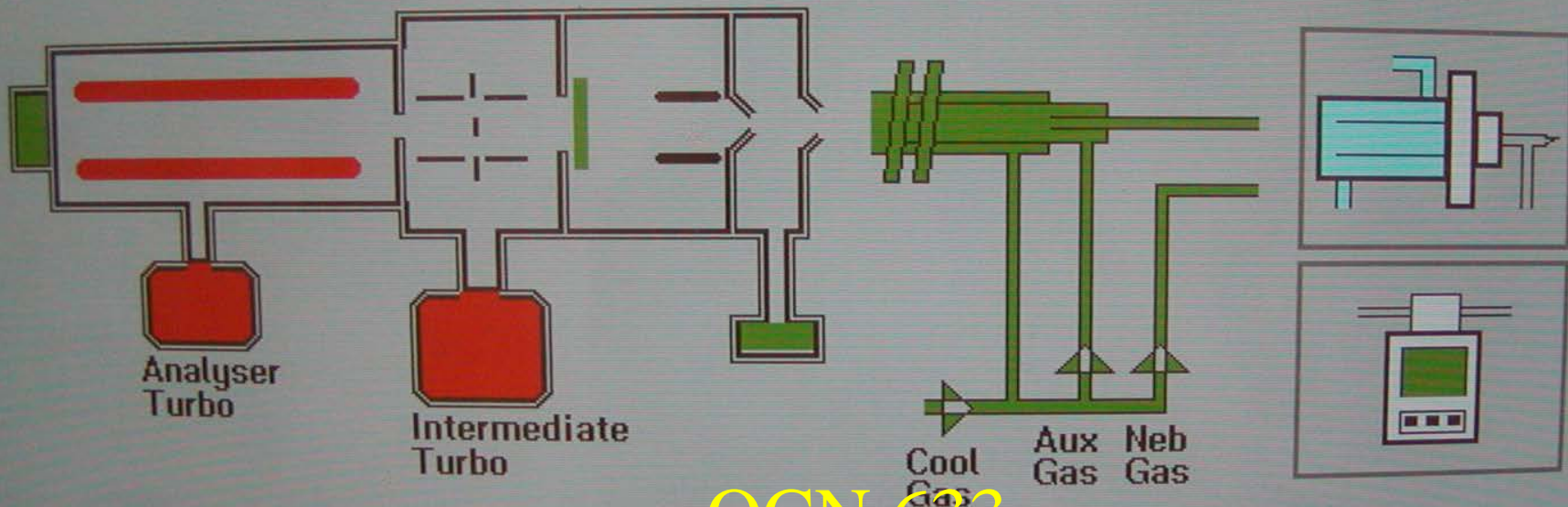


Instrument Control

Spectrometric Methods of Analysis



OCN 633

Fall 2013

Auto-start

Operate

Standby

Pumping

Shutdown

Abort

The instrument is now in pumping mode

Aux Sockets

Interlocks

Calib

Tune

Resets

Engineer

Help

Plasma Emission and Plasma Mass Spectroscopy

- Two fields of elemental analysis undergoing the most study...
- Myriad analytical applications
- Three categories of plasma-based methods (ICP-OES, ICP-AFS, and ICP-MS) have in common the use of a plasma as the means to cause excitation and/or ionization of the analyte.
- A. Montaser, and D.W. Golightly: *Inductively Coupled Plasmas in Analytical Atomic Spectrometry* VCH Publishers

ICP Methods

Approach set of ideal requirements for elemental analysis:

- applicable to nearly all elements
- simultaneous or rapid-sequential multielement determination of (major, minor and trace) elements without change of operating conditions
- no interelement interference effects (**allegedly**)
- applicable to μL or μg size samples
- applicable to solids, liquids, and gases with minimal preparation
- capable of rapid analysis (amenable to process control)
- acceptable precision and accuracy

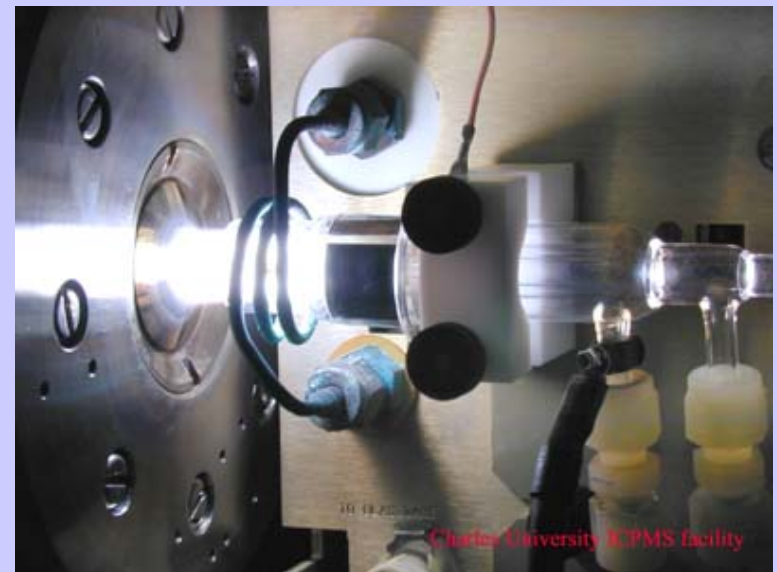
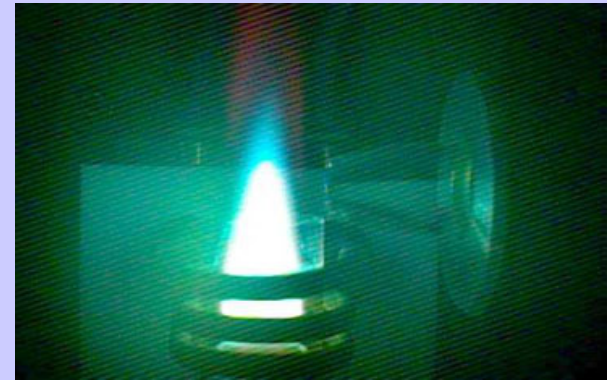
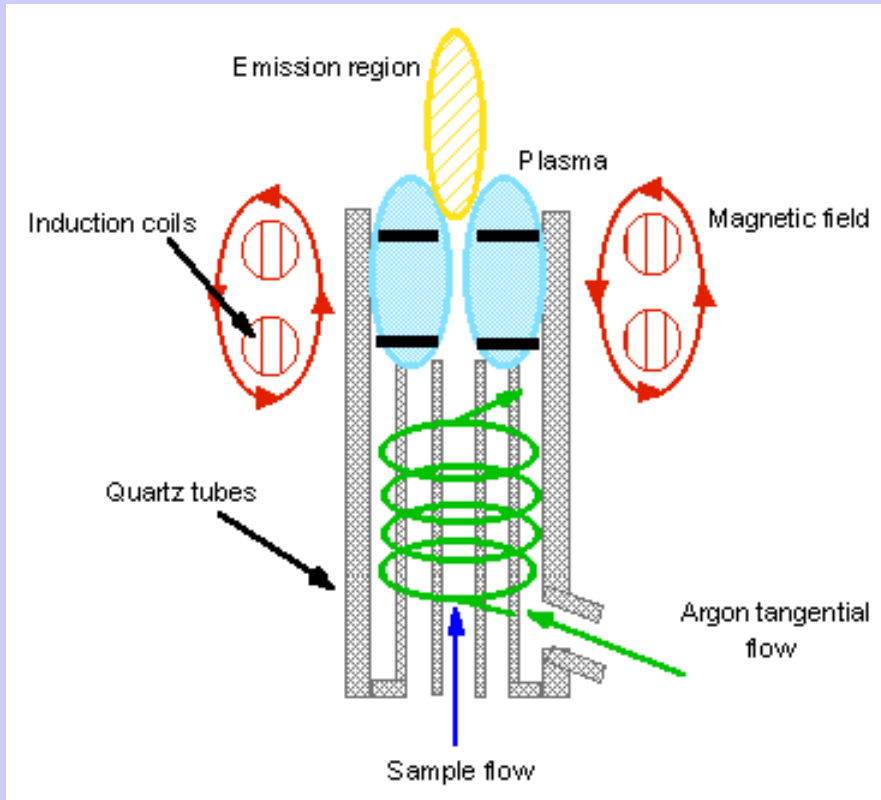
ICP

- Probably the single-most important factor in the popularity of plasma spectrochemistry is the remarkable selectivities and sensitivities achievable on a routine basis
- Unique axial channel of the ICP is mainly responsible for some of its desirable characteristics (relative freedom from matrix interferences, low detection limits, LDR = 4-5, and precision of 1-3% relative)

Inductively Coupled Argon Plasma

- Described as early as 1956 but not commercially developed until the mid 1970's
- Ar flows through open tube concentric with a RF coil, which sets up an oscillating electromagnetic field
- Ionization of Ar is initiated with Tesla discharge (or other appropriate means to introduce a few electrons into torch)
- Ar ions generated by the Tesla are caught in an oscillating EM field
- Rapid changes in magnetic field induces eddy currents in the gas
- Resistance to the eddy current flow produces Joule heating
- Rapidly changing magnetic field sets up oscillation of Ar ions... collisions with other unionized Ar which become ionized.... etc...
- The number of ions increases rapidly → steady state is reached...
- Once the ionizing temperatures have been reached the process is self-sustaining, this is now a PLASMA...

