Trace element analysis of geological materials by ICP-MS I

DSP analytical geochemistry

C9067

Markéta Holá, MU Brno

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Outline

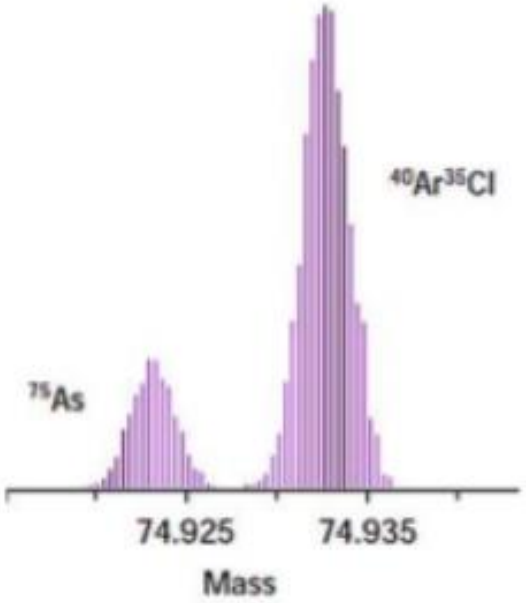
1. Mass spectrometry. General introduction and history.
2. Ion sources for mass spectrometry. Inductively coupled plasma.
3. Interface. Ion optics. Mass discrimination. Vacuum system.
4. Spectral interferences. Resolution, ion resolution calculations.
5. Mass analyzers. Elimination of spectral interferences.
6. Non-spectral interference.
7. Detectors, expression of results.
8. Introduction of samples into plasma.
9. Laser ablation for ICP-MS.
10. Excursion in the laboratory.

Interferences

ICP-MS

- **Spectral**

mass overlap of the interfering particle and the measured isotope (same m/z - indistinguishable from each other)



- **Non-spectral**

influencing the signal intensity of the analyte by the presence of various substances in the sample matrix

Non-spectral interferences

matrix effect

- **Matrix of sample solutions** to be analyzed
  - Total content of dissolved solids **< 1 – 2 g/l (< 0.2 %)**
  - Acid concentration < 10 % (tipically 2-5 %)
- **‘Heavier’ matrices**:
  - **Irreversible effects** (Clogging torch, sampling cone aperture, …)
  - **Reversible effects** (Very pronounced matrix effects or non-spectral interferences
    =Matrix-induced signal suppression or enhancement
  - **Dilution required**

