Ion Sources

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

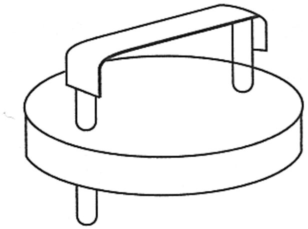
- It should have high efficiency in generating ions of the element of interest (or a range of elements).
- All of the ions should have the same energy.
- It should produce an ion beam with low divergence.
- The ions should be the same charge (preferably +1 for positive ions or -1 for negative ions) so 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.

- The two main types are solid and gas sources
- Both types use heat, photons, electrons, or energetic ions or atoms to ionize the sample
- In the case of solid samples a step of volatilization, atomization or vaporization must occur before or during the ionization process
- For solid samples the most common type of ion source for high precision work is the Thermal Ionization Source or Solid Source
- For gas samples the most common source is the electron bombardment source

Thermal Ionization or Solid Sources

- This type of source uses high temperatures to volatize and ionize elements that can be put into a solid form
- This covers much of the periodic table and strictly only the noble gases could not be run by a solid source. However, many elements (H, C, N, O, S and a few others) are best analyzed isotopically as gases.

- In the most common form of thermal ionization the element of interest (e.g., Sr) is deposited in liquid form (usually in an inorganic acid such as HNO_3) as a dissolved compound of the element onto a filament made of a refractory metal
- Electric current flowing through the filament heats it to high temperature (400 to 2000 C, depending on the element), this causes the volatilization of the element, a small fraction of which are ionized (in our case as + ions).
- Actual filament set-up and geometry:



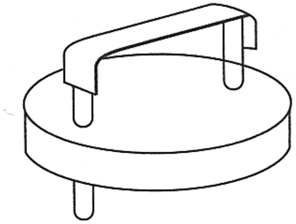
- Typical dimensions for the filament (with a fair amount of variation) are: thickness-0.03 mm, width-1.0 mm and length-5 to 10 mm.

- The sample in liquid form is deposited onto the center of the filament and dried down usually in air but sometimes also in a neutral atmosphere (N_2 or Ar).

- After loading the filament is placed in the source of the mass spectrometer (usually along with many other filaments so that more than one sample can be run in sequence).

- An electric current passed through the filament heats the sample to a high enough temperature to volatize the element of interest off of the filament usually as a monatomic species but also sometimes as a polyatomic species (e.g., Nd as NdO^+).

- As a consequence of the volatilization process some of the resulting vapor is ionized.



- A starting point for understanding the efficiency of this process has usually been the Langmuir Equation (or its slight variant the Langmuir-Saha equation):

$$\frac{N_{+}}{N_{0}} = \exp\left(\frac{W - I}{kT}\right)$$

Where: W is the work function of the filament, filament + matrix or matrix (usually in eV)

I is the ionization potential of the element being analyzed (also in eV)

K is the Boltzman constant (approx. 8.62 x 10^{-5} eV/ K)

T is the temperature in K

N_0 is the number of unionized atoms of the element of interest in the vapor phase above the filament

N_+ is the number of singly charged ions of the element in the vapor phase above the filament

A Long Boring Discussion of the Langmuir Equation

- Langmuir's original equation was developed from measurements of an elemental vapor (generated elsewhere) contacting a clean hot metal surface.
- On a solid source filament volatilization and ionization occur on the same surface
- This surface is a complex mix of the filament, the element of interest and the matrix in which it was loaded.
- The work function of a typical solid source filament can be highly variable.
- In spite of these warnings the Langmuir equation is reasonably good at predicting the N_+/N_0 for a number of elements to within a factor of 10 or so (sometimes better).
- For some elements (for example Sr) the ratio is significantly higher than predicted suggesting that the work function is also higher than expected.

Langmuir Discussion continued

- Langmuir equation is a ratio not an absolute amount.

$$\frac{N_+}{N_0} \propto \exp\left(\frac{W - I}{kT}\right)$$

- Volatilization rates increase with higher temperatures so both N_+ and N_0 will increase at higher temperatures while the ratio N_+/N_0 will go up or down depending on the values of W and I.

- The prediction is that for elements with low I (e.g., Rb), ionization efficiency will go down with increased temperature (again remember that N_+ will go up just not as fast as N_0).

- For elements with high I, increased efficiency is favored by high T. This is balanced by that fact that higher T means higher volatilization rates and therefore decreased sample lifetime.

- The meaning of I can also be questionable in some circumstances (e.g., what is I for NdO).