Inductively Coupled Argon Plasma



- By the early 1990's there were over 6000 commercially installed ICP facilities (the technique was introduced in 1974... (excludes research-built instruments))
- ICP methods largely replaced AAS/AES in most laboratories
- Despite the great popularity of the ICP, there are still areas where much further research is needed
 - e.g., sample introduction, and diagnostic and mechanistic studies of processes prevailing in the ICP
- sample introduction remains a very **ineffective** process in ICP spectrometry
- Study of fundamental discharge processes allows to devise better sources

- The electronic temperature in the ICP is in the range of 5,000-15,000 K
- High T only occurs within annular discharge and in the "hole" temperature is believed to be lower than the maximum (~ 8,000-10,000K)
- Because the plasma is made of Ar^+ and electrons it is easy for other free atoms to ionize
- Ionization is followed by excitation of ions and the resultant emission of light from ionic transitions often provides the best sensitivities (for ICP-OES).
- In mass spectrometric applications, the ions are introduced into a the mass spectrometer focused, and then mass filtered.

Advantages of plasmas relative to other (optical or ion) sources

- much hotter than flames or electrical discharges
- capable of exciting all metals and metalloids (non-metals also to lesser extent)
- much more stable and reproducible than signal from electrical discharge ES
- lower background and fewer interference effects
- steady state signal with continuous sample introduction
- amenable to multi-element (simultaneous or sequential)
- sensitivity (generally) much greater in ICP-OES than in AAS; extremely good for ICP-MS (especially with the newer high resolution magnetic sector instruments)

Instrumentation for ICP-OES

- Similar yet significantly different from in other optical methods such as AAS and flame AES...
- One of the most important characteristics of ICP-OES spectrometers is the need for high resolution
- High (optical) resolution is achieved by several means (e.g., double monochromators, echelle spectrometers, holographic gratings)
- Basic design consists of sample introduction, Ar gas systems, induction coil and associated RF generator, torch, and optical system for wavelength isolation and detection + assorted whistles and bells...
- RF generators are oscillators that generate an alternating current at a desired frequency

ICP-OES Design

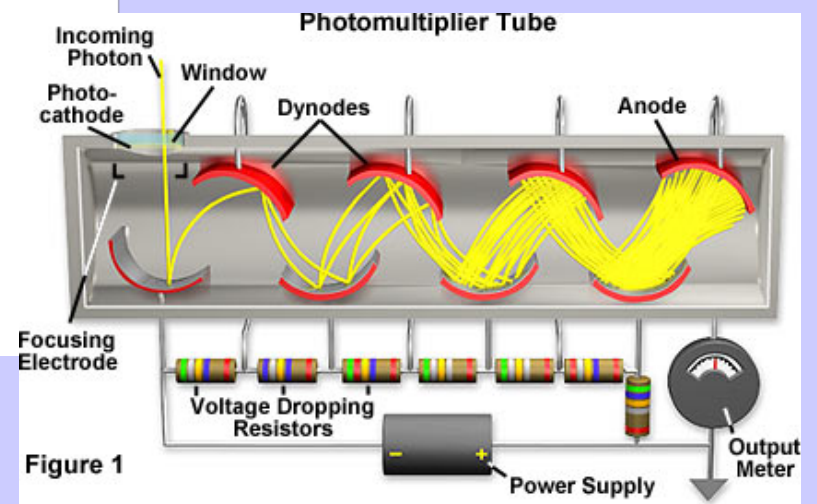
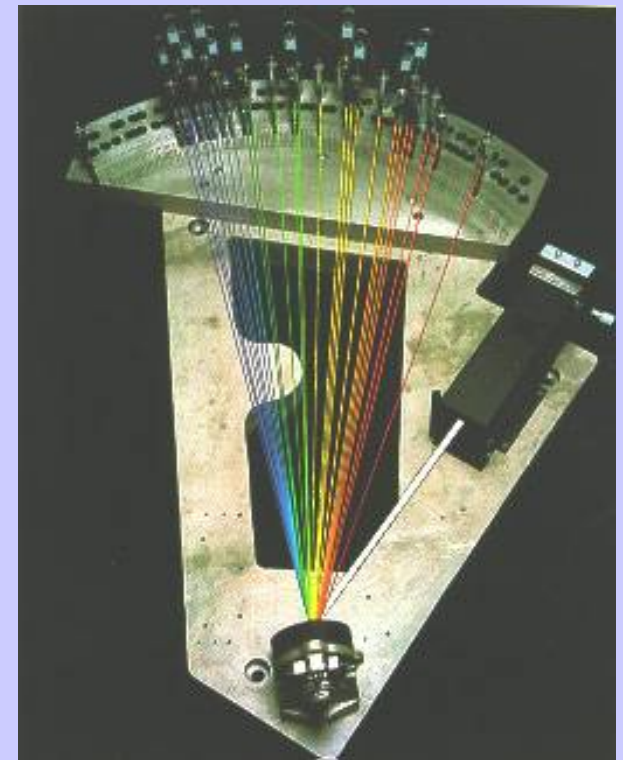
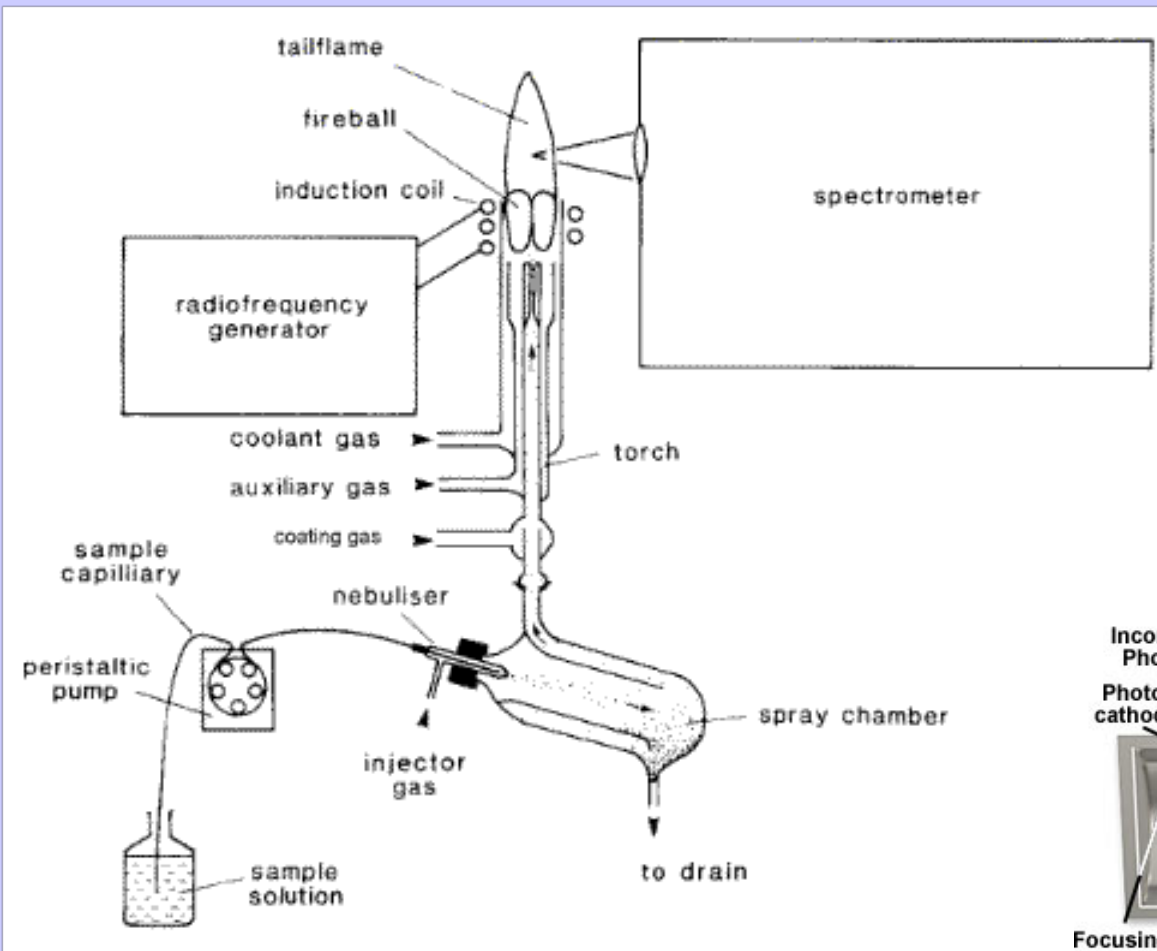
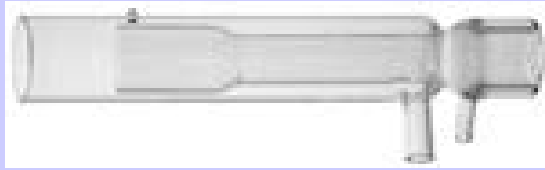


