the ion beam around a “photon stop” (a circular barrier in the ion path that photons crash into but ions are bent around), or by electrostatically bending the ion beam before it enters the detector.

G. Isobaric interferences in ICPMS

1. Because quadrupole mass resolution is a little bit better than 1 amu, any element having a m/e value within 0.5 amu of the isotope of the element of interest will interfere. In many cases, you can avoid these inter-elemental isobaric interferences by using a different isotope of the element you are interested in, or by measuring another isotope of the interfering element and subtracting from the mass of interest on the basis of the known isotope ratio of the interfering element. Alternatively, by using a high-resolution magnetic sector instrument, you can resolve some interferences (see later)
2. In addition to elements in the sample, elements in the solvent (often a mineral acid such as HNO₃, HCl, H₂SO₄, H₃PO₄) and plasma gas (Ar with impurities C, N, O, Ne, Kr, Xe,...) can interfere.
3. The elements in the sample and plasma gas can combine to form interfering polyatomic molecular species which form when the ion beam is cooling in the vacuum interface, e.g.:

Ar₂⁺ (mainly mass 80 but also at 76 and 78) ArCl⁺ (mainly masses 75 and 77);
 ArO⁺ (mainly mass 56); POH⁺ (mainly mass 48), ClO⁺ (mainly 53, 55), ClOH⁺
 (mainly masses 54 and 56), ArN⁺ (mainly mass 54), ArCl⁺ (mainly masses 75 and

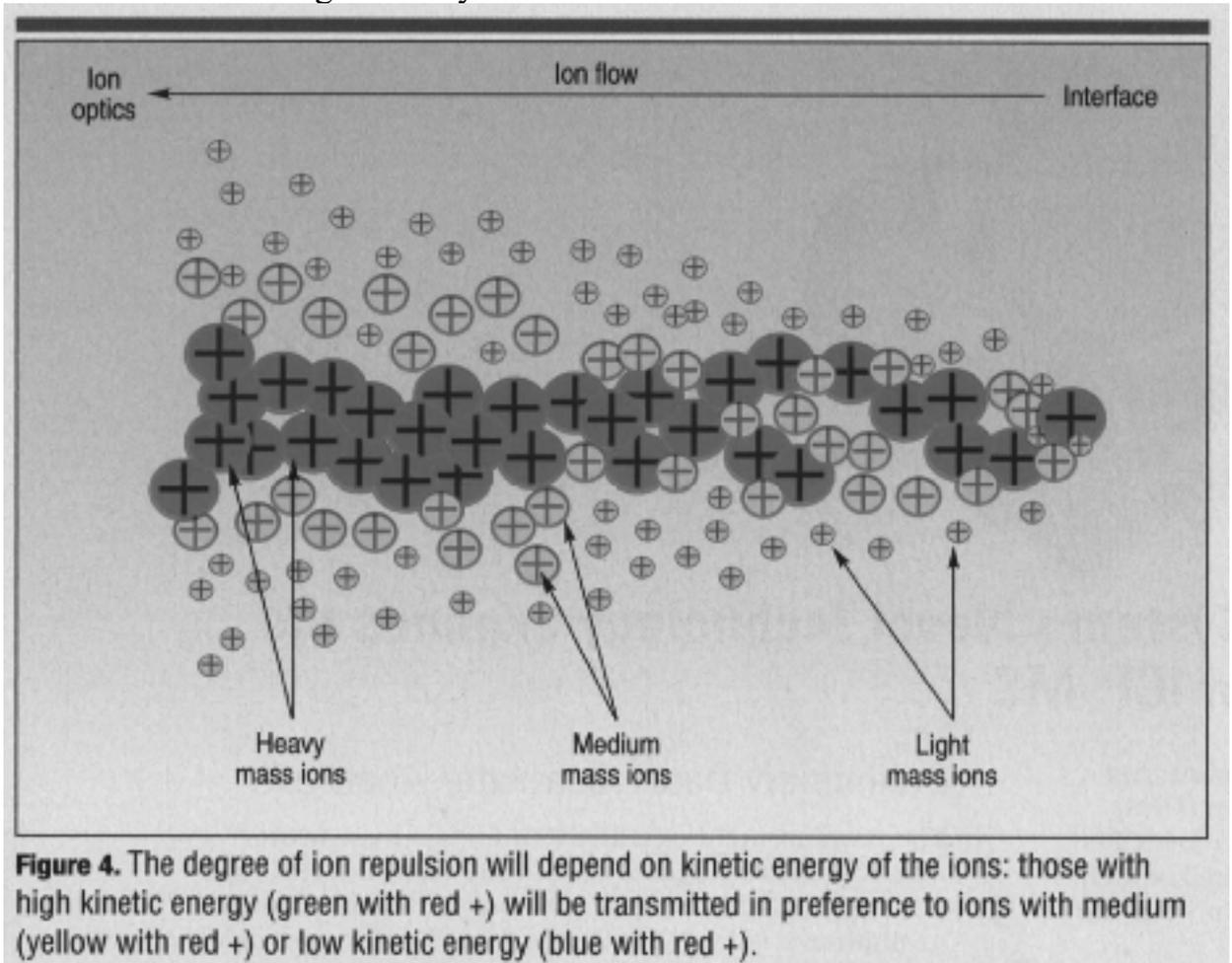
77), NaAr, MgAr⁺ and many other bizarre, non-intuitive species. Note that minor isotope interferences also exist: e.g. ³⁶Ar¹⁴N⁺ and ⁴⁰Ar¹⁸O⁺). Nitric acid is often considered the “preferred” ICPMS acid because it has the fewest polyatomic interferences (but it is obviously not desirable for ⁵⁴Fe/⁵⁶Fe isotope measurements because of ⁴⁰Ar¹⁴N⁺)

