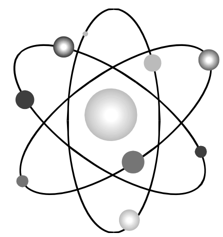
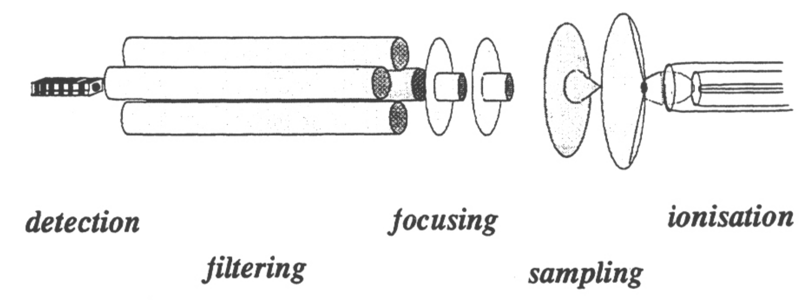
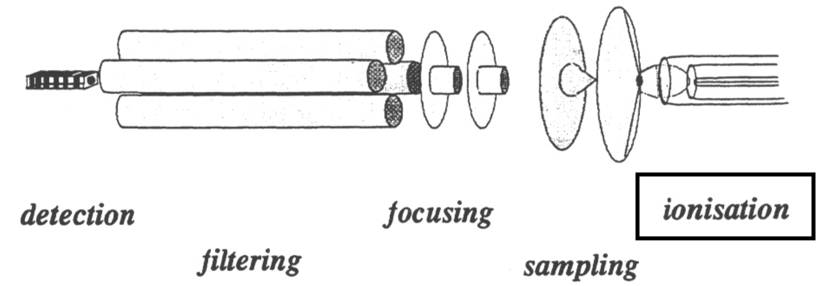
An Overview of ICP/MS



Basic Components of an ICP-Mass Spectrometer



Basic Components of an ICP-Mass Spectrometer



•A fine aerosol of sample is introduced into the plasma via a combination of nebulizer, spray chamber, and torch.

•The plasma, normally an Argon plasma, is of sufficient energy to ionize the sample atoms.

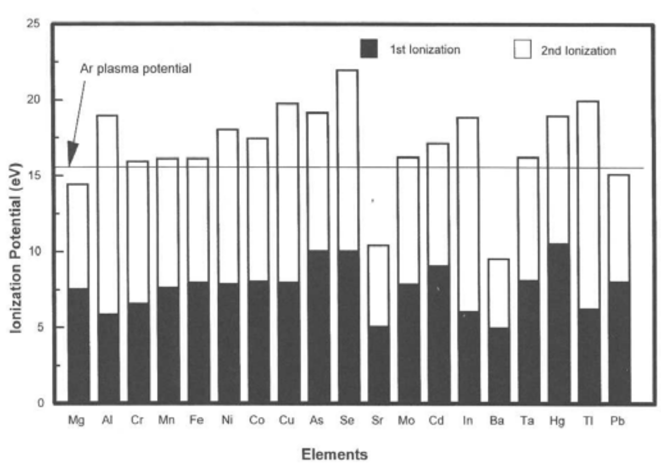
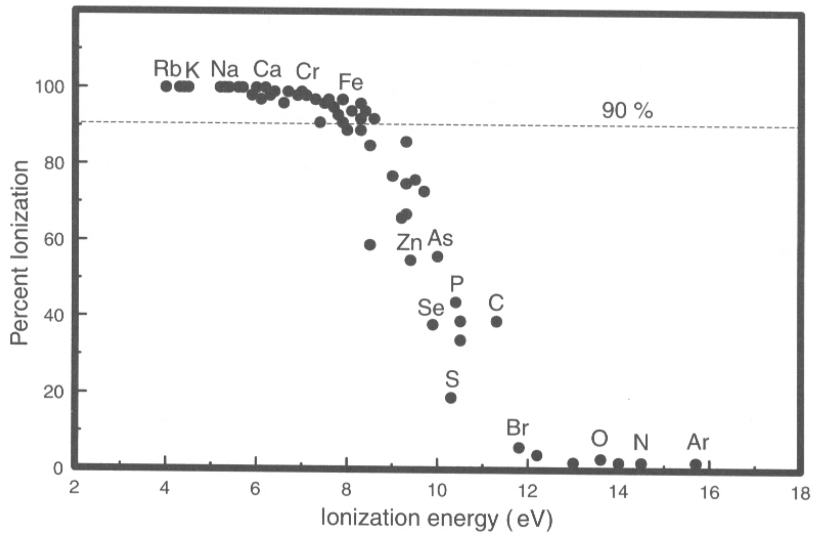
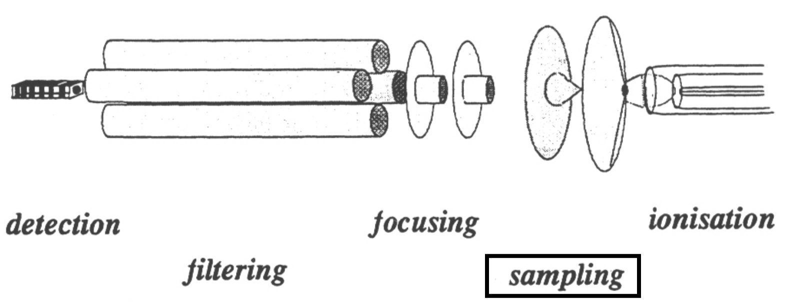


Figure 9.2 First and second ionization potentials of selected metals. (From Reference 16, with permission.)