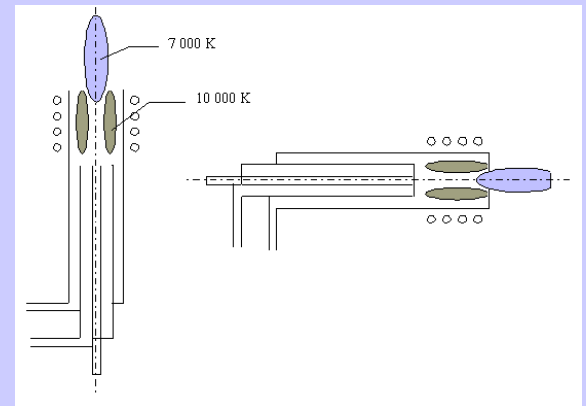
Figure 1



ICP Torches



- many designs available, all follow same principle
- Three streams of Ar gas flow through three concentric quartz tubes leading to the RF coil
- The functions of the streams are:
 1. sample transport
 2. plasma gas (i.e., that which forms the plasma) and torch coolant
 3. auxiliary flow gas to position plasma vertically in the torch
- Flow rates $\sim 0.4\text{-}1.5$ L/min, ~ 15 L/min, and highly variable respectively.
(On the VG-PQ2S ICP-MS system in my lab we use ~ 0.9 L/min, $\sim 14\text{-}15$ L/min, and $0.8\text{-}1.3$ L/min, respectively)



Sample Introduction

- The general principles of other flame methods are applicable... however, a few differences exist.
- Overwhelmingly... the sample is in liquid form.
- Techniques exist for gas and solid introduction
- Routine techniques for direct solid introduction are lacking.
- Laser ablation is the most promising means of dealing with solids on a repetitive and site-specific basis.
- Analyte transport efficiency in ICP-OES and ICP-MS using conventional nebulization is typically lower than in flame (optical) methods.
- Pneumatic nebulizers (concentric or cross flow design)

Pneumatic Nebulizers

- *Pneumatic* is defined as “of or relating to or using air or a similar gas”
- *Nebulizer* is derived from the Latin *nebula*, and is defined as 'an instrument for converting a liquid into a fine spray”
- A pneumatic nebulizer is literally an instrument for converting a liquid into a fine spray that uses a gas as the driving force.

ICP Pneumatic Nebulizers

Some of the more popular types include

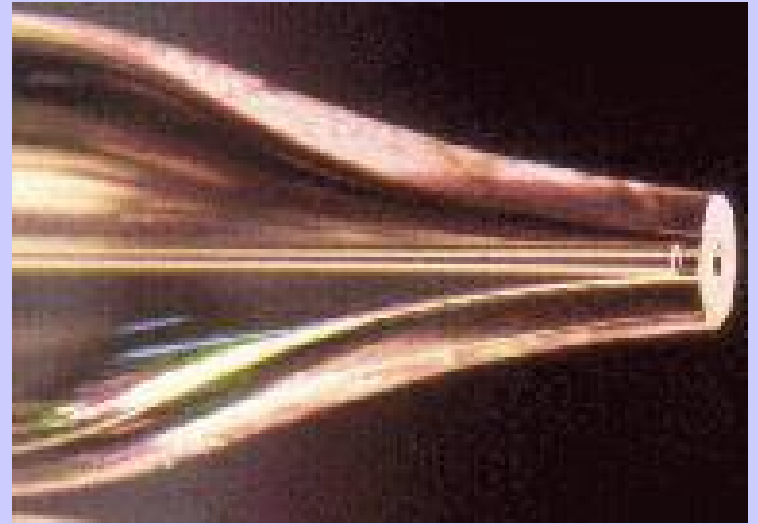
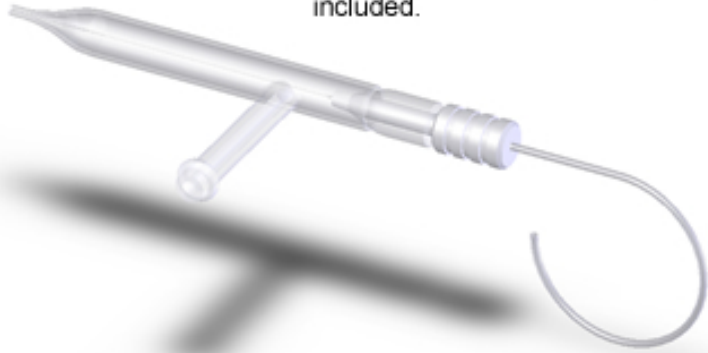
- Concentric glass
- Concentric PFA
- Fixed Cross-Flow
- Lichte (modified)
- Micro-concentric glass
- Adjustable Cross-Flow
- High-Pressure Fixed Cross-Flow (MAK)
- Babington V-Groove (high solids)
- GMK Babington (high solids)
- Hildebrand dual grid (high solids)
- Ebdon slurry (high solids)
- Cone Spray (high solids)

Most Common Nebulizers

- **Cross Flow Nebulizer:** the standard “old style” nebulizer that is based on AA technology... (from the 60’s)
- **Concentric (e.g., Meinhard) Nebulizer:** generally recommended for low TDS samples because the inner capillary can be clogged by particles or high TDS. Fragile and not resistant to hydrofluoric acid. Meinhard or its offshoot (the gas expansion nebulizer) are most commonly used in ICP-MS.
- **Babington Nebulizer:** can be used to introduce samples with high matrix and high TDS level samples because of its structure. Components made of PEEK, therefore is resistant to many sample types including hydrofluoric acid

Meinhard Nebulizer

Quick disconnect sample inlets are available on nebulizers with the "QD" designation. PTFE connector and PTFE tubing are included.

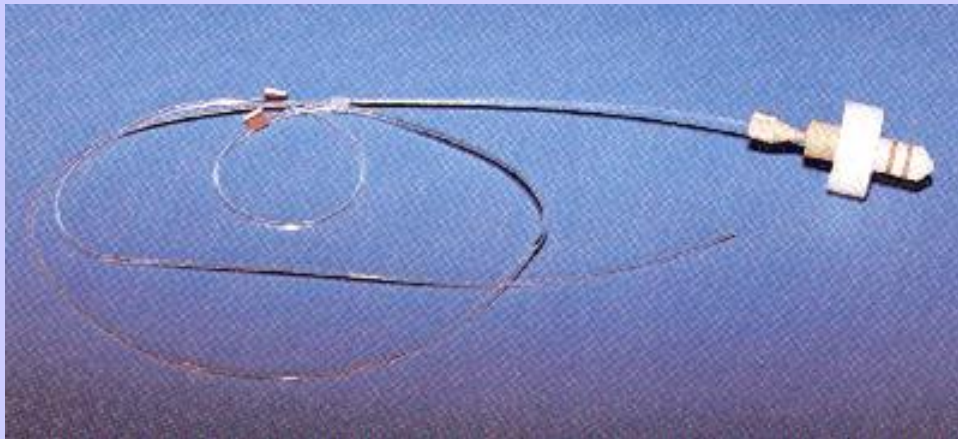


Savillex Cross Flow Nebulizer

Microconcentric Nebulizers (MCN)



The Aspire (by CETAC) is a highly chemically resistant PFA MCN designed for the introduction of small volume samples (< 1 mL) to an ICP-AES or ICP-MS instrument for trace element analysis.



The MCN-100 (also by CETAC) is a low flow, high efficiency MCN, allowing high sensitivity analysis on very small sample volumes.

Ultrasonic Nebulization

- Ultrasonic nebulization is another sample introduction technique, in which a piezoelectric crystal is driven at 0.2-10 MHz and used to break up liquid films into an aerosol



Common Spray Chambers

- Scott (single or double pass) spray chamber
- Cyclonic spray chamber



- Material: Quartz/Borosilicate glass or Teflon (shown)
- Volume: ~90-100 ml
- Physical reproducibility ~1%
- Uptake range ~700-1000 $\mu\text{l}/\text{min}$
- Water cooled jacket on glass/quartz models



- Material: Borosilicate glass
- Volume: 20ml
- Physical reproducibility ~1%
- Uptake range ~20 to 1000 $\mu\text{l}/\text{min}$