Non-spectral interferences

matrix effect

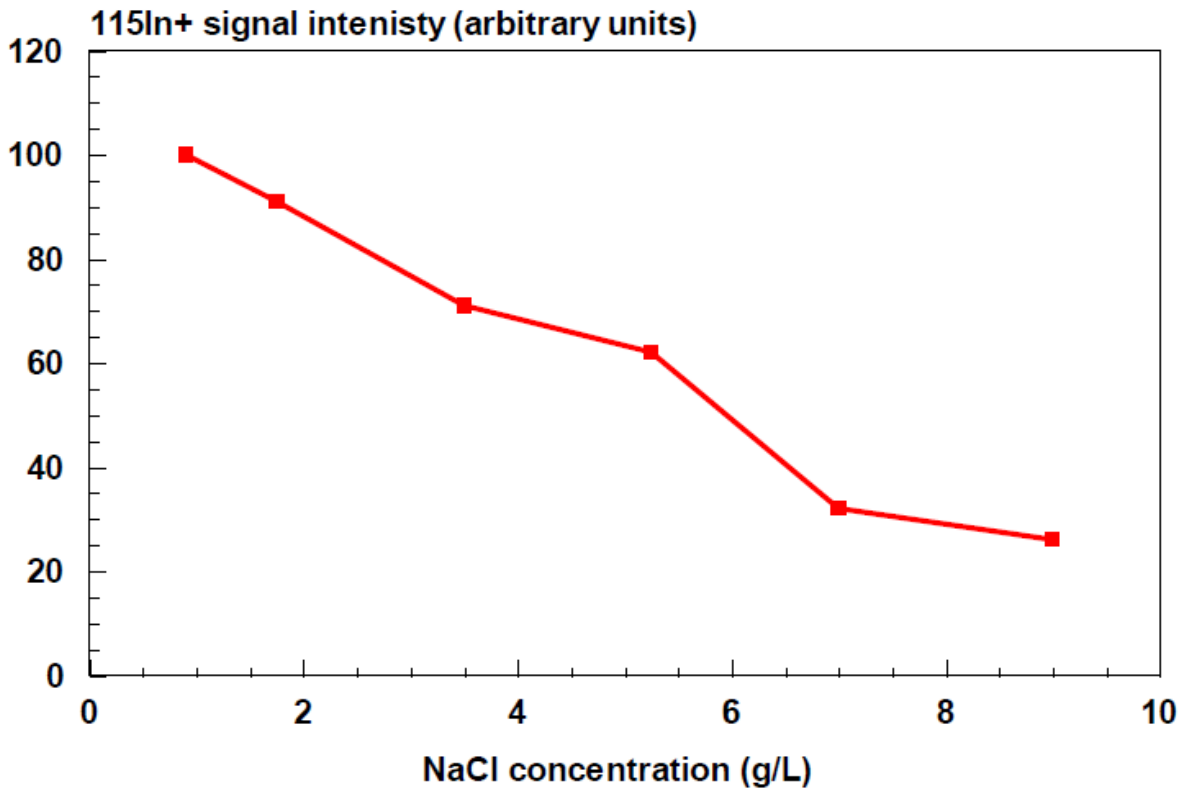
- **Physical effects** - Difference in viscosity between sample & standard
  - difference in nebulization efficiency
  - difference in droplet size distribution
- **Shift in ionization equilibrium**
- **Ambipolar diffusion in ICP**
- **Shift of zone of maximum M^+ density**
- **Space charge effects during ion extraction**
- Specific effects

Non-spectral interferences

matrix effect

Physical effects

- Matrix-induced signal suppression or enhancement



Non-spectral interferences

matrix effect

Shift in ionization equilibrium

- Ionization equilibrium in ICP

$$M \rightleftharpoons M^+ + e^-$$

addition of easily ionizable matrix element (e.g., Na)