- There is also some evidence of an isotopic effect on I, the I of ^{87}Sr may differ from the I of ^{86}Sr (the ionization potential of ^{2}D is 0.005eV higher than ^{1}H).

A Long Boring Discussion about the Work Function

- W, the work function, is a measure of the energy needed to remove an electron from the surface of a material (usually a metal) to a short distance from the surface.

- Unlike ionization potential, which is dependent only on the properties of an individual atom, the work function is highly dependent on other properties of the material such as crystal structure and surface characteristics (e.g., composition, grain size and texture.

- High work function means that it is difficult to remove an electron from the metal surface. This explains why a high work function and low ionization potential give high ionization efficiencies.

- Surprisingly, the work function of many metals is approximately ½ the ionization potential but the work function of the surface depends on the matrix.

$$\frac{N_{+}}{N_0} \propto \exp\left(\frac{(W - I)}{kT}\right)$$

Work Function Continued

- Raising the work function is the major way to improve ionization efficiency.

- The oxides of many elements are used to improve ionization efficiency (e.g., Ta_2O_5 for Sr and SiO_2 for Pb).

- Do they raise the work function of the surface, or is there some other effect?

- Metals used as filaments:

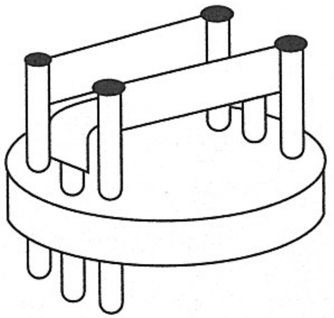
Metal	Work Function	Melting Point
Rhenium (Re)	4.96 eV	3180°C
Tantalum (Ta)	4.25 eV	2996°C
Tungsten (W)	4.55 eV	3407°C

- Sample loaded on filament with solvent (e.g., dilute HNO_3), ionization enhancer (Ta_2O_5, SiO_2 or some other matrix), and a glue (usually dilute H_3PO_4).

- In the mass spectrometer the filament is raised to a high positive voltage, this accelerates the positive ions away from the filament and determines their final energy.

Double and Triple Filaments

- The use of more than one filament is intended to separate the process of volatization from ionization and approach more closely to a Langmuir type of ionization.



- The side filament(s) is run at temperature low enough to provide useful volatization, while the center filament is run at high temperature to generate ions. This is useful for elements with high ionization potentials where the high temperature needed for efficient ionization would result in high volatization rates.

- Multiple filaments are also useful for elements that do not volatilize as monatomic species such as Nd. Nd usually ionizes from the filament as NdO+. Nd can be analyzed as the oxide but this introduces problems with corrections for overlaps. In triple filament mode Nd can be run as Nd+, the NdO+ is reduced to Nd+ at the hot center filament.

Advantages of Thermal Ionization:

1. Many filaments can be prepared and placed in MS source
2. Nearly all elements that can be put in solid form can be analyzed
3. Very high efficiency for some elements
4. All of the sample is subject to ionization
5. Ions are very mono-energetic
6. MS can be operated at high vacuum
7. Accelerating voltage can be high

Disadvantages of Thermal Ionization:

1. Some elements have very low efficiencies
2. Mass dependent evaporation (fractionation)
3. Sample dissipates as it is analyzed
4. Samples can behave erratically due to impurities (which effect ionization efficiency), sample changes during analysis, and the quality of loading.
5. Filament geometry effect beam intensity (Source geometry changes between samples
6. Source must be vented to change samples