4. Molecular interferences can be minimized using a hexapole collision cell (or quadrupole or hexapole reaction cells): a hexapole confining cell just downstream of the skimmer cone can allow a “collision gas” to interact with the ion beam at higher pressures “... thus reducing the ion energy spread of the ions as they emerge from the skimmer, and breaking up molecular species before they reach the mass analyzer. As a result, a mass spectrum free from argon interferences is achieved, which in turn allows much lower detection limits for what would otherwise have been ‘difficult’ elements.” (quote from Micromass product literature)
Example: ⁴⁰Ar¹⁶O⁺ is minimized with collisions with Ar gas, and additions of H₂ collision gas can eliminate it entirely when residual ArO⁺ is converted to ArOH⁺)
5. “Abundance sensitivity”: if a very small peak (e.g. ²³⁴U) occurs near a very large peak (e.g. ²³⁵U), the larger peak will “tail” into the larger peak, largely because of ions that are scattered by gas molecules (although some may instead bounce off the walls). This tail will give a false high signal on the smaller peak.
Quadrupole mass spectrometers have very good abundance sensitivity, but magnetic sector mass spectrometers are poorer at high masses. One strategy for minimizing this problem is the “WARP” filter (wide angle retarding potential), which takes the “higher angle, lower-energy” ions out of the ion path.

H. Other interferences in ICPMS

1. Although ionization is high (>90% for many elements), it is not complete and some inter-element ionization interferences can occur.
2. Interface transmission interferences
 - a. In addition to factors that influence ionization, mass-dependent interferences occur via factors influencing the transmission of elements into the ion beam.
 - b. Space-charge effects: the beam of positively charged ions suffers from mutual repulsion. Light elements with less momentum are lost laterally more rapidly than heavier elements; this factor contributes to a generally lower sensitivity for light elements compared to heavy elements, and accounts for several inter-element interferences (e.g., a solution containing high concentrations of uranium depresses the sensitivity for lithium).
 - c. A high concentration of ions in the beam can lead to "space charge effects" (a result of the total positive charge of an bit of space inside of the vacuum system). Most of the ions in the plasma are Ar⁺ ions, which are an inevitable product of an Ar plasma. Mass charge effects lead to the preferential loss of light ions (which can leave the space more rapidly than the heavy ions). This is one reason why the sensitivity of ICPMS is lower for light ions than for

positive ions. - hence high concentrations of U can depress the signal for Li. In addition, if the sample itself contains a high concentration of heavy elements (e.g. U), the light ion sensitivity is even lower than it would be in a solution containing no heavy ions.



source: Beginner's guide to ICPMS, Pt. V, Spectroscopy magazine

- d. These interferences, being dependent on the geometry of the ion beam, can be quite dependent on the specific instrumentation used, and even upon the specific tuning conditions employed (nebulizer flow, position of torch relative to sample cone); interferences reported on one instrumental configuration may not apply to different instruments, or to the same instrument in a different configuration. But in general on modern instruments, most interferences are mass-dependent, an "internal standard" at a nearby mass can correct for most of these interferences.
- I. The bottom line is that ICPMS is not an interference-free method. As with FAAS, GFAAS, and ICP-OES, one must be aware of interferences and how to control them.
1. Minimize polyatomics:
 - a. Minimize acid interferences for elements of interest.
 - b. Use appropriate collision gases if possible

- c. Purify the sample of elements that produce interfering polyatomic interferences.
 - d. Use pure acid blank correction for polyatomics produced by acid.
2. Compensate for ionization and transmission interferences:
- a. Use the internal standard method to minimizing mass-dependent matrix interferences.
 - b. Use standard additions method to correct for “sensitivity” interferences.
 - c. Use the isotope dilution method to avoid all “sensitivity” interferences (and sample recovery issues during processing).