In ICP-MS, the aim is to maximize singly-charged ions and minimize multiply-charged ions. The instrument measures m/z (mass per unit charge), so a doubly-charged ion will be detected at a mass which is 1/2 that of its singly-charged counterpart.



Basic Components of an ICP-Mass Spectrometer



- Two interface cones, each with an orifice size of 0.4-1.2 mm, aid in the transmitting of ions from the atmospheric pressure plasma (at 760 torr) to the low-pressure operating zones of the mass spectrometer (at 10^{-5} -10^{-6} torr).
- The sampling interface is designed to maintain the composition and integrity of the ion stream by limiting the kinetic energy spread of the ions and limiting production of polyatomic species.

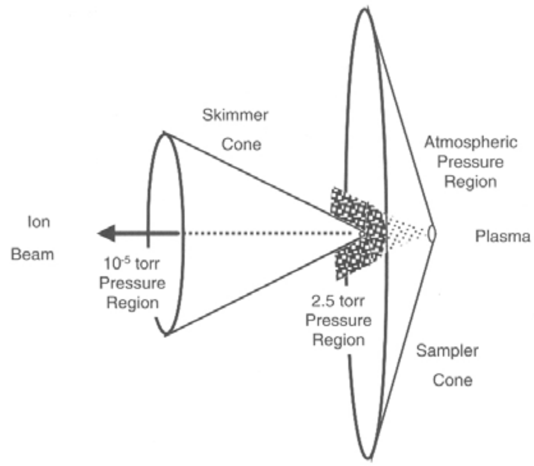


FIGURE 4.2 ICP interface cones, showing the ion beam.

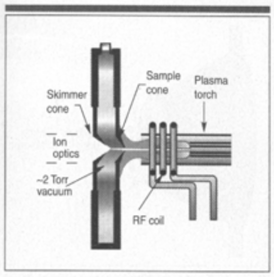


Figure 2. Detailed view of the interface region.

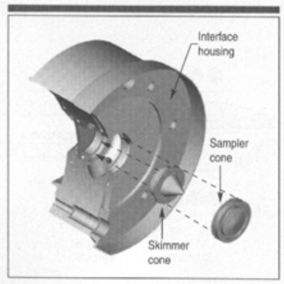


Figure 3. Close-up view of the sampler and skimmer cones. (Courtesy PerkinElmer Instruments, Norwalk, CT.)

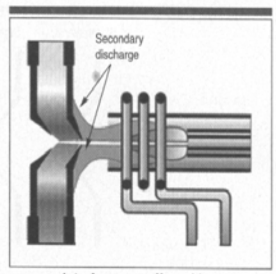


Figure 4. Interface area affected by secondary discharge.

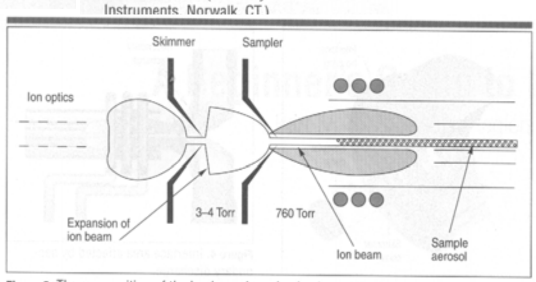
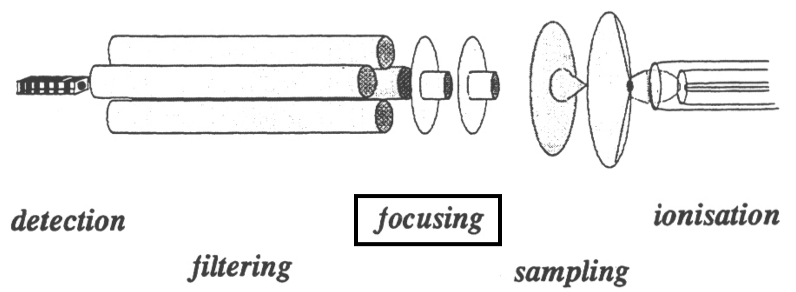


Figure 6. The composition of the ion beam is maintained, assuming a neutral plasma.

<u>Basic Components of an ICP-Mass Spectrometer</u>



•The lenses electrostatically steer the maximum number of analyte ions from the sampling region to the mass separation (filtering) device, while minimizing the transport of unwanted matrix/solvent components and non-analyte-based species, such as particulates, neutral species and photons.

•Electrons are diffused out of the ion beam, leaving a positively charged beam, whose ions are focused back towards the center of the ion beam.