electron density ↑

- ionization constant

$$K_M = \frac{n_i \cdot n_e}{n_a}$$

- ionization efficiency

$$\alpha = \frac{n_i}{n_i + n_a} = \frac{K_M}{K_M + n_e}$$

K_M: constant

n_e: constant

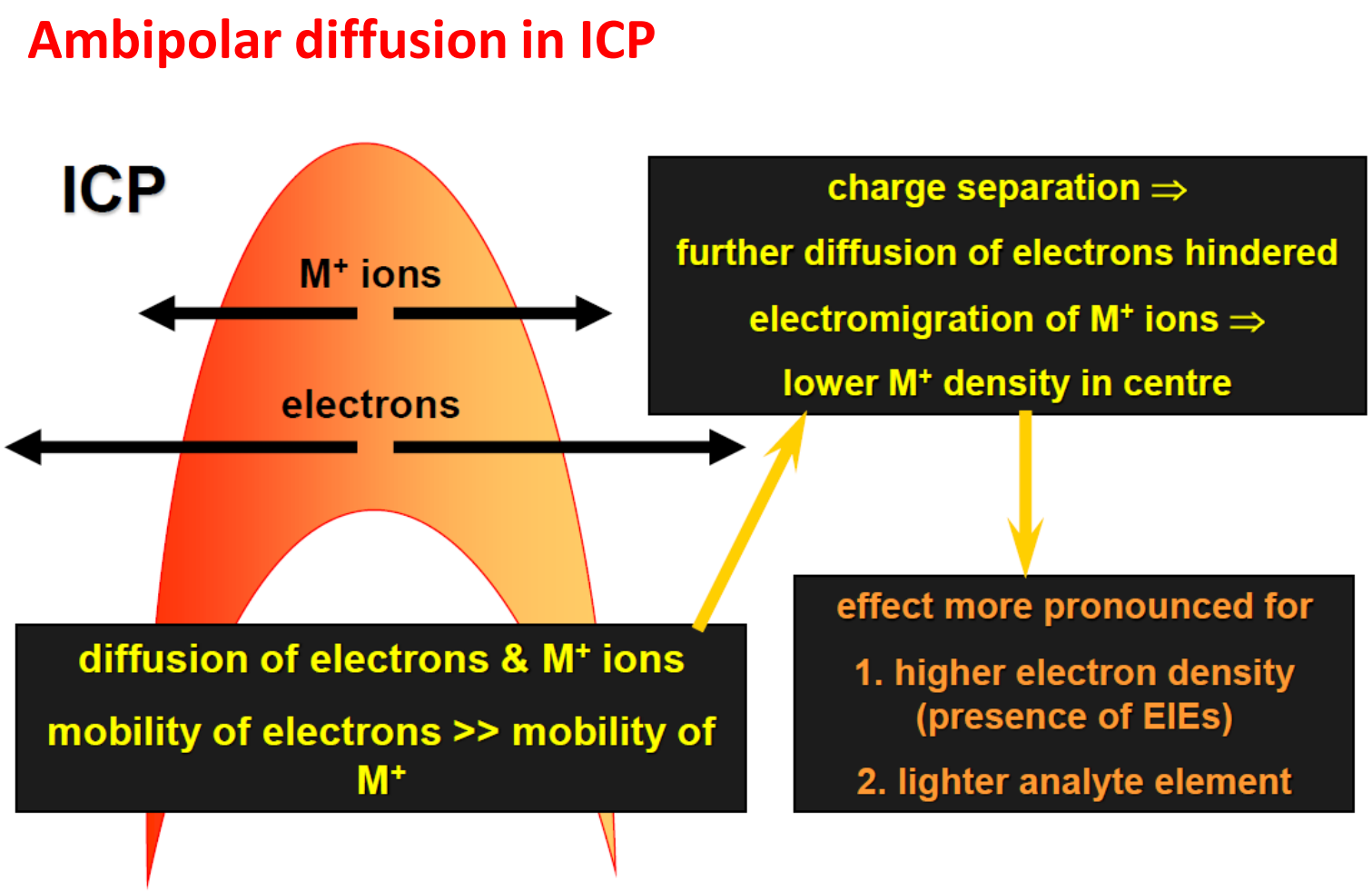
α → decreased

K_M → increased

suppression most pronounced for high IP analyte elements

Non-spectral interferences

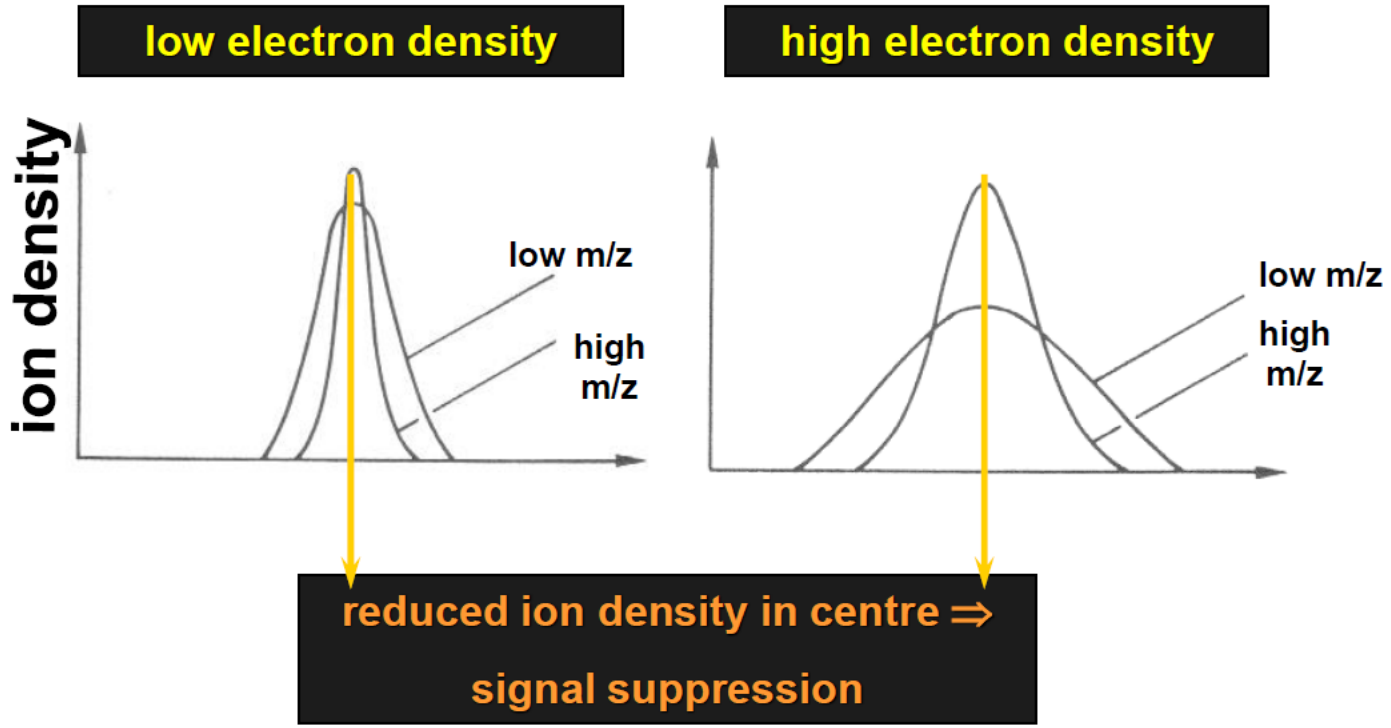
matrix effect



Non-spectral interferences

matrix effect

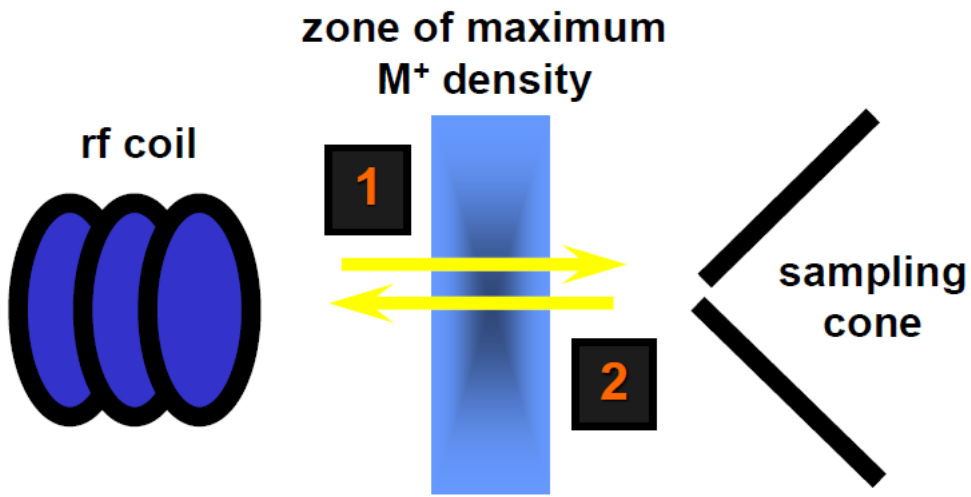
