I. Overview of ICPMS technology

plasma

ion optics

mass analyzer

detector

high temperature ionizes atoms

interface: atm. pressure-> high vacuum creates ion beam in vacuum

shapes beam, selects or modifies ion energy

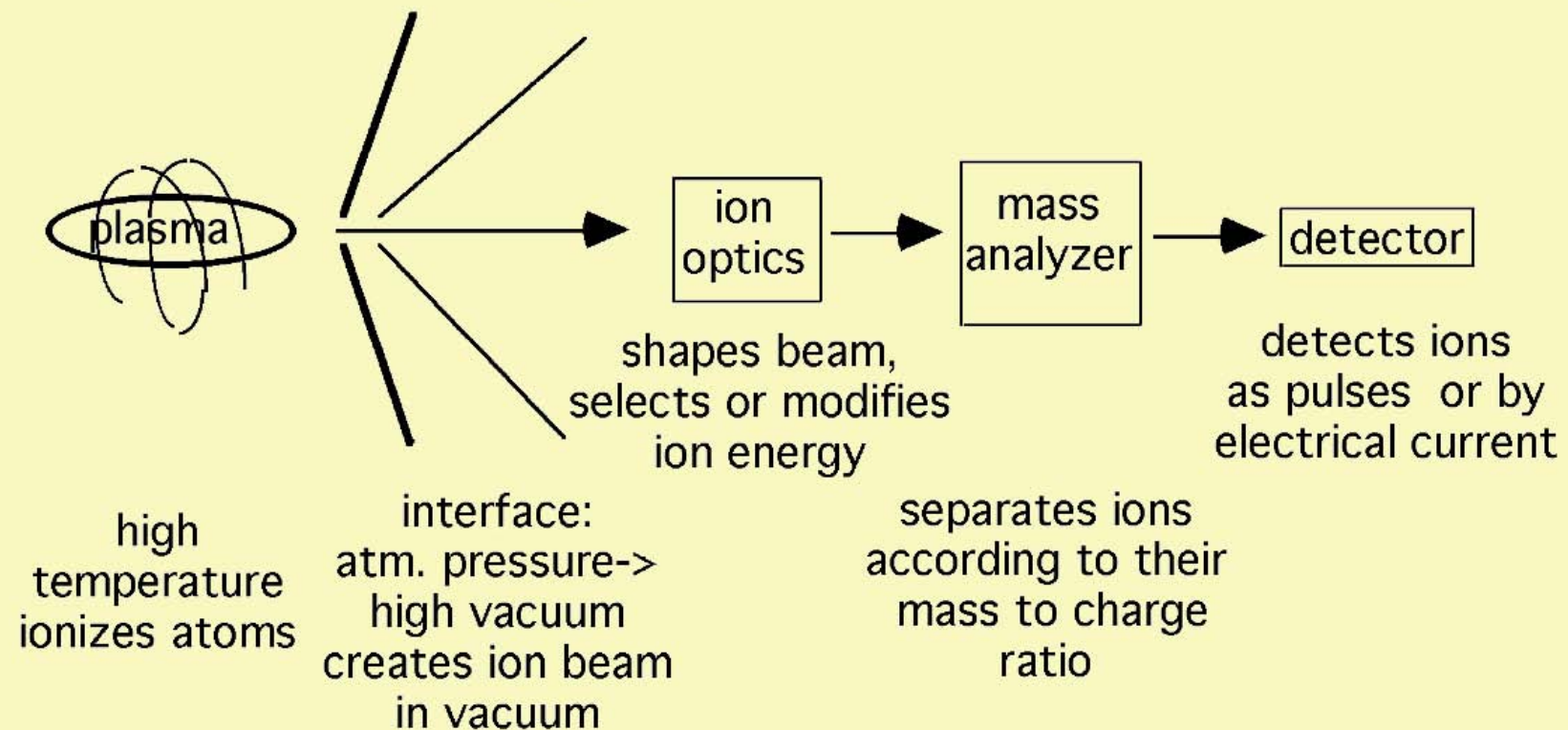separates ions according to their mass to charge ratio

detects ions as pulses or by electrical current

Isobaric interferences in ICPMS

1.At the highest sensitivity, any ion having a m/e value within 0.1 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 high-resolution on a magnetic sector instrument, you can resolve some interferences (e.g. $^{40}Ar^{16}O^+$ from $^{56}Fe^+$)

2. In addition to elements in the sample, elements in the solvent (often a mineral acid such as HNO_3, HCl, H_2SO_4, H_3PO_4) and plasma gas (Ar with impurities C, N, O, Ne, Kr, Xe,...) can interfere.

Isobaric interferences in ICPMS

3. The elements in the sample (including H and O) and plasma gas (Ar and its impurities) can combine to form interfering polyatomic molecular species which form when the ion beam is cooling in the vacuum interface, e.g.:

Ar_2^+ (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. $^{36}Ar^{14}N^+$ and $^{40}Ar^{18}O^+$). Nitric acid is often considered the "preferred" ICPMS acid because it has the fewest polyatomic interferences (but may not desirable for $^{54}Fe/^{56}Fe$ isotope measurements because of $^{40}Ar^{14}N^+$)