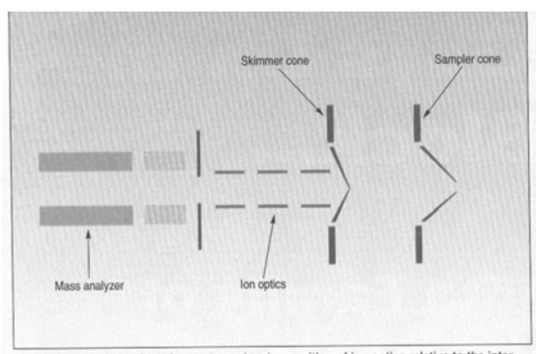


Figure 2. A generic ion focusing system, showing position of ion optics relative to the interface cones and mass analyzer.

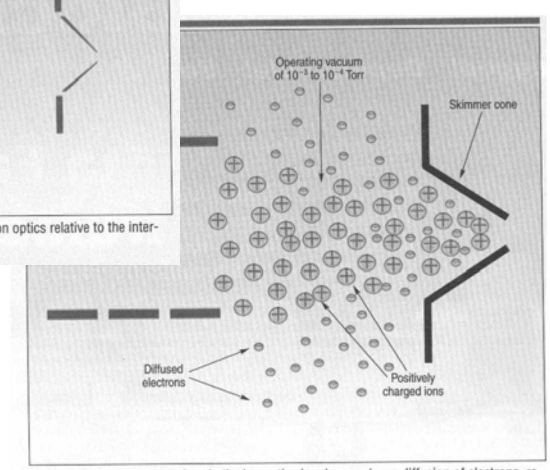


Figure 3. Extreme pressure drop in the ion optic chamber produces diffusion of electrons, resulting in a positively charged ion beam.

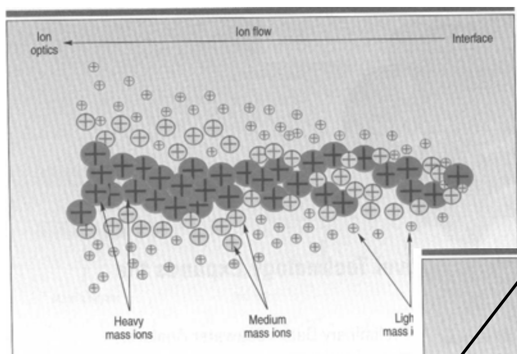


Figure 4. The degree of ion repulsion will depend on kinetic energy of the i high kinetic energy (green with red +) will be transmitted in preference to (yellow with red +) or low kinetic energy (blue with red +).

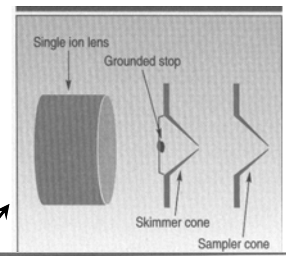


Figure 6. Schematic of a single ion lens and grounded stop system (not to scale [courtesy of PerkinElmer Instruments (Norwalk, CT)]).

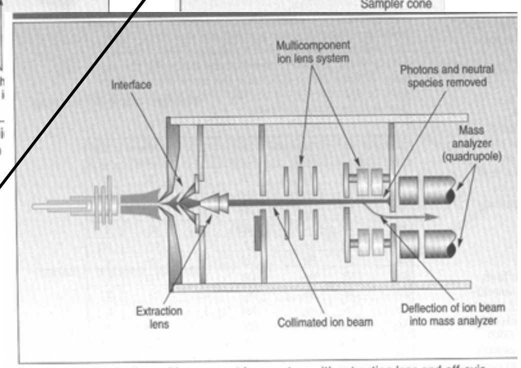
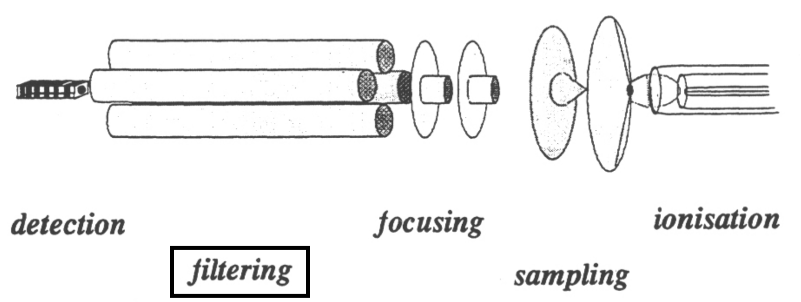


Figure 5. Schematic of a multicomponent lens system with extraction lens and off-axis quadrupole mass analyzer (courtesy of Agilent Technologies [Wilmington, DE]).

Basic Components of an ICP-Mass Spectrometer



•Separates ions based on their m/z (mass to charge) ratios. Only one mass (m/z) is allowed to reach the detector at any given time.

•Quadrupole mass filter is most common (90%) and economical, but there are also magnetic sector, time-of-flight, and collision/reaction cell systems.