Ambipolar diffusion in ICP



Non-spectral interferences

matrix effect

Shift of zone of maximum ion density



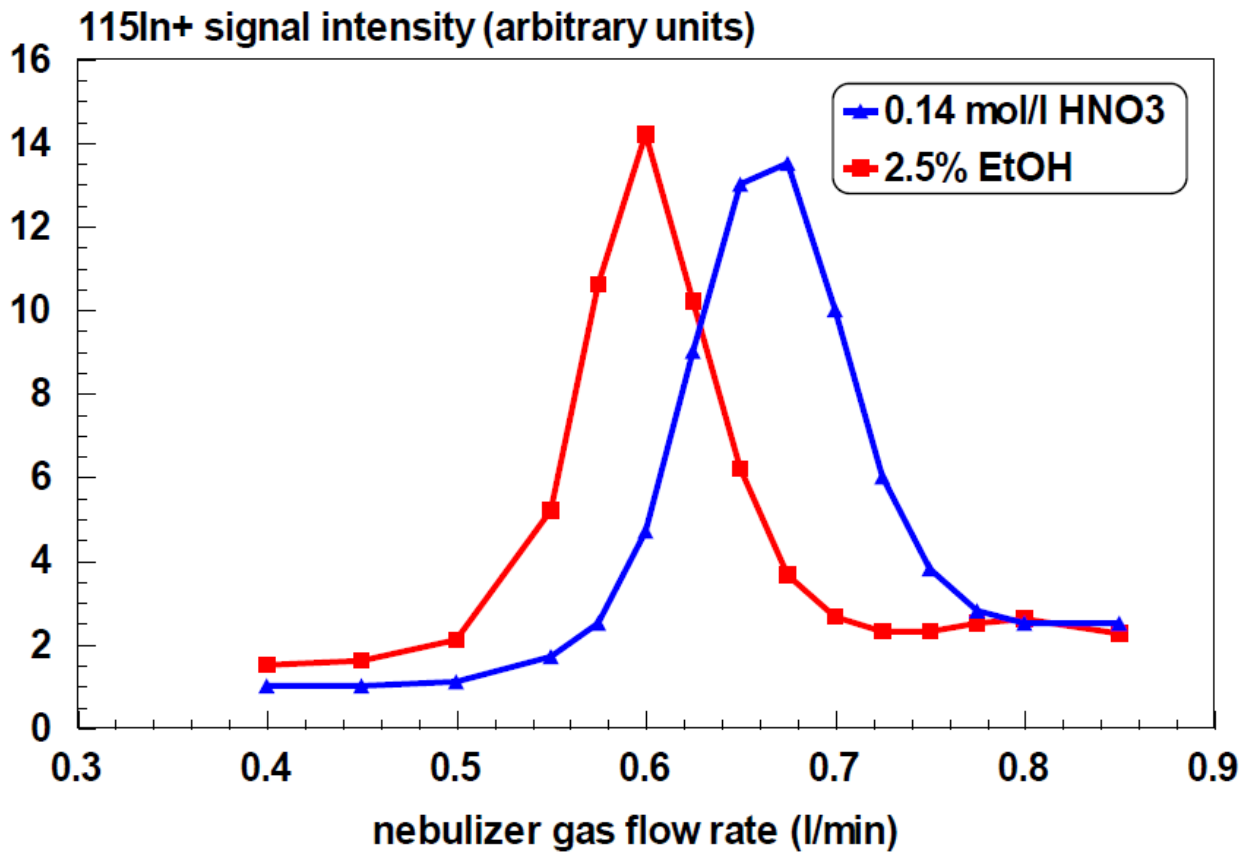
1. Lower temperature ⇒ ionization requires longer residence time in ICP ⇒ M^+ zone moved downstream

2. Higher temperature ⇒ ionization after shorter residence time in ICP ⇒ M^+ zone moved upstream

Non-spectral interferences

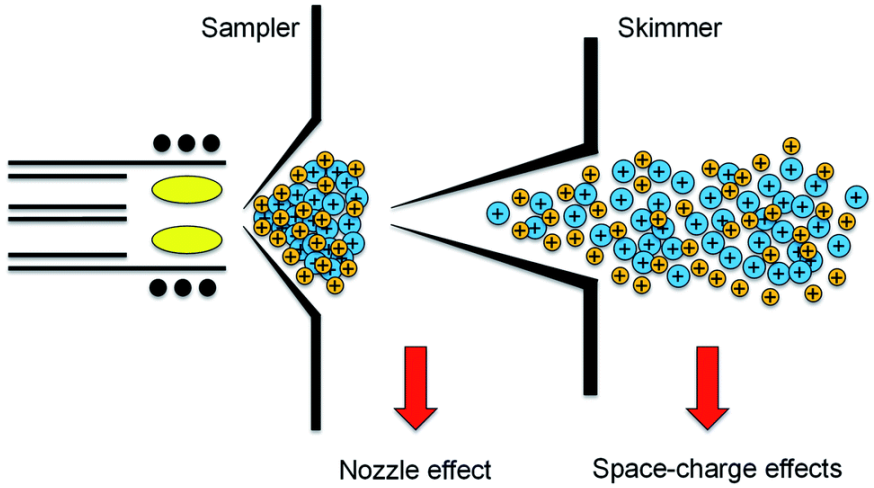
matrix effect

Shift of zone of maximum ion density



MASS DISCRIMINATION

- The phenomenon of non-stoichiometric transition of ions through the mass spectrometer depending on their mass
- **Origins in ICP-MS**:
  - plasma nozzle effect
  - space charge effects in the interface during supersonic expansion of ions through the sampler cone
  - Coulombic repulsion
- **Results in ICP-MS**: measured isotope ratio shows significant bias to the true value
- **Numerical Correction needed**:
  - mass bias drifts with time (**time and matrix dependent**)
  - Instrumental Isotope Fractionation (IIF)