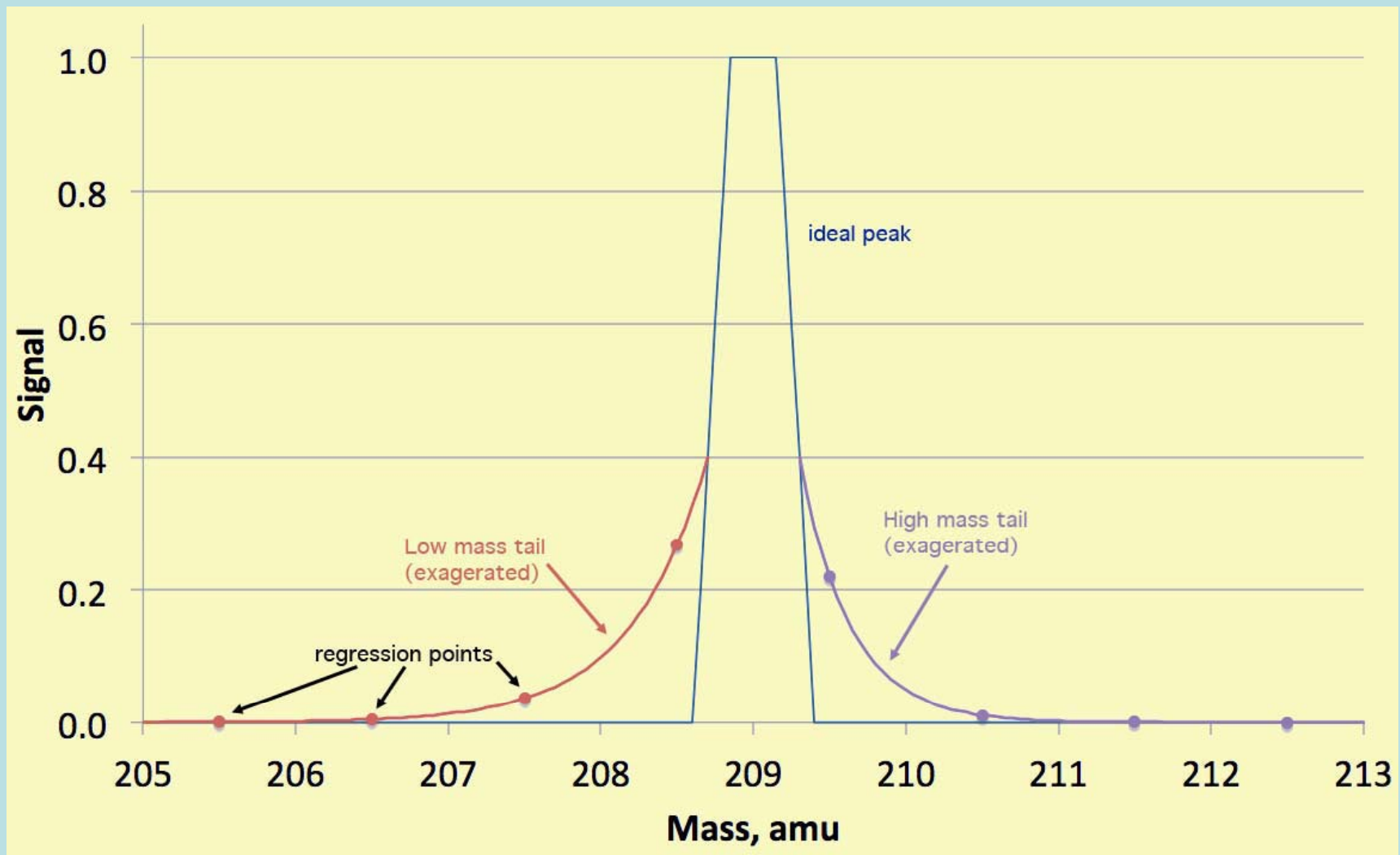# Isobaric interferences in ICPMS

4. Molecular interferences can be minimized using a collision cell: 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: $^{40}Ar^{16}O^+$ is minimized with collisions with Ar gas, and additions of H_2 collision gas can eliminate it entirely when residual ArO^+ is converted to Ar and $ArOH^+$)

Tailing interferences in ICPMS

"Abundance sensitivity": if a very small peak (e.g. ^{234}U) occurs near a very large peak (e.g. ^{235}U), the larger peak will "tail" into the larger peak, because of ions that are scattered by residual gas molecules in the vacuum (some others may bounce off the walls). This tail will give a false high signal on the smaller peak. 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, but this solution cannot be employed on systems that do not have a narrow energy spread.

Tailing interferences in ICPMS

Tailing interferences can be evaluated by using a mono-isotopic element near the mass of interest, e.g. ^{209}Bi can be used to estimate tailing for Pb:

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 for some elements in some matrices (e.g., Cd, Zn).

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).

Other interferences in ICPMS

c. A high concentration of ions in the beam can lead to "space charge effects" (a result of the total positive charge of the ion beam inside of the vacuum system). Most of the ions in the plasma are Ar^+ ions, which are an inevitable product of an Ar plasma. Space charge leads to the preferential loss of light ions (which are repelled from the beam more rapidly than the heavy ions). This is one reason why the sensitivity of ICPMS is lower for light ions than for positive ions. High concentrations of U can depress the signal for Li, but high concentrations of Li do not affect U very much.

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.

Mimimizing interferences in ICPMS

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 available on your instrument

    c. Purify the sample of elements that produce interfering polyatomic interferences.

    d. Use pure acid blank correction for polyatomics produced by acid, water, and plasma gases.

Mimimizing interferences in ICPMS

2. Compensate for ionization and transmission interferences:

    a. Use the internal standard method to minimize
       mass-dependent matrix interferences (e.g. addition
       of known amount of indium). Works best if added
       element is near the same mass as the analyte element.

    b. Use standard additions method for analyte element
       to correct for sensitivity interferences.

    c. Use the isotope dilution method to avoid all
       sensitivity interferences and sample recovery
       issues during processing.

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