Ion Sources

Some characteristics of ion sources (especially in high precision work):

• It should have high efficiency in generating ions of the element of interest (or a range of elements).

• All of the ions should have the same energy.

• It should produce an ion beam with low divergence.

• The ions should be the same charge (preferably +1 for positive ions or -1 for negative ions) so we separate by mass and not m/q.

• The ion beam should be stable.

• The ion beam should have isotopic ratios the same as the sample.
Thermal Ionization MS

- **Advantages**
  - Extremely Stable
  - Generally less prone to isotopic fractionation effects than other sources
  - Thermalized ions (narrow energy range)

- **Disadvantages**
  - Complicated sample preparation
  - Incomplete isotope (elemental) coverage
    » Inconsistent positive or negative ionization efficiencies across periodic table
Inductively Coupled Plasma MS

**Advantages**
- High sensitivity
- Nearly complete isotope coverage
- Liquid, solid or gas samples
- Short analysis times
- Less “art”

**Disadvantages**
- Isobaric interferences
- Relatively noisy
- Wide ion energy spread
- Inefficient
- Spectral complexity
So what is the ICP?

- What equipment does it require?
- How does it operate?
- What are its features?
- How does it work with MS?
Basic ICP Instrument

Sample Introduction System → ICP → Spectrometric System

Readout System
Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES)
Types of ICP Nebulizers

- Concentric pneumatic
- Cross-flow pneumatic
- Ultrasonic (high sensitivity)
- High-solids (V-groove, Babington, etc.)
- ......
Types of ICP Spray Chambers

- Scott-type
- High-efficiency
- Cyclonic
- Desolvating
- ......
The Inductively Coupled Plasma

- A plasma is a hot, partially ionized gas.
- The ICP is an argon-based, radio frequency plasma.
- The input rf frequency is either 27 or 40 MHz at powers from 1 to 2 kW.
- The plasma is formed and contained in a three tube quartz touch.
- The temperature in the central analyte channel ranges from about 6000 to 8000° K.
- At these temperatures most elements are largely atomized and ionized
The ICP Torch and Plasma
THE STEPS
THE STEPS
ICP torch, nebulizer, spray chamber
Inductively Coupled Plasma (ICP)

- Tail Flame
- YO
- Normal Analytical Zone
- Y +
- $\text{Y}^+$
- $\text{Y}$
- Induction (Load) Coil
- Sample Aerosol
- $\text{e}^- + \text{Ar} \leftrightarrow \text{Ar}^+ + 2\text{e}^-$
Inductively Coupled Plasma (ICP)
Inductively Coupled Plasma - Mass Spectrometry
The image contains a periodic table with detection limit ranges for various elements. The table includes atomic symbols, isotopic abundance, and most abundant isotopes. The table is labeled as "Detection Limit Ranges" with color codes indicating different concentration levels:

- Blue: < 0.1 ppt
- Light green: 0.1-1 ppt
- Yellow: 1-10 ppt
- Orange: 10-100 ppt
- Pink: 0.1-1 ppb
- Purple: 1-10 ppb

The table includes elements from Be to Lu. The periodic table is part of a document related to "Ultratrace Analysis" and mentions ELAN 9000 and ELAN DRC II detection limits.

The bottom of the image contains the text "DRC-e performance typically between DRC II and ELAN 9000."
ICP-MS
Interface
Cones
Supersonic Expansion

Diagram:
- Mach Disk
- Barrel Shock
- Sampling Plate
- Observation Flow

Notations:
- Y_R
- Y_M
- Y_B
- X_M
- X_max
Consequences of Expansion

\[ KE_{Ar} = \frac{5}{2} kT \]

Small ions

Large ions

\[ KE = 0.5 MV^2 \]

So \( KE_{M^+} = kM^+ \)
Plasma Offset (Rectification)

Mass Spectrometer

\[ + \quad e^- \]
Plasma Offset (Rectification)

Mass Spectrometer

Ar$^+$
Ion Energies Depend on Mass

27 MHz - open symbols
40 MHz - closed symbols

“hot” plasma

- “cold” plasma
Ion Currents in ICP-MS
Spectral Characteristics of ICP-MS

- Basic Background Species
  - argon, water, and air.
  - $\text{N}_2^+$, $\text{Ar}^+$, $\text{ArO}^+$, $\text{Ar}_2^+$

- Interelement Spectral Overlaps
  - isobaric overlaps.
  - element oxides and hydroxides.

- Matrix Induced Spectral Overlaps
  - chlorine and sulfur based species.
  - $\text{ClO}^+$, $\text{SO}_2^+$

- Argon - Matrix Related Species
  - $\text{ArNa}^+$, $\text{ArCl}^+$
ICP-MS Background: 5% HCl
ICP-MS
Background: 5% $\text{H}_2\text{SO}_4$
Oxide and Hydroxide Species

- Problems Caused by Oxides
  - spectral interferences.
  - can result in the implementation of inappropriate isobaric corrections.

- Oxides Formed From
  - plasma gases.
  - air entrainment.
  - sample solvent.
  - matrix components of the sample.
  - the sought-for-elements in the sample.
Variables Affecting Oxide Levels

- Oxide Levels Depend On:
  - injector gas flow rate.
  - forward power.
  - sampler - skimmer spacing.
  - sampler orifice size.
  - plasma gas composition.
  - aerosol processing.
  - solvent load.
  - oxygen level.

All these experimental variables can be used, to some extent, to control oxide levels in ICP-MS.
Matrix Induced Signal Changes

A high concentration of a concomitant:
- generally, suppression of the analyte signal is observed.
- the suppression is more serious with heavier matrix elements.
- light analytes are more seriously affected.
- the effects may be minimized by:
  - reducing the nebulizer flow rate.
  - using an internal standard.
  - using dilute solutions.
Matrix Effects in ICP-MS
ICP-MS Options for Isotope Ratios

- **Multi-collector sector-field spectrometer**
  - Offered by Thermo (Neptune), GV, and Nu
  - Isotope-ratio precision ~0.002% rsd (20 ppm)

- **Time-of-flight mass spectrometer**
  - Leco & GBC
  - Isotope-ratio precision ~0.05% rsd analog
  - Isotope-ratio precision ~0.01% rsd counting

- **Array-detector sector field**
  - Not yet commercially available
  - Isotope-ratio precision ~0.007% rsd
Nu Instruments MC-ICP-MS
Leco Renaissance ICP-TOFMS
GBC Optimass ICP-TOFMS