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MASS BIAS CORRECTION

- specific isotope amount ratio is used to **calibrate** the amount ratio of another pair of isotopes (same or different element) - **SSB (Sample-standard bracketing) correction**
- **mass bias**: time-dependent, mass-dependent

Correction factor:

linear correction law $K_{i/j} = 1 + f(t)(m_i - m_j)$

Russell's law $K_{i/j} = (\frac{m_i}{m_j})^{f(t)}$

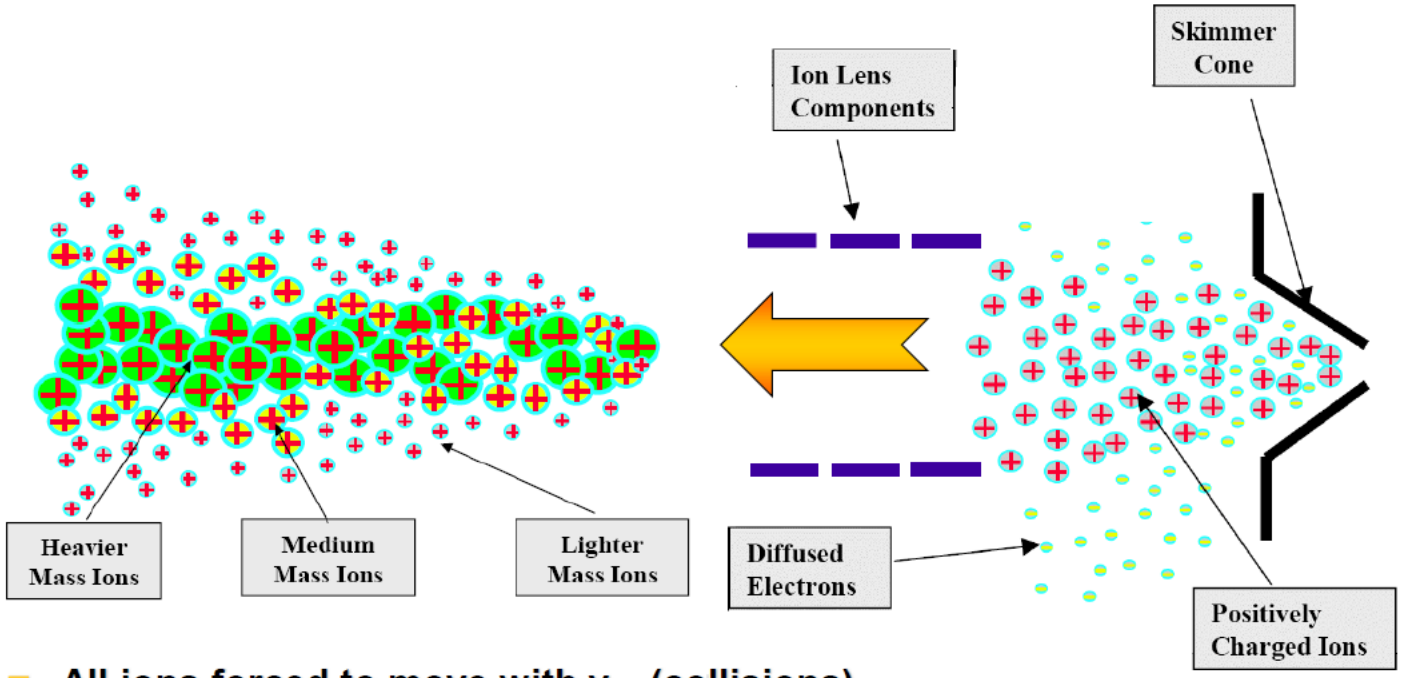
exponential law $\ln K_{i/j} = f(t)(m_i^n - m_j^n)$