Gas Sources

- Dietz-Nier Source

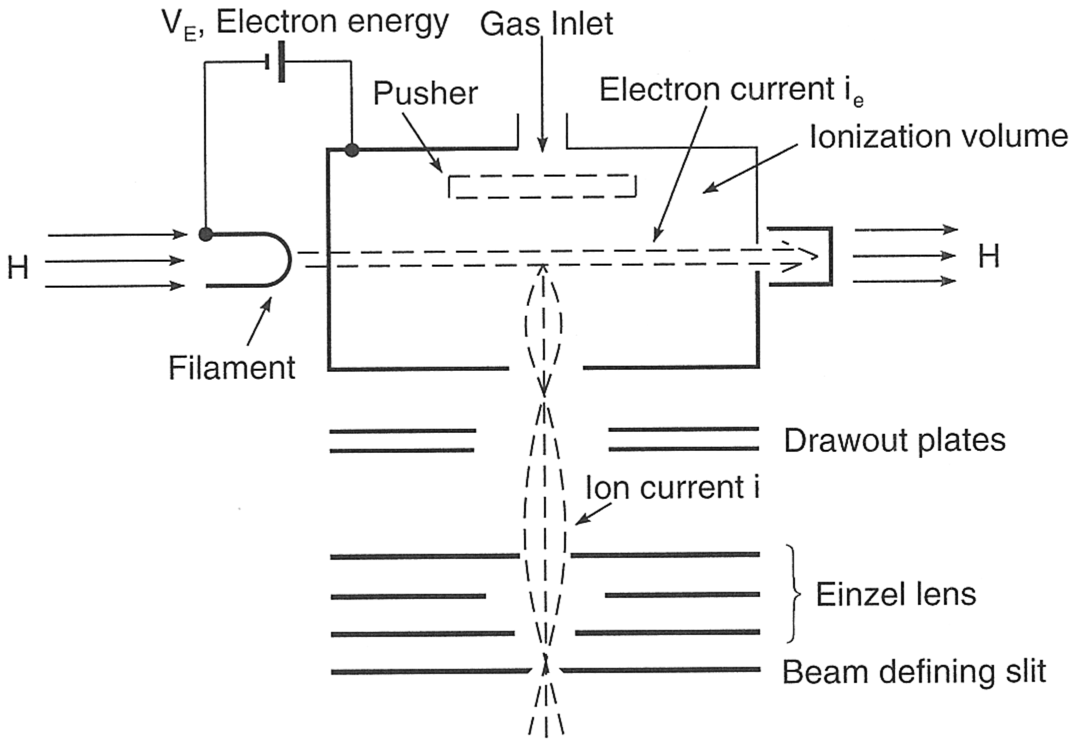


Figure 3.6. Schematics of an electron impact ion source

Advantages of Gas Source:

- High ionization efficiency (in electron beam)
- Works for most gases (and liquids that can be readily volatilized)
- Mono-energetic beam
- Long sample life
- Fixed Source Geometry-efficiency and beam characteristics are constant over long periods of time
- Mass dependent fractionation relatively constant
- Mass Spectrometer rarely needs to be vented

Disadvantages of a Gas Source:

- Total efficiency is low
- Ions can interact with gas in the rest of the spectrometer
- Memory effects
- Ionization not very selective
- Ionization efficiency affected by other gases
- Charges higher than +1 common

Other types of Electron Impact Sources

- Most other kinds of EI sources are designed to improve the efficiency of ionization
- This is usually done by increasing the current of electrons, the size of the ionization region or the path length of the electrons
- Often this involves exposing the ions to the filament or to other processes that raises their temperature
- This results in a wider energy spread than the Nier source

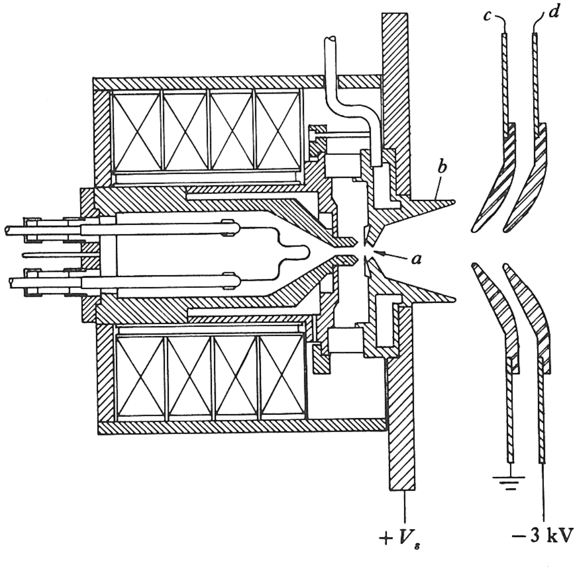
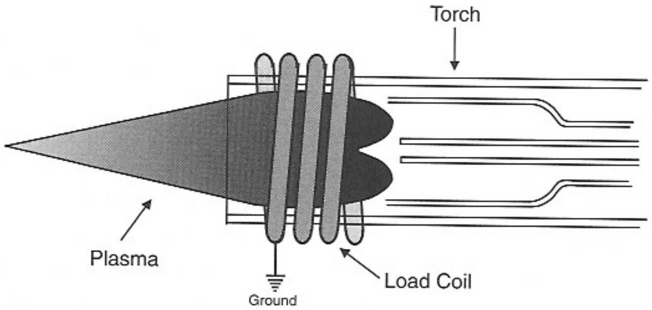
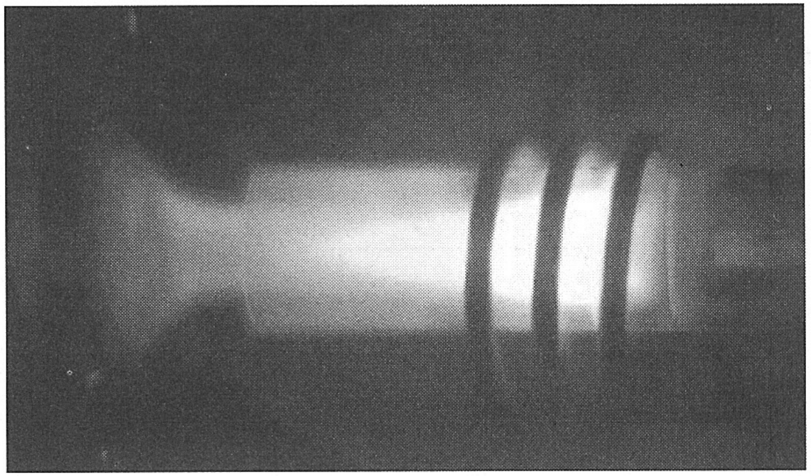