Isotope dilution equation for analysis of an element by spiking natural element ($f_{238\text{U}}=0.993$) with an isotope-enriched spike ^{235}U -enriched spike, then measuring the isotope ratio R:

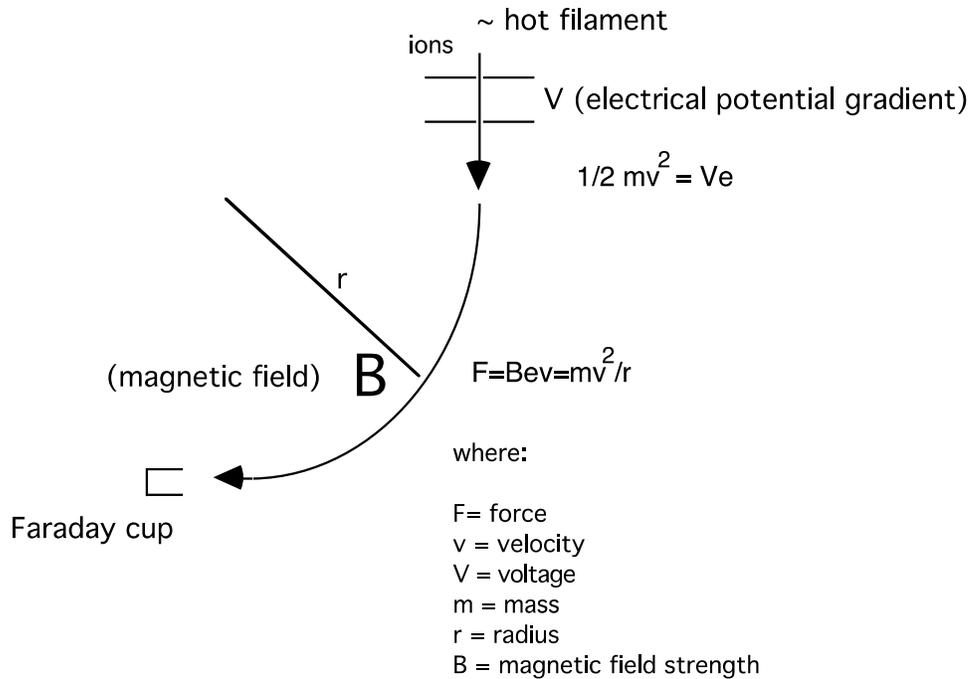
Isotope dilution equation:

$$C_{\text{sample}} = \frac{f_{\text{spike}}}{f_{\text{natural}}} [C_{\text{spike}}] \left(\frac{\text{spike volume}}{\text{sample volume}} \right) \left[\frac{R_{\text{measured}} - R_{\text{spike}}}{R_{\text{natural}} - R_{\text{measured}}} \right]$$

where f is the fraction of the element occurring as the denominator isotope in the ratio measured for the sample or spike, C_{spike} is the concentration of the element in the spiking solution, R_{measured} is the isotope ratio measured in the spiked sample., R_{spike} is the isotope ratio of the spike, and R_{natural} is the isotope ratio of the naturally-occurring element.

IV. Magnetic-sector ICPMS

A. Magnetic sector mass spectrometer:



Hence

$$M/e = 4.824 \times 10^{-5} r^2 B^2 / V$$

where

M = atomic mass units

e = electronic charge (1,2,3,...)

r = radius (centimeters)

V = acceleration potential (volts)

B = magnetic field strength (gauss)

- B. One solution to the isobaric interference problem is to employ a magnetic-sector mass spectrometer with higher mass resolving capability ($\Delta m/m > 3000$). A higher vacuum is required, the instrument is more expensive than a quadrupole ($\sim 2-4x$), and magnetic field scans occur more slowly (seconds rather than milliseconds). But magnetic sector instruments can distinguish between species such as $^{32}\text{S}^{16}\text{O}^+$, $^{31}\text{P}^{16}\text{O}^{1}\text{H}^+$, and $^{48}\text{Ti}^+$, or $^{40}\text{Ar}^{16}\text{O}^+$ (55.957 amu) and $^{56}\text{Fe}^+$ (55.935 amu), for example.
- C. In order to improve mass scanning speeds, these instruments sometimes employ electrostatic scanning whereby the accelerating voltage of the mass spectrometer is varied instead of the magnetic field strength. Although this method can scan as fast as the quadrupole, it has a more limited AMU range ($\pm 30\%$ of the central mass).