- **principle**: calibrator with known isotope amount ratio is measured to obtain the *f(t)* value as a difference between known and measured value; this *f(t)* value is then used to calculate the correction factor $K_{i/j}$
- **Matrix effect:** target element needs to be isolated – separation process

Non-spectral interferences

matrix effect

Space charge effects during ion extraction



- All ions forced to move with v_{Ar} (collisions)
  - $E_{kin} = ½ mv^2$ and hence, $f(m_{ion})$
- Electrostatic repulsion between positively charged ions
  - Defocusing of ion beam
  - Lighter ions preferentially lost

Non-spectral interferences

matrix effect

Elimination of matrix effect:

- **Trace / matrix separation**
  - (Chromatographic) separation technique
    Labor-intensive & time-consuming
    Increased risk of contamination & analyte losses
  - Alternative sample introduction technique
    e.g., ETV, hydride generation
- **Dilution**
  - Not $c_{analyte}/c_{matrix}$, but c_{matrix} is determining factor
  - Deterioration of LODs
- **Use of internal standard**
- **Appropriate calibration techniques**
  - Single standard addition
  - Isotope dilution

Non-spectral interferences

matrix effect

Use of internal standard:

- **Element** (same concentration) **added to sample, standard, blank**
- Assumption - Undergoes same suppression / enhancement as analyte
- Selection - Most important criterion: **close agreement in m/z**
- Further conditions

  Not present in sample

  No precipitation, no volatilization

  No spectral overlap
- **All calculations with $I_{analyte}$ / $I_{internal\ standard}$**
- Additional advantage: improved precision - Correction for signal drift & instrument instability

ICP-Q-MS Users Guide

Sample Collection and Preparation

No Particles:

Samples for solution mode ICP-Q-MS should be particulate free in order to prevent clogging of sample tubing and the nebulizer capillaries (particularly for concentric and micro-concentric types).

Samples containing solids (even nanoparticles) will not ionize the same way as liquid samples, and thus can negatively affect quantitative analysis. Particles may be removed by filtration or by centrifugation and decanting.

ICP-Q-MS Users Guide

Sample Collection and Preparation

Dilute Samples in 1-2 % Nitric Acid:

Sample solutions should ideally share a matrix similar to calibration standards. Commercially available single and multielement standards often have matrices comprised of 1-5% nitric acid.

Acidification prevents dissolved species from readily sorbing onto tubing and container walls. Nitric acid is preferred because it generates fewer polyatomic interferences compared to other acids.

ICP-Q-MS Users Guide

Sample Collection and Preparation

Dilute Samples to <<< 0.2 wt% (2000 ppm; preferably ≤200 ppm) Total Dissolved Solids:

It is important to limit total dissolved sample contents in order to minimize matrix effects that can affect the consistency of ionization in the plasma as well as focusing and collimation of the ion beam beyond the interface region of the ICP-Q-MS.

Dilution is also important to ensure that measurement conditions remain consistent throughout the analytical session. Analysis of high TDS samples can rapidly deposit coatings onto sampler and skimmer cones that change orifice shapes and flow dynamics. Such deposits can also constitute a contamination source if partially ionized during subsequent analyses.

Example: salinity of seewater 3.5 % (35 000 ppm). Dilution 175x to obtain 200 ppm. Will trace elements be detectable?

ICP-Q-MS Users Guide

Sample Collection and Preparation

Plan Quality Control in Advance:

Quality control statistics typically derive from analyses of method blanks, matrix spikes, and certified reference materials of known concentration. Method (or procedural) blanks, sample processed identically to real samples except that no sample is actually added, provide a measure of all processing-related contamination (airborne, reagents/acids, labware, personal) that could potentially contribute to measured concentrations. Matrix spikes provide a means of evaluating the extent to which quantitative results may suffer as a result of matrix differences between samples and calibrations standards. Quality control standards are often analyzed periodically throughout a run of unknowns. Accuracy and precision obtainable by the data acquisition method can be evaluated from recoveries and standard deviations relative to certified concentrations. Reference standards should be independently sourced from stocks used for calibration standards.