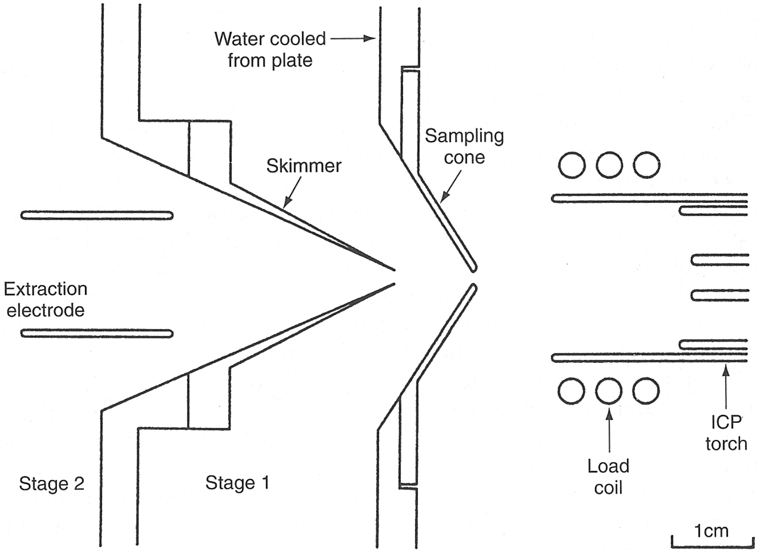
Fig. 3.11. Duoplasmatron ion source and extraction system (after Rose & Galejs, 1965): *a*, anode aperture; *b*, plasma expansion cone; *c*, extractor electrode; *d*, suppression electrode.

Other Kinds of Ion Sources

- Inductively Coupled Plasma (ICP) Source:







ICP

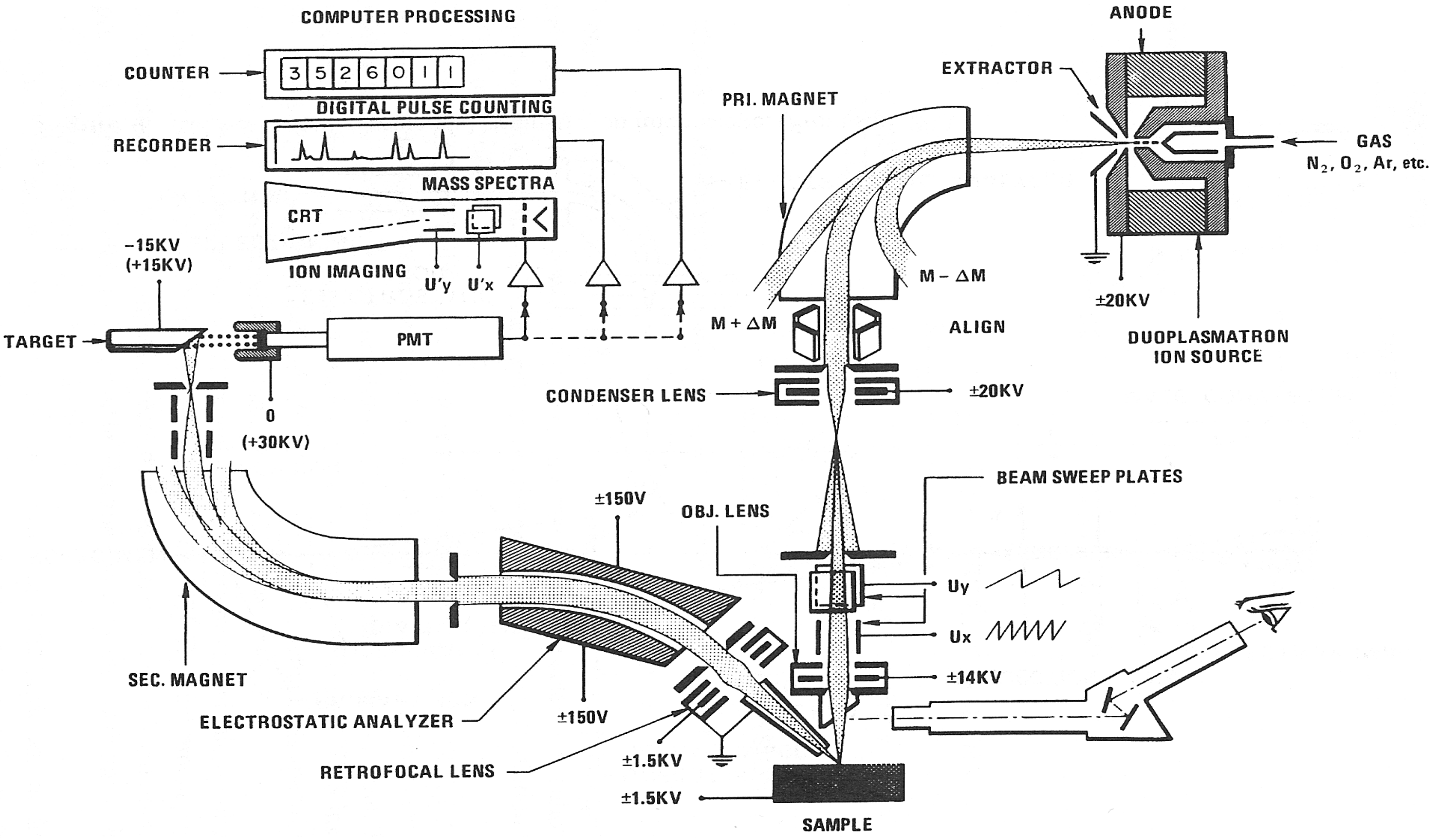
- Advantages:
  - High ionization efficiency
  - Rapid sample throughput
  - Solids, liquids and gases can be analyzed on the same MS
  - In situ analyses possible

- Disadvantages:
  - Some efficiency lost during sample input
  - Wide energy range and transverse velocity (e.g., space charge effects) for the ions—energy filtering and beam shaping increase complexity
  - For magnetic sectors source must start at ground since the plasma is conductive
  - Differential pumping is necessary at the source since it is open to atmosphere
  - Mass overlaps common (e.g., ArO^+ and Fe^+ at mass 56)

- These disadvantages can be gotten around

Other Sources continued

- Secondary Ion Mass Spectrometry (SIMS):



SIMS

- Advantages:
  - In situ analyses possible, little sample preparation
  - High spatial precision
  - Mapping
  - High ionization efficiency

- Disadvantages:
  - Complex (two mass spectrometers)
  - Energy filtering and beam shaping necessary
  - Efficiencies matrix dependent
  - Mass overlaps common

- Again these disadvantages can be gotten around

After the Ions are Generated

- Ions generated on filament or in ionization chamber must be focused and collimated
- Characteristics of this process:
  - High Efficiency
  - Low Divergence angle (< 5^o)
  - Well defined beam shape

- These characteristics are met by passing the ions thru a series of plates with slits, the voltages on the plates can varied allowing control of the paths of the ions.