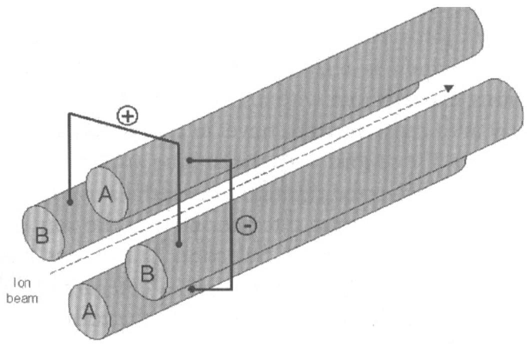


FIGURE 4.4 Quadrupole mass filter.

DC (direct current) and RF (radio frequency) fields are applied to quadrupole rods

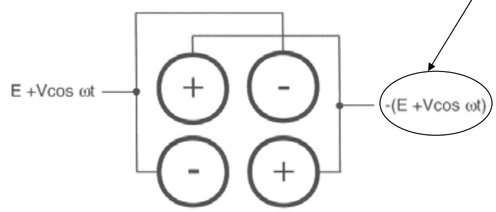


FIGURE 4.5 End-on view of quadrupole rods with electrical connections.

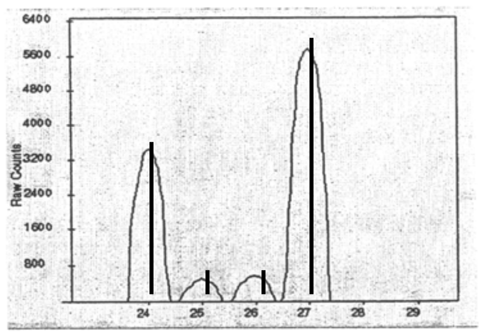
Table I. Illustrative values for air at 20 ° C.

Pressure (in Torr)	Gas density (molecules per mL)	Mean free path (cm)	Time to monolayer (s)
$\boxed{760}$	2.7×10^{19}	$\boxed{7 \times 10^{-6}}$	3.3×10^{-9}
10^{-3}	3.5×10^{13}	5	2.5×10^{-3}
$\boxed{10^{-6}}$	3.5×10^{10}	$\boxed{5 \times 10^{3}}$	2.5
10^{-9}	3.5×10^{7}	5×10^{6}	2.5×10^{3}

Mean Free Path: defines the distance a gas atom or molecule travels between collisions.

- At atmospheric pressure, as in the plasma, the mean free path is 0.000007 cm, so atoms and molecules collide after traveling a very short distance.
- In the quadrupole region, where the pressure is 10^{-6} torr, the mean free path is 5000 cm, so atoms and molecules can easily travel the entire length of the quadrupole rods and into the detector without colliding with other molecules.

figure 9.8 - Good mass calibration



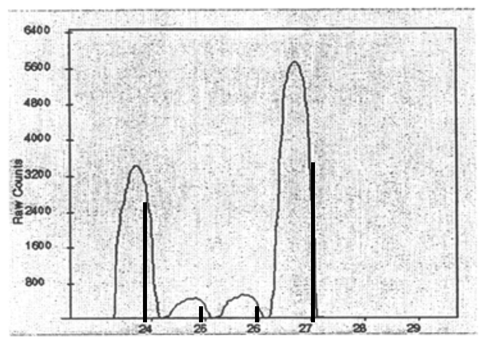
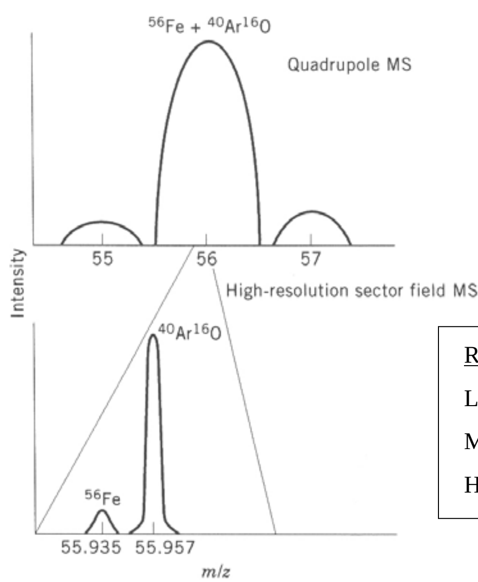


figure 9.9 - Poor mass calibration



<u>Resolution comparisons</u>

Low resolution: 300-400

Medium resolution: 3000-4000

High resolution: 8000-10,000

Figure 6.34 Comparison of mass spectra of Fe obtained with a quadrupole MS and with a high-resolution magnetic MS.