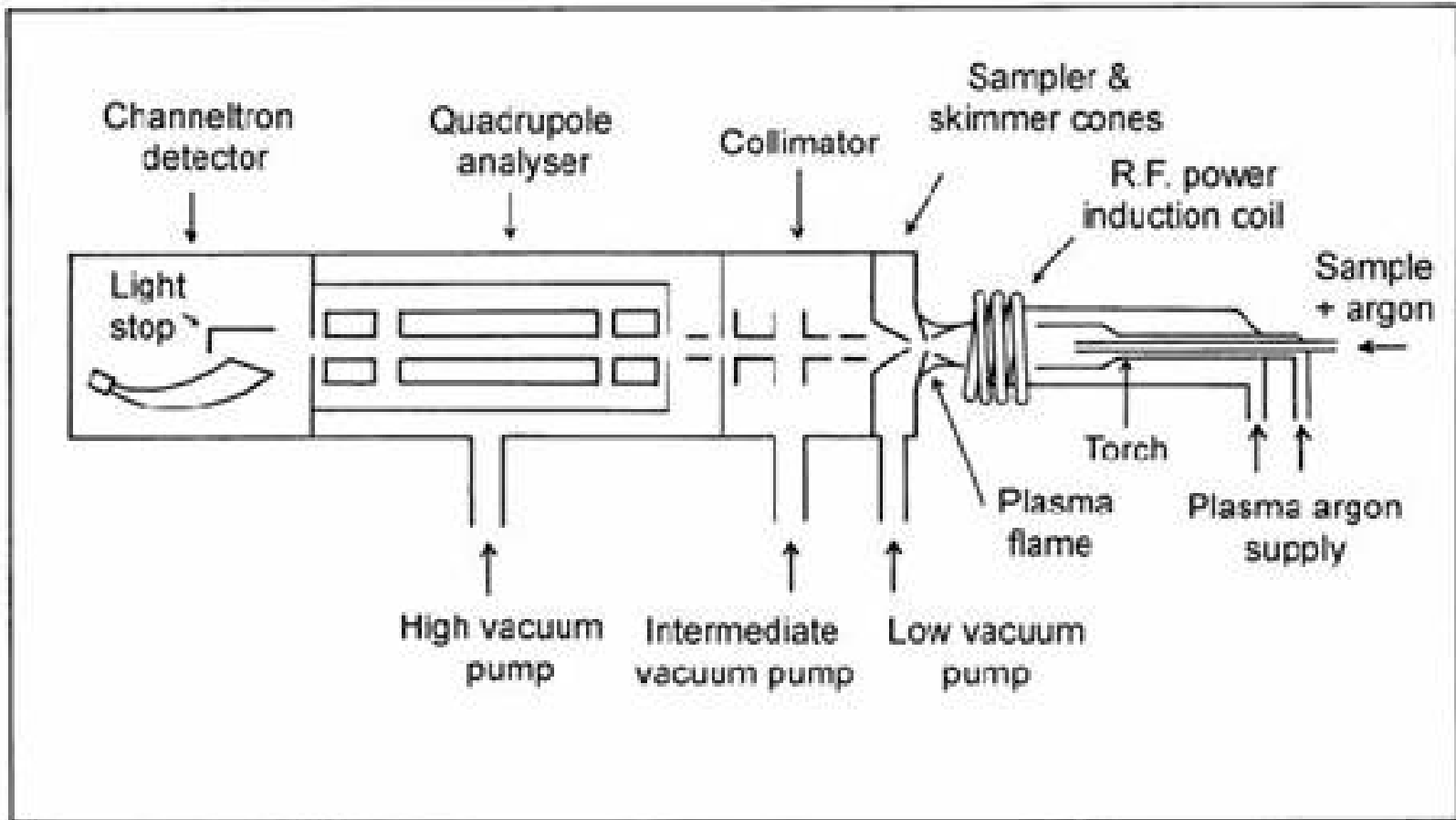
ICP-MS

- Detection limits of 10-100 pg/mL routinely with 1 pg/mL achievable with fairly little effort on the newer machines (this is 100 to 1000 better than ICP-OES)
- Mass spectra are considerably simpler than optical spectra (particularly true with lanthanides)
- Isotope abundance spectra provide a rapid qualitative tool.
- LDR of 6 decades (allegedly, but not really)
- The ICP is an excellent ion source. Efficiencies of ionization range from near quantitative for about 40 elements and quite favorable for many more (see table 10.2 in handout)

ICP-MS

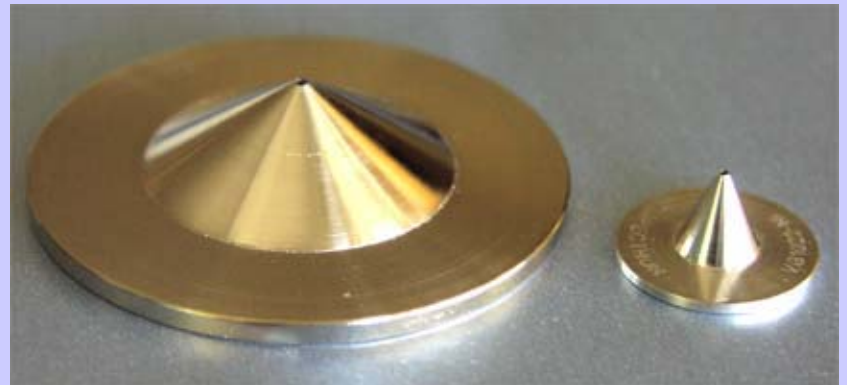
- Systems are similar in design with a quadrupole (or magnetic sector) ms interfaced with the ICP through a set of metallic cones.
- Biggest problem with ICPMS is interfacing ICP (high pressure and temperature) with MS (low pressure and temperature).

ICP-MS Schematic



CONES

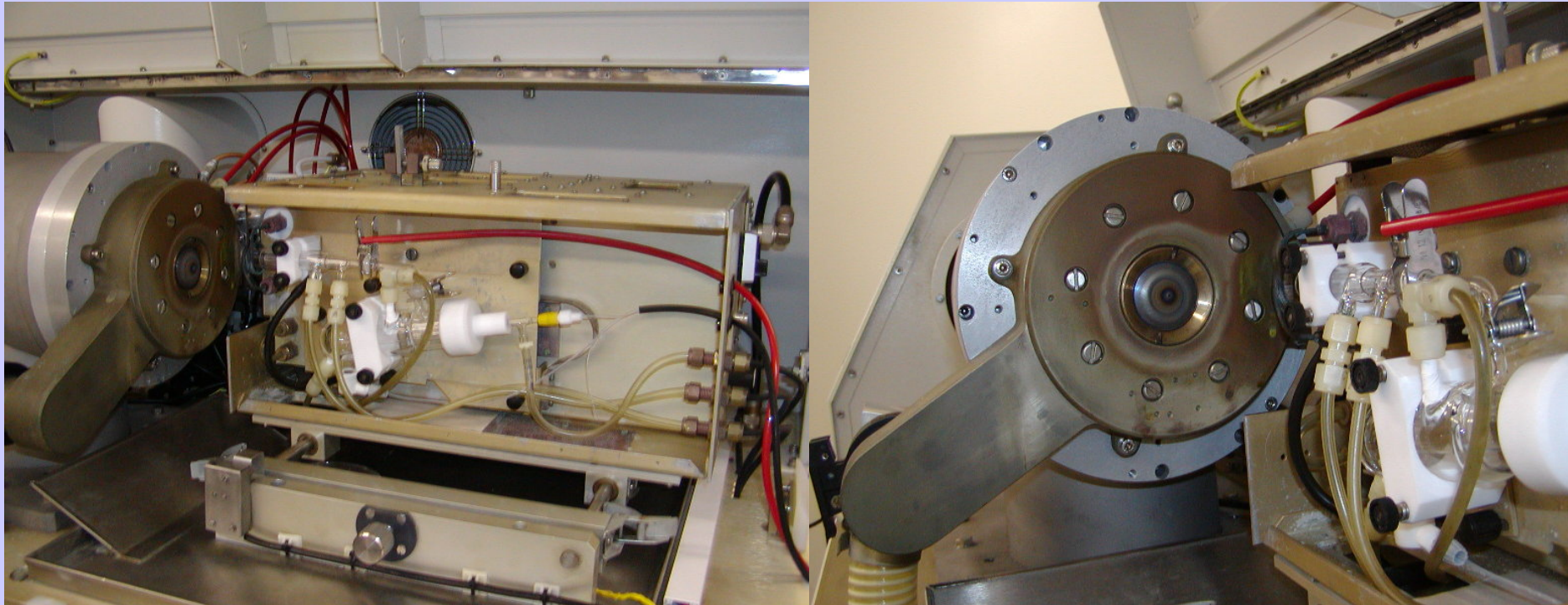
- First cone is a *sampling cone* with an orifice of 1mm and the whole interface is water cooled
- Second cone is a *skimmer cone* placed 2-10 mm behind the sampling cone
- Latter has same diameter orifice as sampling cone but is more sharply tapered.
- Region between two cones is evacuated to 1 torr or less