- D. These instruments also have lower counter background count rates (~ 0.1 cps compared to $\sim 3-30$ for a quadrupole instrument), resulting in improved detection limits.
- E. The energy spread of the ions coming in from the plasma is relatively large, but the magnetic sector mass spectrometer requires a narrow spread. Most designs use an electrostatic focusing sector to pre-select a narrower energy range (this results in some loss of transmission). One other design uses a “hexapole collision cell” to collide the incoming ions with thermal gas to reduce the energy spread (this design has a very high transmission).
- F. Although these instruments deliver square-topped peaks (images of the slit), fluctuations in the plasma prevent this method from having much better isotope ratio performance when a single detector is used because the ion current fluctuates during the time over which the scan is performed.
- G. A more expensive ($\sim \$750K$) variant overcomes the plasma fluctuation problem by using multiple-collectors with a magnetic-sector ICPMS. This device collects several m/e levels simultaneously. Because the ratio of ions is determined instantaneously, plasma fluctuations do not affect these isotope ratios. This instrument is almost as stable as a TIMS mass spectrometer, but has the particular advantage of high ionization efficiency for almost all elements and very rapid isotope ratio determination (minutes compared to hours).
- H. Isotope mass fractionation in ICPMS, and correction strategies
1. During the step from plasma formation to ion beam detection, rather large isotope mass fractionations occur in ICPMS with discrimination in favor of heavier isotopes. The effect is largest at low masses and smallest at high masses and depends on the instrument, analytical conditions, and sample matrix; these fractionations can change relatively quickly even on the same instrument.
 2. Example: on our IsoProbe, mass fractionation is about +5% per amu at mass 55 and about +1% per amu at mass 207.
 3. For some purposes that don't require precision to better than 10%, these fractionations are often ignored and assumed to be taken care of by similar fractionations in the elemental standards. However, for the most precise analyses using isotope dilution or natural stable isotope ratio determinations, it is necessary to compensate for this mass fractionation before the isotope ratio is computed. For very high precision data, these mass fractionations can vary from sample to sample.
 4. These fractionations are typically calculated using either “natural” isotope ratios (where the natural isotope ratio variations are typically small compared to the desired precision; this approach is typically used in isotope dilution measurements where the spiked ratio variations are large compared to natural isotope variations) or by using a standard of known isotopic composition. For the highest accuracy, an “internal” standard should be used. For example thallium (masses 203 and 205) is often added to

Pb isotope samples (masses 204, 206, 207, 208). Mass fractionation is typically interpolated/extrapolated using the “exponential” formula:

$$R_{true} = R_{measured} \left(\frac{M_2}{M_1} \right)^\beta$$

where

R_{true} is the known true isotope ratio of isotopes with masses M_1 and M_2 ,
 $R_{measured}$ is their isotope ratio signal measured by the mass spectrometer, and
 β is a constant determined from a known isotope ratio in the same sample

IV. Alternative sample introduction techniques

- A. Because the conventional concentric glass nebulizer/spray chamber throws away 99% of the sample, higher sensitivity can be achieved by alternative sample introduction techniques, which may also have other advantages.
- B. Micro Concentric Nebulizer (MCN): similar in principle to the concentric nebulizer, but scaled down dimensionally so the sample draw rate is much lower (~50 μ l per minute compared to 1 ml per minute) and the efficiency of conversion to fine droplets is higher. The signal intensity for this device is similar to the conventional nebulizer, but because the sample size is much smaller, the mass detection limits (absolute mass required for detection) are much lower. Disadvantage: it is easy to clog the nebulizer with fine particles.
- C. Desolvators: because the plasma is partially cooled by the water droplets, and because the water contributes molecular interferences, it is advantageous to desolvate the mist before introducing it into the plasma. The conventional spray chamber achieves this to some extent, but alternative desolvators are more effective: infrared heating and flow past a water-permeable membrane. These devices can result in order-of-magnitude higher signals. Disadvantage: not always as stable a signal, and more difficulty with inter-sample carryover.
- D. Electrothermal Vaporizers (ETV): essentially, a graphite furnace used as the source for the ICPMS. It has the advantages of complete desolvation, small sample size, efficient sample transport, and concentration of the signal into a few seconds duration (getting signals above noise levels) – hence it has excellent detection limits, perhaps unsurpassed. Disadvantages: slow, less precise, and requires more knowledge of sample preparation and temperature programming.

- E. Laser ablation: a powerful laser can be focused onto a 10-100 μm spot and pulsed to ablate a small crater; the ejecta can be caught up into the Ar flow and introduced into the ICPMS. This has the advantages of analyzing solid samples without dissolution, a capability for determining spatial heterogeneity, and a dry plasma (hence excellent detection limits and relative freedom from solvent-induced molecular interferences). Disadvantage: more difficult to calibrate, as the interaction of the laser beam and the sample depends very strongly on the composition of the sample and its geometrical characteristics.
- F. Solid slurry: a slurry of finely divided particles can be introduced into the plasma. If the particles are small enough, they will decompose in the plasma. This method has the advantage of not requiring dissolution of solid samples. Disadvantages: particles have to be very small; more matrix interferences; more difficult to standardize.

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