TABLE 6.2 Resolution Required to Separate Analyte Ions from Interfering Ions

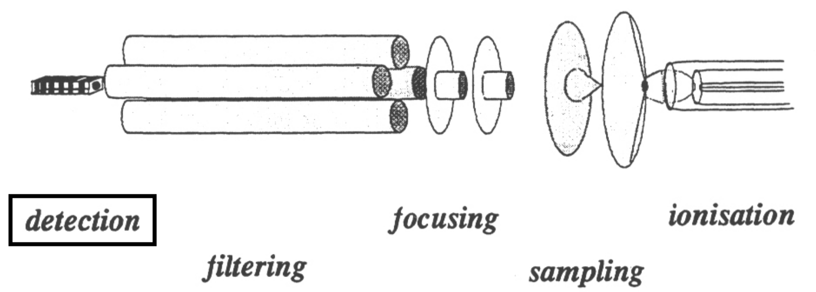
Isotope	Mass[a]	Interference	Mass[a,b]	Resolution Required[b]
^{28}Si	27.9769284	$^{14}N_2$	28.006148	960
		$^{12}C^{16}O$	27.994915	1600
^{31}P	30.9737634	$^{14}N^{16}O^{1}H$	31.005814	970
^{32}S	31.9720718	$^{16}O_2$	31.989829	1800
^{39}K	38.9637079	$^{38}Ar^{1}H$	38.970557	5700
^{40}Ca	39.9625907	^{40}Ar	39.962383	193000
		^{40}K	39.963999	29000
^{48}Ti	47.9479467	$^{32}S^{16}O$	47.966986	2600
		$^{34}S^{14}N$	47.970942	2100
^{51}V	50.9439625	$^{35}Cl^{16}O$	50.963767	2600
		$^{37}Cl^{14}N$	50.968977	2100
^{52}Cr	51.9405097	$^{40}Ar^{12}C$	51.962383	2400
		$^{35}Cl^{16}O^{1}H$	51.971592	1700
^{53}Cr	52.9406510	$^{37}Cl^{16}O$	52.960817	2700
^{55}Mn	54.9380463	$^{40}Ar^{15}N$	54.962492	2300
		$^{37}Cl^{18}O$	54.965062	2100
		$^{40}Ar^{14}N^{1}H$	54.973282	1600
^{56}Fe	55.9349393	$^{40}Ar^{16}O$	55.957298	2500
^{58}Ni	57.9353471	$^{40}Ar^{18}O$	57.961542	2250
^{59}Co	58.9331978	$^{40}Ar^{18}O^{1}H$	58.969368	1650
^{63}Cu	62.9295992	$^{40}Ar^{23}Na$	62.952153	2800
^{64}Zn	63.9291454	$^{32}S^{16}O_2$	63.961901	2000
		$^{32}S_2$	63.944144	4300
^{69}Ga	68.9255809	$^{37}Cl^{16}O_2$	68.955732	2300
^{74}Ge	73.9211788	$^{40}Ar^{34}S$	73.930251	8200
^{75}As	74.9215955	$^{40}Ar^{35}Cl$	74.931236	7800
^{80}Se	79.9165205	$^{40}Ar_2$	79.924766	9700

[a] Isotopic masses from A.H. Wapstra and K. Bos, *At. Data Nuclear Data Tables*, 19, 175 (1977).
[b] Values are rounded.

Table I. Resolution required to resolve some common polyatomic interferences from a selected group of isotopes.

Isotope	Matrix	Interference	Resolution	Transmission
^{39}K	H_2O	^{38}ArH	5570	6%
^{40}Ca	H_2O	^{40}Ar	199,800	0%
^{44}Ca	HNO_3	$^{14}N^{14}N\,^{16}O$	970	80%
^{56}Fe	H_2O	$^{40}Ar^{16}O$	2504	18%
^{31}P	H_2O	$^{15}N^{16}O$	1460	53%
^{34}S	H_2O	$^{16}O^{18}O$	1300	65%
^{75}As	HCl	$^{40}Ar^{35}Cl$	7725	2%
^{51}V	HCl	$^{35}Cl^{16}O$	2572	18%
^{64}Zn	H_2SO_4	$^{32}S^{16}O^{16}O$	1950	42%
^{24}Mg	Organics	$^{12}C^{12}C$	1600	50%
^{52}Cr	Organics	$^{40}Ar^{12}C$	2370	20%
^{55}Mn	HNO_3	$^{40}Ar^{15}N$	2300	20%

Basic Components of an ICP-Mass Spectrometer



•Most ICP-MS detection systems use electron multipliers, which convert ion currents into electrical signals.

•The magnitude of the electrical signal is proportional to the number of analyte ions present in the sample.

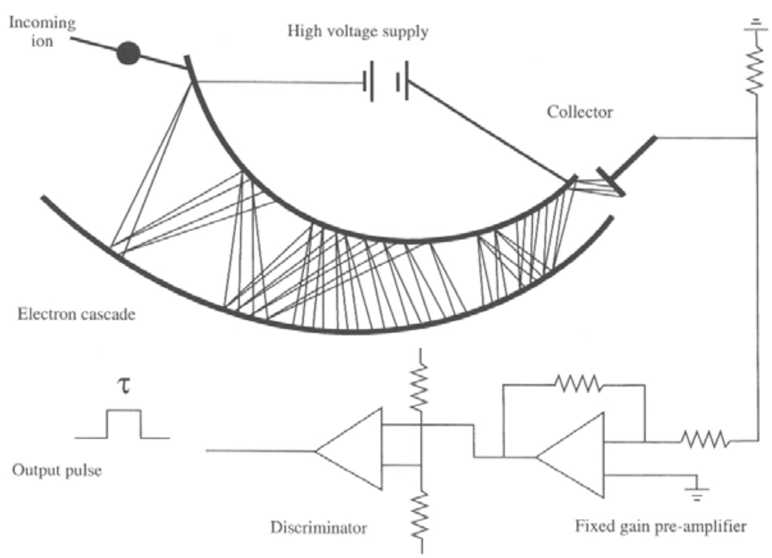


Figure 6.29 Continuous dynode electron multiplier.