Model VG-PQ2S ICP-MS



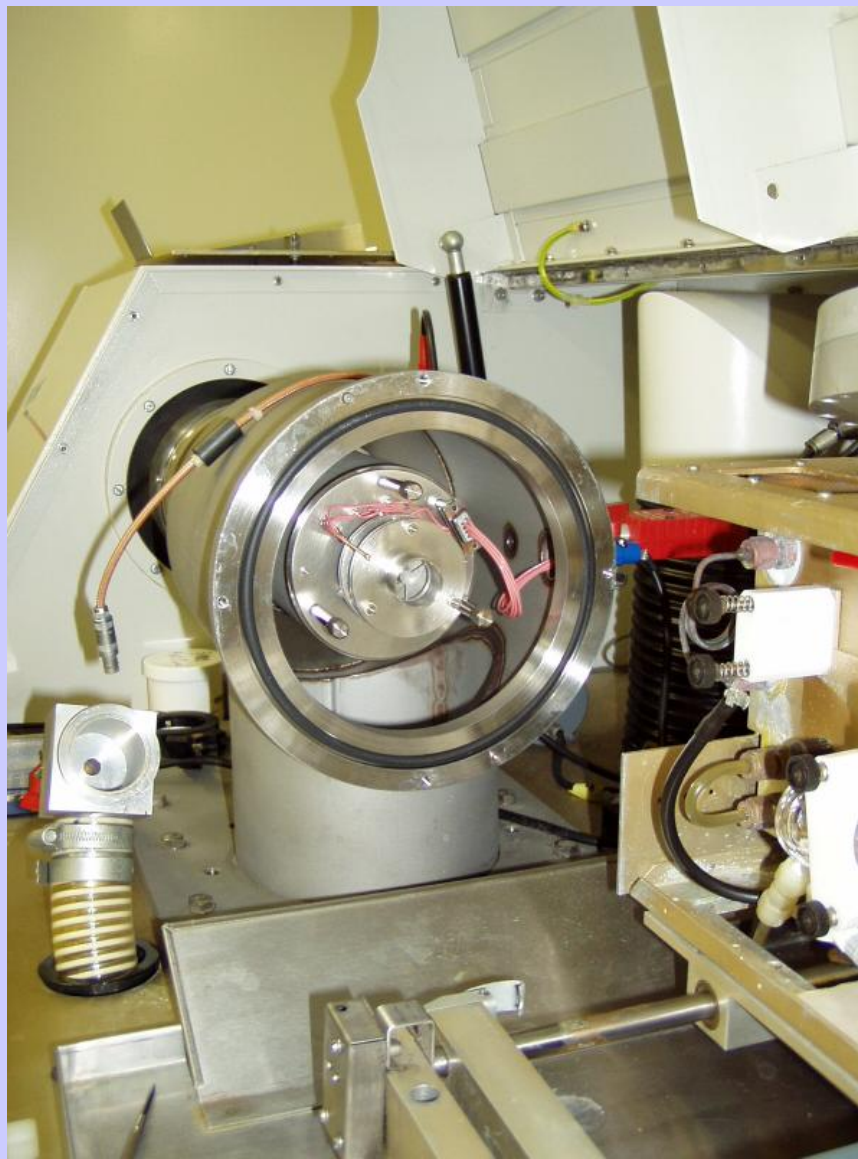
Torch Box (left) and Expansion Chamber (right) of VG-PQ2S ICP-MS



Torch box contains nebulizer (yellow tip), spray chamber, and torch, and associated gas/water lines and the load coil

High Vacuum Part...

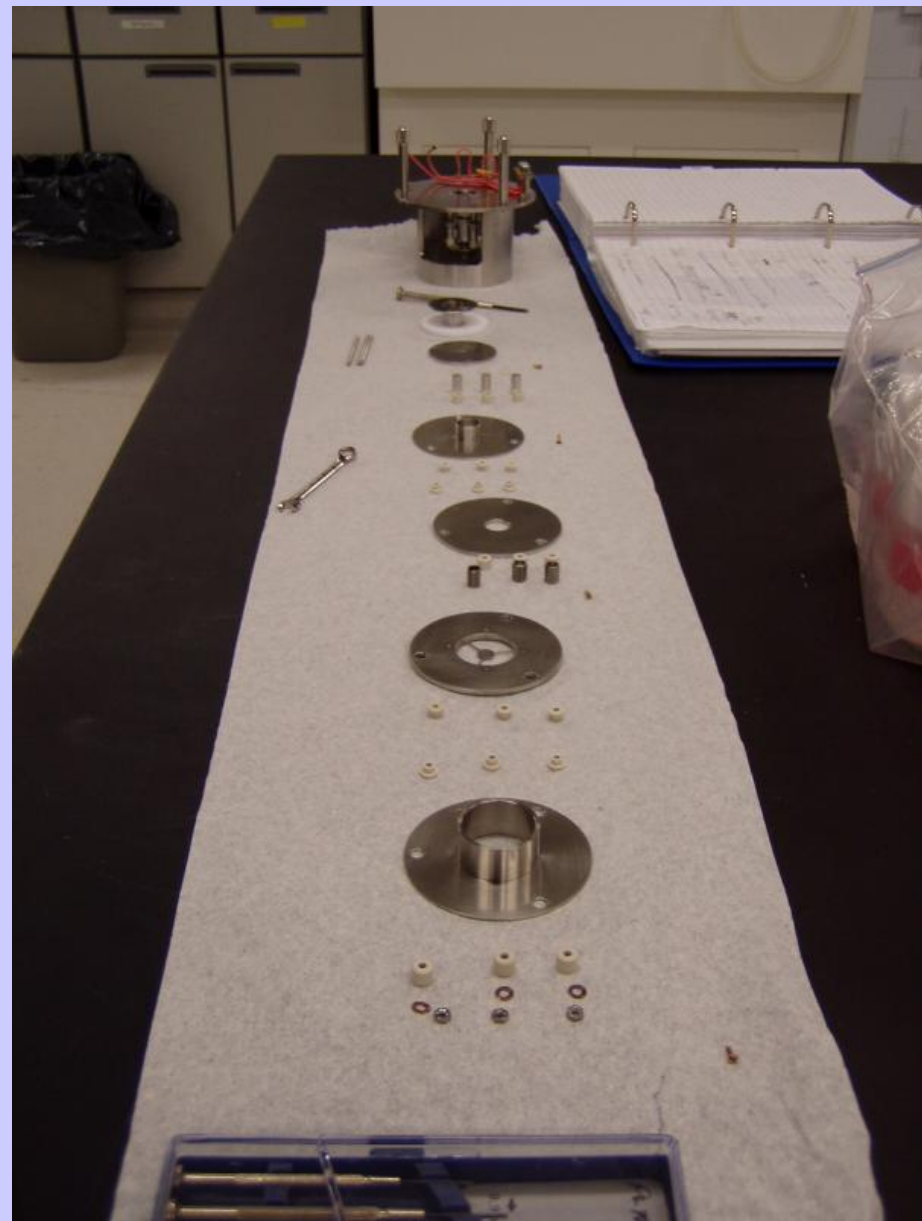
- High vacuum (i.e., low P) part of mass spec. following the skimmer contains input ion optics, the quadrupole, and the ion detector
- Main part of system is kept at approximately $<10^{-6}$ torr. (Sciex use one stage cryogenic pumping whereas VG use two stages of mechanical pumping)
- Input ion optics consist of ion lenses and a Bessel box to block photon passage
- Further reduction in photon noise is achieved by deflection of ions exiting the quadrupole to an off-axis detector