- Two general design philosophies: short and long

- An example of a short lens

- General characteristics:

  Short focal distance compared to beam width

  Simple and efficient

  However, tends to have wide divergence angle

4a

- An example of a long lens:

- General characteristics:

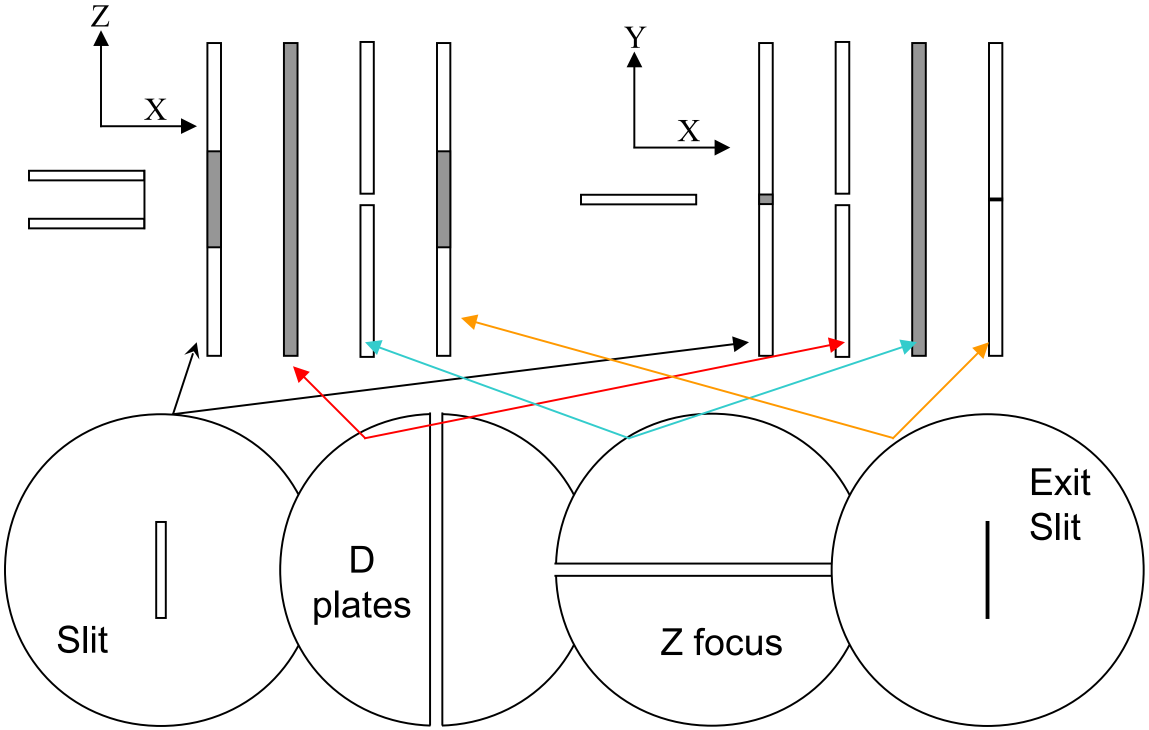
  Long focal length compared to beam width

  Less efficient

  Low divergence angle

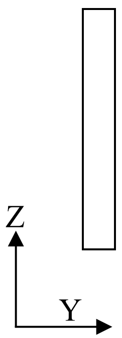
Ion Source View

highly schematic

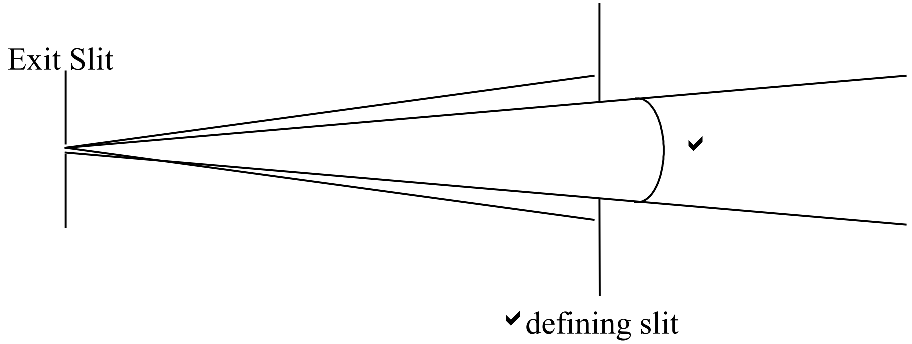


Beam Characteristics

- At the exit slit the beam has a rectangular shape:
- This provides for maximum ion transmission and minimum beam width at the focal plane



- However, various effects cause the divergence angle (✓angle) to be larger
- A defining slit is placed in the flight tube



Fractionation

- Measured isotope ratio is rarely the isotope ratio of the sample
- Variation of measured ratio from true is called fractionation
- Many reasons:

  In source:
    - Gas source-mass dependent ionization efficiency due to energy and momentum conservation
      - Effect of magnetic field
      - Size of effect?
    - Solid source-Volatilization major factor
    - Mass dependent ionization potentials?
    - Lens effects?

- Talk about fractionation or biases in other parts as we get to them