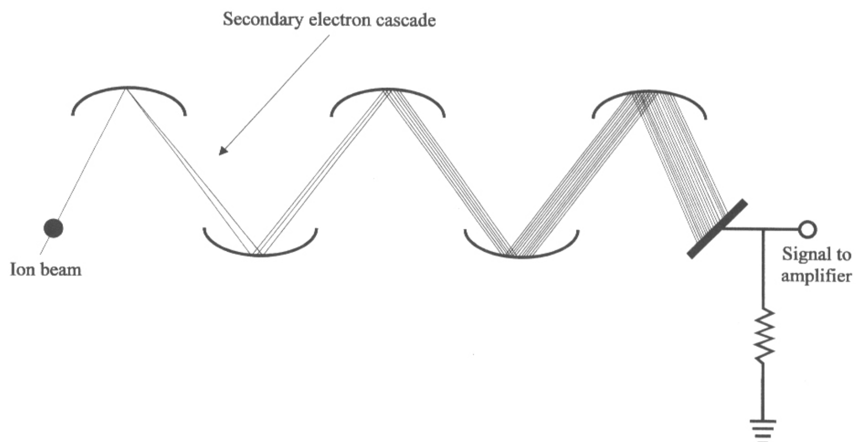


Figure 6.30 Discrete dynode electron multiplier.

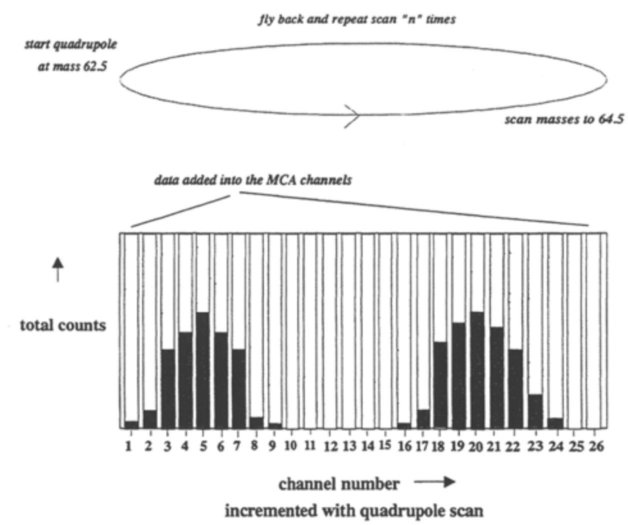
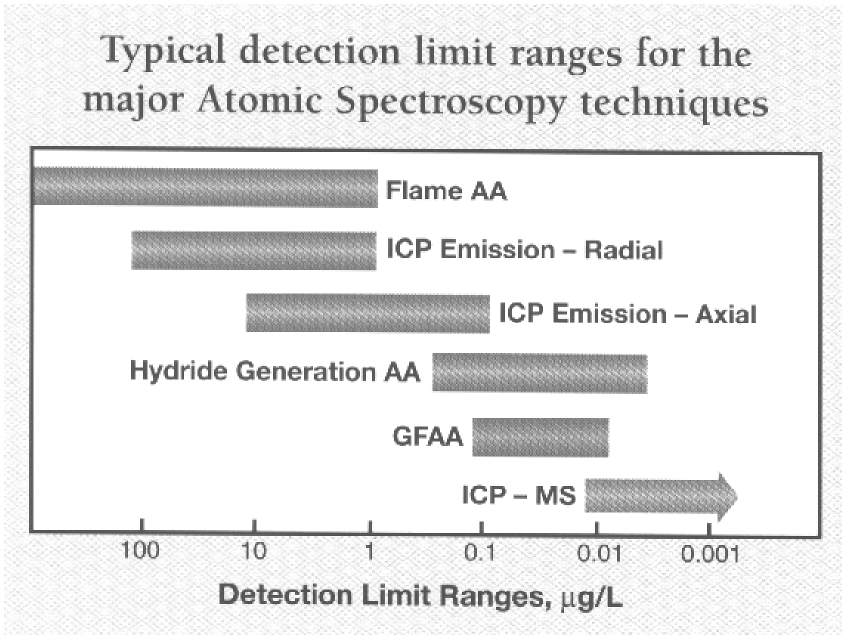