View of Lens Stack in High Vacuum Chamber of VG-PQ2S

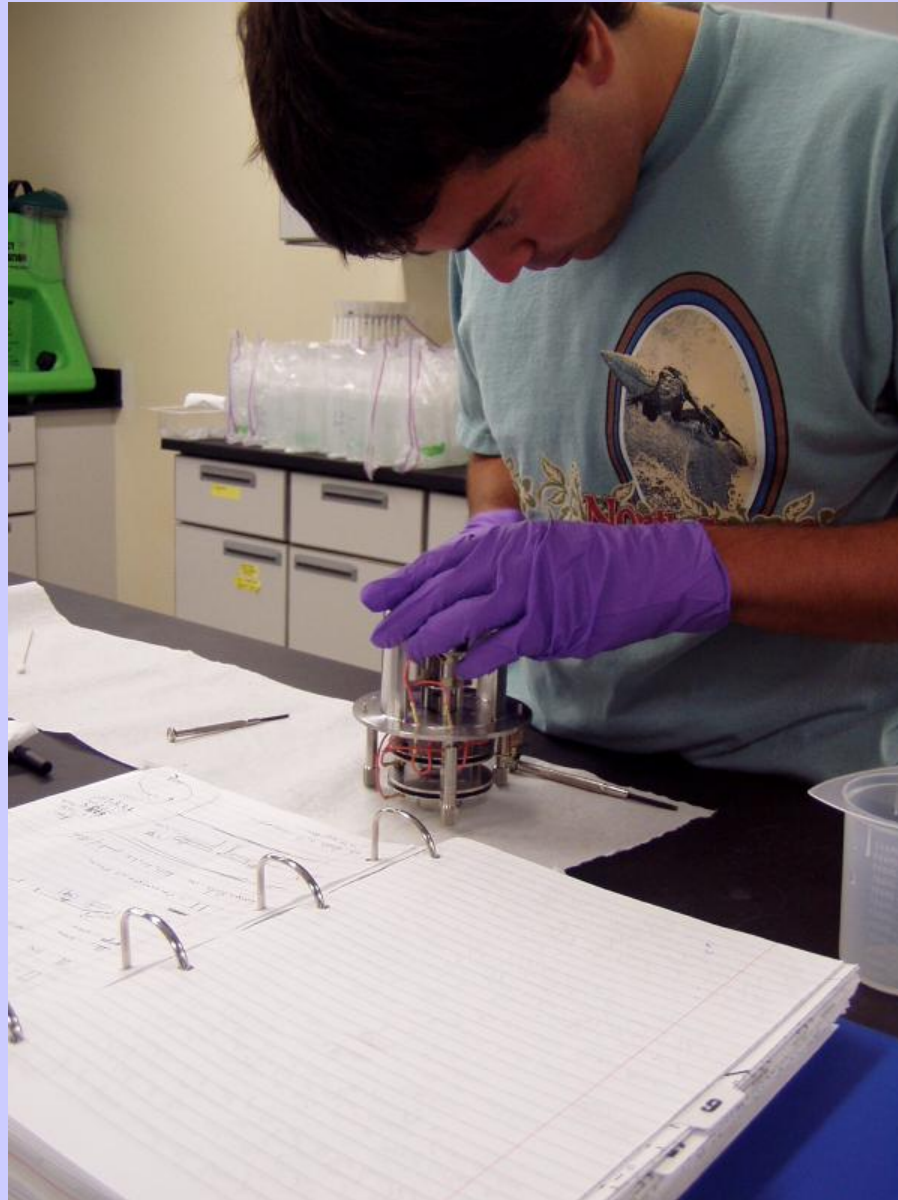
Lens Stack of VG-PQ2S





Lens Stack of VG-PQ2S

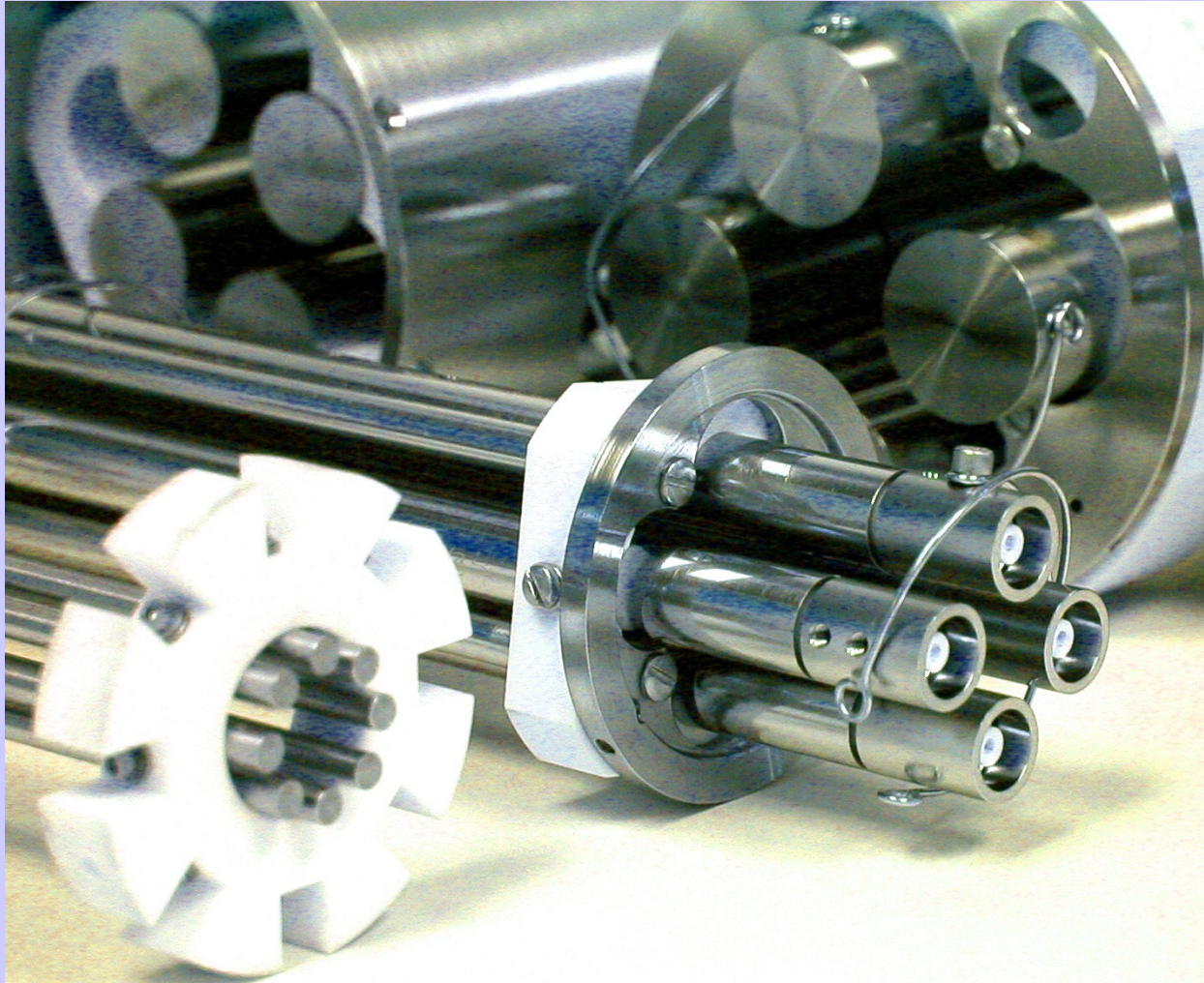
Assembly of Lens Stack



Ion Focusing...

- Because of similar characteristics for different elements, it is possible to use compromise settings for analysis of elements that span 3 rows of the periodic table and have significantly different masses and ionization potentials
- Input optic voltages are very important... settings depend on instrument design and type of input ion optics.
- One of the critical values is in the voltage on the photon stop in the Bessel box (optimized setting is dependent on mass)

Quadrupole Mass Filter



Detection and Interferences

- Although spectral simplicity is ICP-MS's biggest claim to fame, spectral overlaps do occur although not nearly as bad as in ICP-OES
- Molecular species and doubly charged ions can cause some problems
- Isobaric interferences occur as a result of the isotopic composition of various elements (can also occur from oxide formation, doubly charged ions, and combination products with Ar)
- e.g.: mass 48 for both Ti and Ca; can correct for the Ca contribution by measuring ^{44}Ca and subtract 0.0891 of the measured counts from the 48 mass...

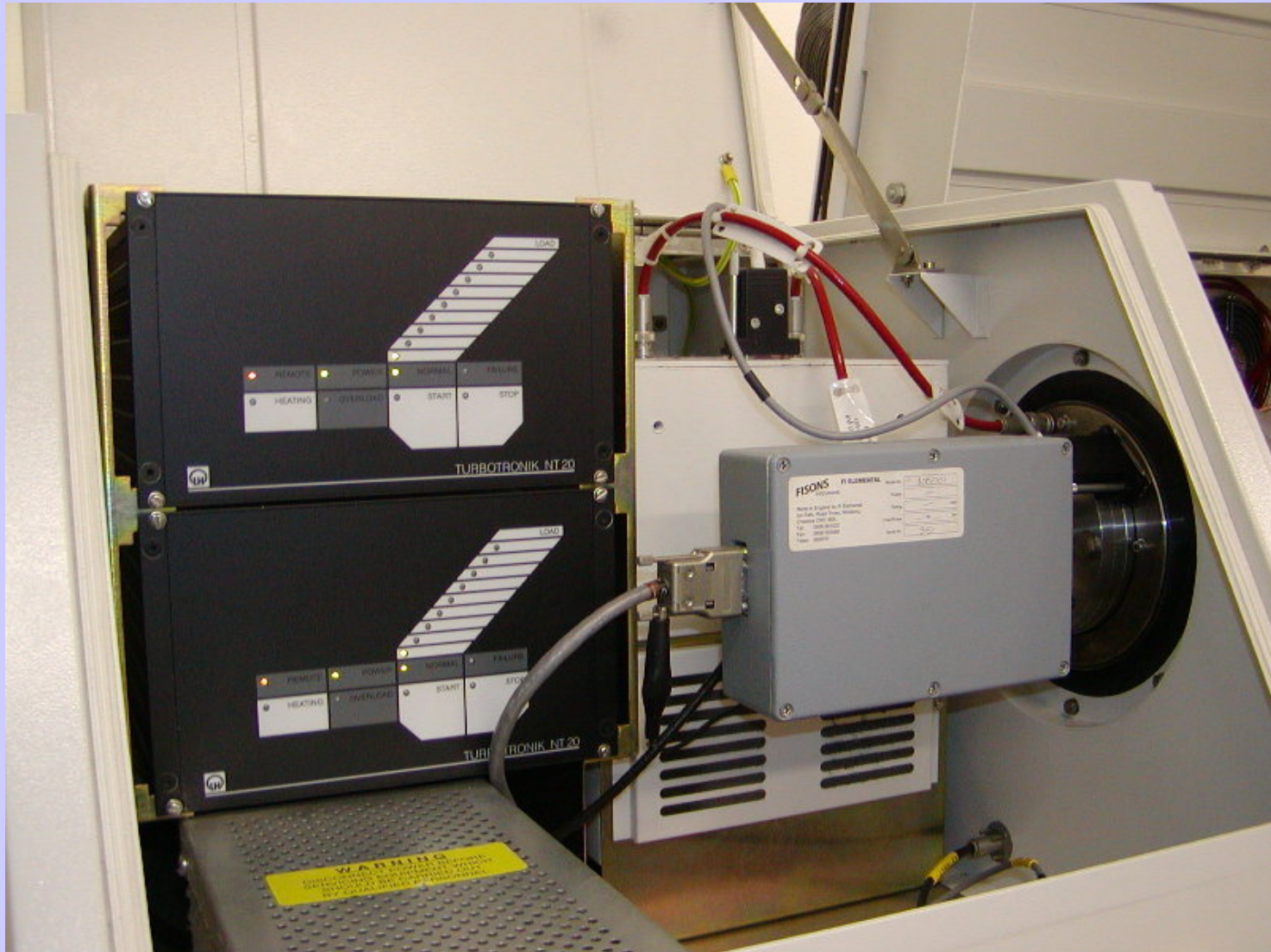
Interferences...