figure 3.1 - MCA Operation



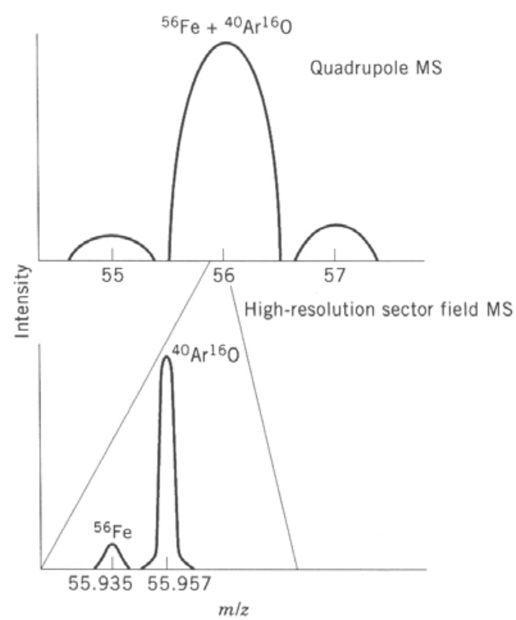
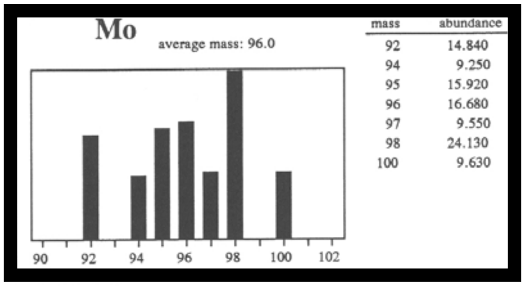
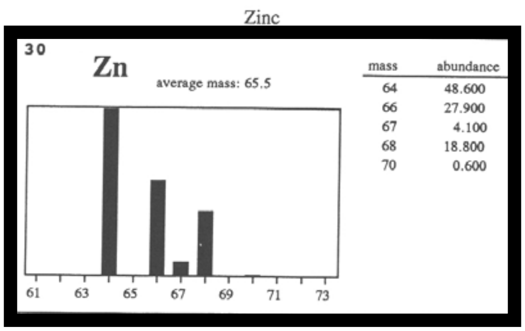


Figure 6.34 Comparison of mass spectra of Fe obtained with a quadrupole MS and with a high-resolution magnetic MS.





Natural Isotopes

- Isotopes are atoms of the same element, which have different masses.
- Isotopes have different masses by having varying numbers of neutrons in their nuclei.
- Isotopes of elements that occur in nature have a constant abundance relative to one another, referred to as their *relative natural abundance*.

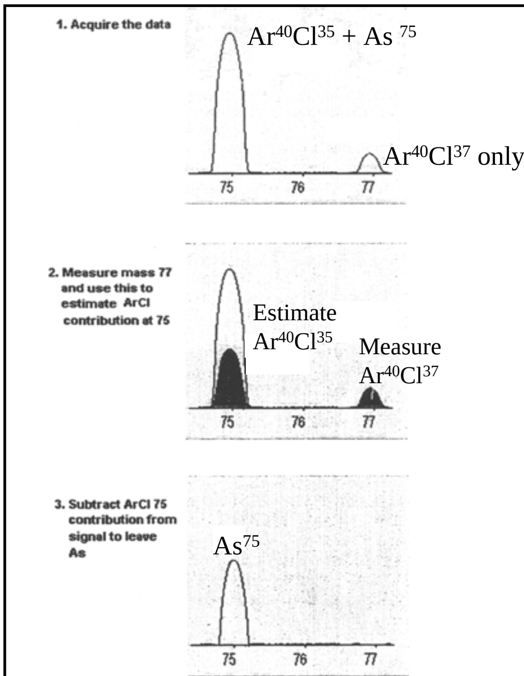


figure 6.1 - Interference correction

Interference Correction Equations

- $Ar^{40}Cl^{35}$ interferes with the analyte of interest, As^{75}, at mass 75.
- Assuming that the other ArCl peak at mass 77 is not itself being interfered with, its peak intensity can be used to estimate the contribution of $Ar^{40}Cl^{35}$ to the peak at mass 75.
- Because Cl^{35} and Cl^{37} are in a fixed natural ratio, the ArCl contribution at mass 75 can be estimated by multiplying the signal at mass 77 by the natural isotope ratio Cl^{35}/Cl^{37}.
- Once the contribution of ArCl at mass 75 is estimated, its intensity can be simply subtracted from the total signal intensity at mass 75, leaving the intensity due to the analyte of interest, As^{75}.