- Matrix composition can also cause problems. Cannot use HCl to dissolve samples containing As or V because the $^{40}\text{Ar}^{35}\text{Cl}$ interferes with ^{75}As and $^{35}\text{Cl}^{16}\text{O}$ interferes with ^{51}V , and both elements are MONOISOTOPIC.
- Oxide and hydroxide formation also can be problematic. Need to minimize the formation of these unwanted species. Usually involves changing in RF power and injector gas flow rate, cooling the spray chamber, etc.

More Interferences...

- matrix induced spectral overlaps
- Example: $^{47}\text{Ti}^{16}\text{O}$ and $^{23}\text{Na}^{40}\text{Ar}$ interferes with ^{63}Cu , $^{49}\text{Ti}^{16}\text{O}$ interferes with ^{65}Cu , $^{16}\text{O}^{40}\text{Ar}$ precludes analysis of ^{56}Fe . There are many other isobaric interferences, especially in the mass range below 80 amu.
- Another problem is the effect of large amounts of a matrix element on the signal from a trace component. This remains poorly understood but impacts background, ionization efficiency of analyte, etc.
- Life is generally good above mass 80...

Detector and Vacuum Control Module on VG-PQ2S



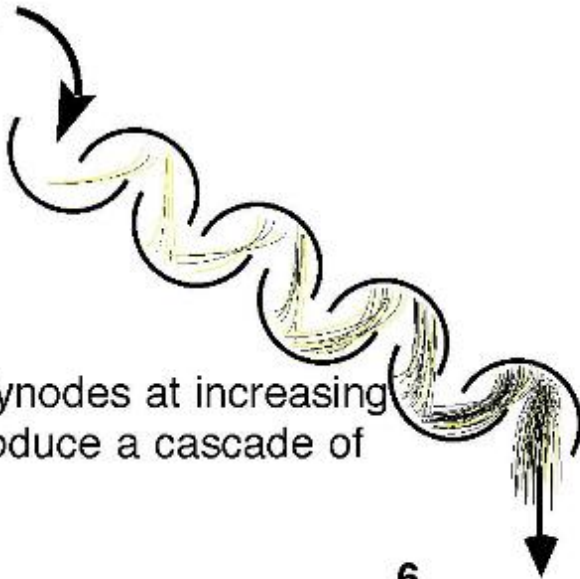
Detection and Ion Focusing

- detection with continuous scanning, peak hopping...
- resolution needed is not high if avoid oxide formation...
0.5 to 1 amu (width at 10% height)
- there are many parameters that affect the operation of an ICP/MS system
- most do not need to be routinely adjusted but forward power, gas flows, and ms input ion-optic voltages have major effects on analyte ion signals
- forward power and gas flows are most important and operate as a paired set of variables (if one is changed the other must also be changed to maximize the signal)

Detectors

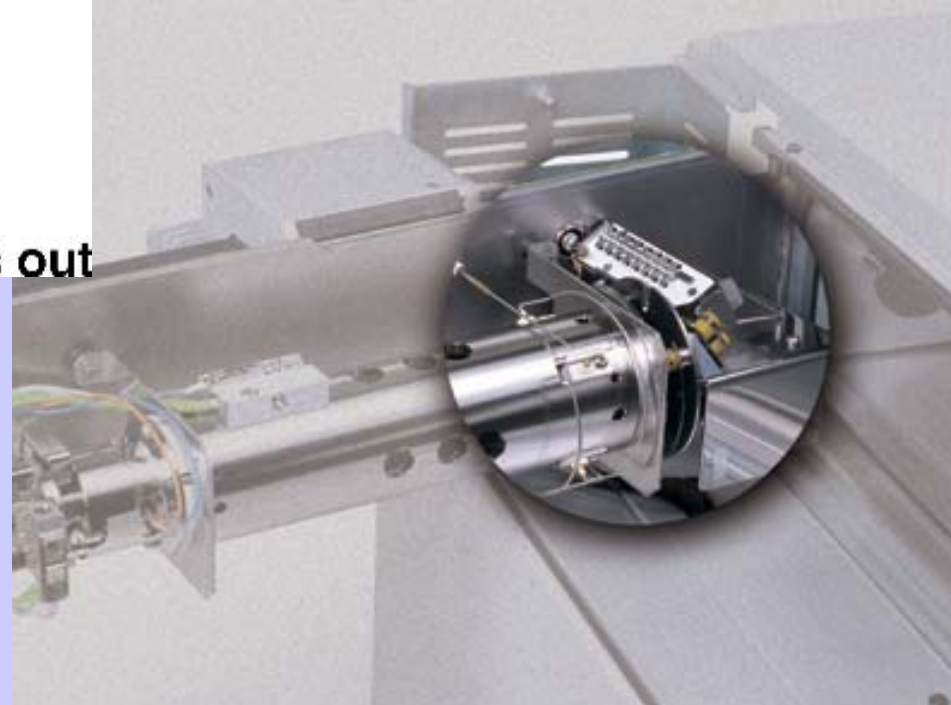
- Channeltron Electron Multiplier

one ion in

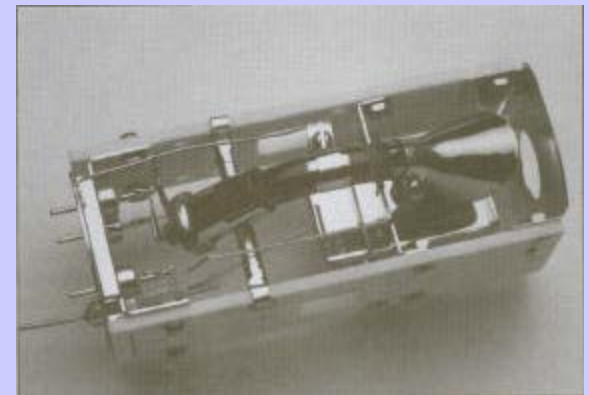


A series of dynodes at increasing potentials produce a cascade of electrons.

10^6 electrons out



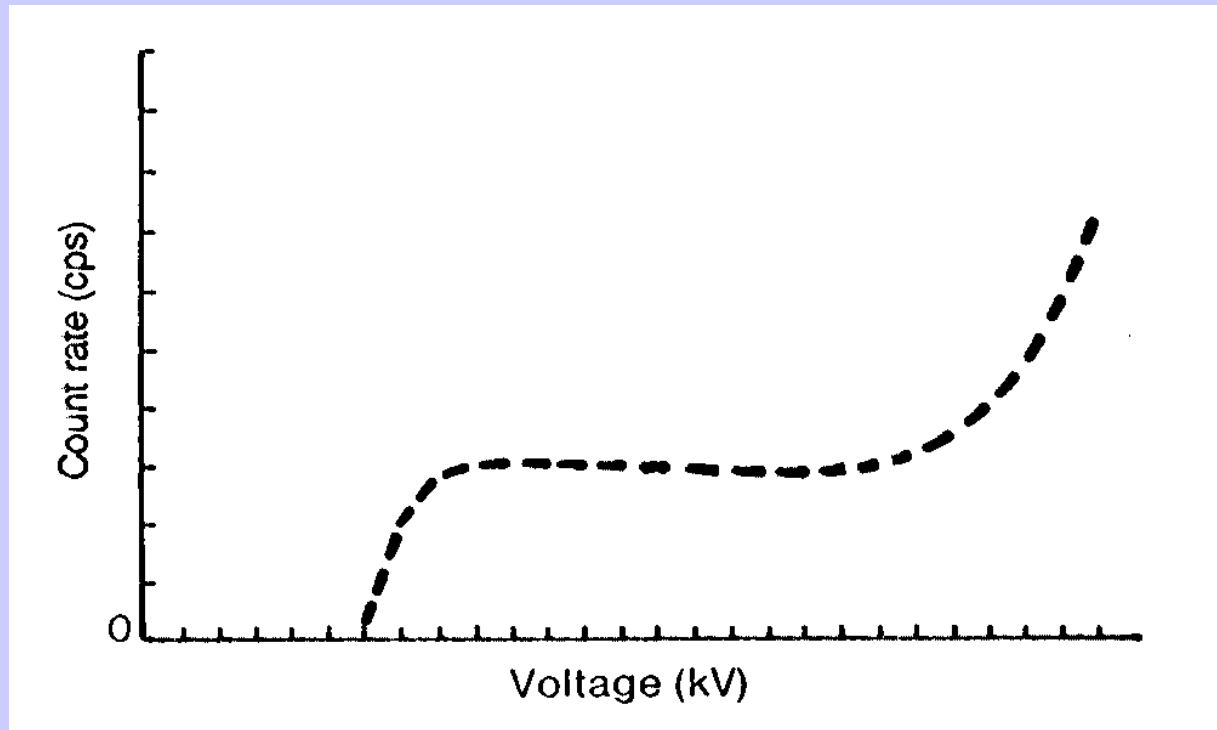
Channeltron Electron Multipliers



Detection Efficiency

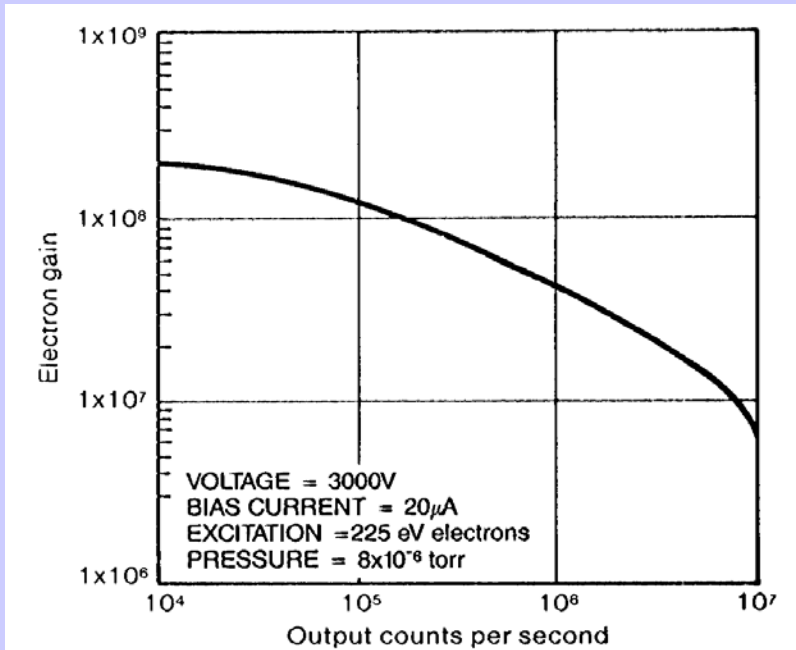
- Detection efficiency is the probability of a charged particle (or photon) incident on the CEM input producing an output pulse. This parameter is strongly dependent upon the energy, mass and velocity of the incident particle as well as the number of charges on the particle and the angle of incidence.
- For mass spectrometry, the most important particles of interest are positive and negative ions. Electron detection efficiency is important in some instances, such as when a conversion dynode is being used and the CEM is detecting secondary electrons emitted from the dynode surface.
- Photon detection can also be important in a negative sense in that it is often a source of unwanted noise (this is why there is a photon stop in the lens stack)

CEM Operating Plateau



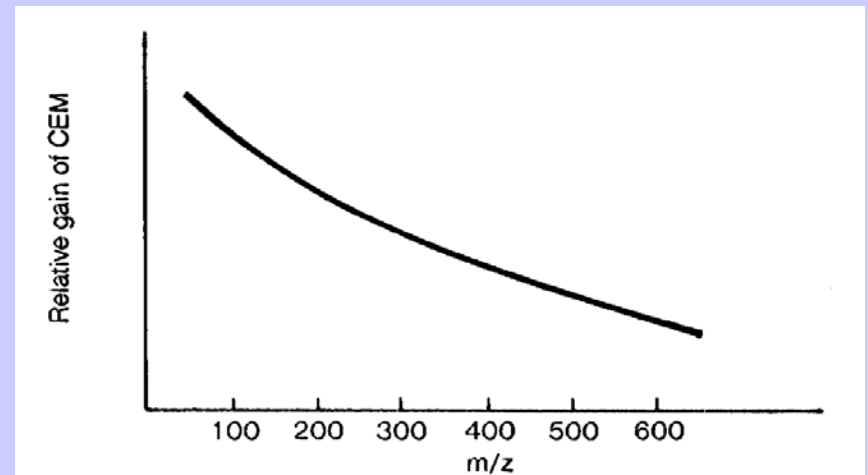
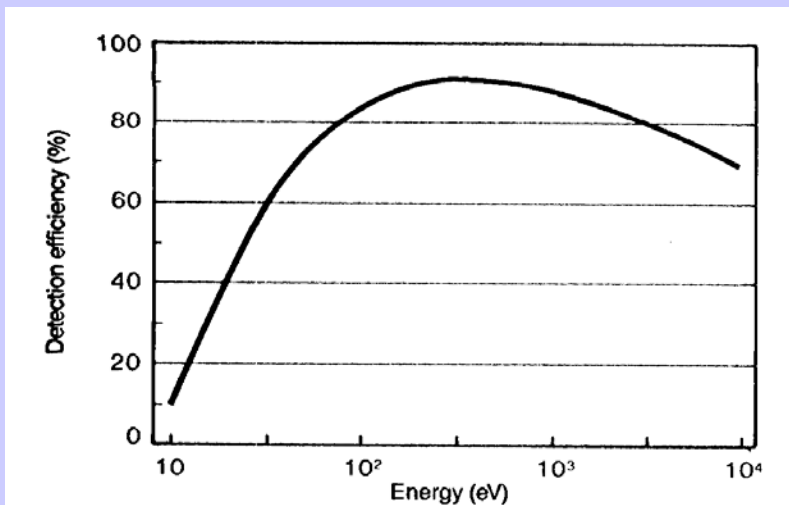
The optimum operating point is about 50-100 volts beyond the “knee” of the curve. As the multiplier ages, the knee moves to the right and the voltage must be increased. Typical lifetime characteristics under ideal conditions are illustrated in Figure 3-20 for either analog or pulse counting operation

Output/Response of CEM

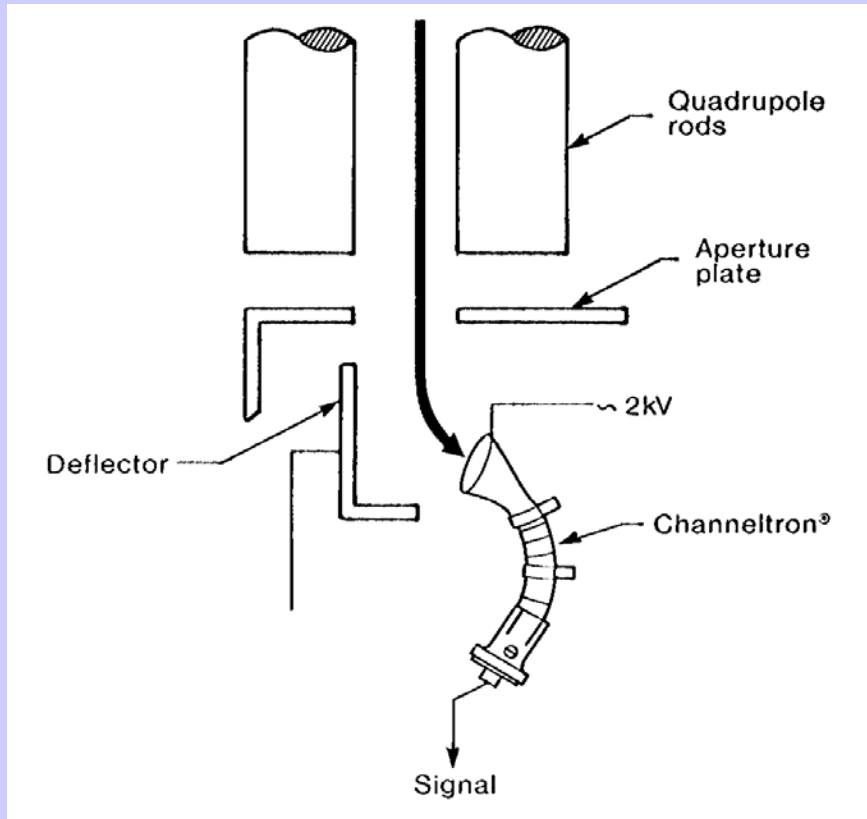


The gain of the CEM is non linear (lower gain at higher count rates)

The detection efficiency of ions is a function of both ion energy or, more properly, ion velocity at the point of impact on the secondary emitting surface and ion mass to charge ratio (m/z)



Detector Alignment



The straight line geometry of most quadrupole MS necessitates mounting the detector off-axis to avoid noise caused by neutrals and/or photons or due to the decay of metastables within the analyzer or detector chamber.

The CEM Input aperture is located out of the line-of-sight of the analyzer exit aperture. This effectively eliminates detection of neutrals and photons.