$$As75=I75-(I77*(75.77/24.23))$$

TABLE 7.3 ***Continued***

Mass Element[b]	H_2O (5% HNO_3)	5% H_2SO_4	5% HCl
45 **Sc(100)**	$^{12}C^{16}O^{16}OH$		
46 **Ti(8.01), Ca(0.004)**	$^{14}N^{16}O^{16}$	$\mathbf{^{32}S^{14}N}$	
47 **Ti(7.33)**		$^{33}S^{14}N$	
48 **Ti(73.81),** Ca(0.187)		$^{34}S^{14}N$, $\mathbf{^{32}S^{14}O}$	
49 Ti(5.5)		$\mathbf{^{33}S^{14}O}$	$\mathbf{^{35}Cl^{14}N}$
50 Ti(5.4), Cr(4.34), V(0.25)	$^{36}Ar^{14}N$	$\mathbf{^{34}S^{14}O}$	
51 **V(99.76)**			$^{37}Cl^{14}N$, $\mathbf{^{35}Cl^{16}O}$
52 **Cr(83.79)**	$\mathbf{^{40}Ar^{12}C}$, $^{36}Ar^{16}O$	$^{36}S^{16}O$	$\mathbf{^{35}Cl^{16}OH}$
53 Cr(9.50)			$\mathbf{^{37}Cl^{16}O}$
54 Fe(5.9), Cr(2.36)	$\mathbf{^{40}Ar^{14}N}$		$\mathbf{^{37}Cl^{16}OH}$
55 **Mn(100)**	$^{40}Ar^{14}NH$		
56 **Fe(91.72)**	$\mathbf{^{40}Ar^{14}O}$		
57 Fe(2.11)			
58 **Ni(68.077),** Fe(0.28)			
59 **Co(100)**			
60 Ni(26.223)			
61 Ni(1.14)			
62 Ni(3.634)			
63 **Cu(69.17)**			
64 **Zn(48.63),** Ni(0.926)		$\mathbf{^{32}S^{14}O^{14}O}$, $^{32}S^{32}S$	
65 Cu(30.83)		$^{33}S^{16}O^{16}O$, $^{32}S^{33}S$	
66 Zn(27.9)		$\mathbf{^{34}S^{14}O^{14}O}$, $^{32}S^{34}S$	
67 Zn(4.1)			$\mathbf{^{35}Cl^{16}O^{16}O}$
68 Zn(18.8)	$^{40}Ar^{14}N^{14}N$	$^{36}S^{16}O^{16}O$, $^{33}S^{36}S$	
69 **Ga(60.108)**			$\mathbf{^{37}Cl^{16}O^{16}O}$
70 Ge(21.24), Zn(0.62)	$^{40}Ar^{14}N^{16}O$		
71 Ga(39.89)			$^{36}Ar^{35}Cl$
72 Ge(27.66)	$^{36}Ar^{36}Ar$	$\mathbf{^{40}Ar^{32}S}$	
73 Ge(7.72)		$^{40}Ar^{33}S$	$^{36}Ar^{37}Cl$
74 **Ge(35.94),** Se(0.89)	$^{36}Ar^{38}Ar$	$\mathbf{^{40}Ar^{34}S}$	
75 **As(100)**			$\mathbf{^{40}Ar^{35}Cl}$
76 Ge(7.44), Se(9.36)	$\mathbf{^{36}Ar^{40}Ar}$	$^{40}Ar^{36}S$	
77 Se(7.63)	$^{36}Ar^{40}ArH$		$\mathbf{^{40}Ar^{37}Cl}$
78 Se(23.77), Kr(0.35)	$\mathbf{^{38}Ar^{40}Ar}$		
79 **Br(50.69)**	$^{38}Ar^{40}ArH$		
80 **Se(49.61),** Kr(2.25)	$\mathbf{^{40}Ar^{40}Ar}$	$\mathbf{^{32}S^{16}O^{16}O^{16}O}$	
81 Br(49.46)	$\mathbf{^{40}Ar^{40}ArH}$	$\mathbf{^{32}S^{16}O^{16}O^{16}OH}$	
82 Kr(11.61), Se(8.74)	$^{40}Ar^{40}ArH_2$	$\mathbf{^{34}S^{16}O^{16}O^{16}O}$	
83 Kr(11.51)		$\mathbf{^{34}S^{16}O^{16}O^{16}OH}$	
84 **Kr(57.03),** Sr(0.56)		$^{36}S^{16}O^{16}O^{16}O$	

[a]Most abundant species designated in boldface.
[b]Percentage natural abundance given in parentheses.

TABLE 7.5 Calcium Oxide and Hydroxide Species and Other Potential Interferences in the Mass Region for Ni Determination

Mass	Element[a]	Interferences
56	Fe(91.72)	^{40}ArO, ^{40}CaO
57	Fe(2.11)	$^{40}ArOH$, $^{40}CaOH$
58	Ni(68.27), Fe(0.28)	^{42}CaO, NaCl
59	Co(100)	^{43}CaO, $^{42}CaOH$
60	Ni(26.223)	$^{43}CaOH$, ^{44}CaO
61	Ni(1.14)	$^{44}CaOH$
62	Ni(3.634)	^{46}CaO, Na_2O, NaK
63	Cu(69.17)	$^{46}CaOH$, $^{40}ArNa$
64	Ni(0.926), Zn(48.63)	$^{32}SO_2$, $^{32}S_2$, ^{48}CaO
65	Cu(30.83)	$^{32}S^{32}S$, $^{33}SO_2$, $^{48}CaOH$

[a]Natural abundances in parentheses.

Advantages of ICP-MS

- Detection limits are 10-100 times superior to those of ICP-AES.
- Ability to provide elemental isotopic ratio information.
- Roughly 25 elements can be analyzed in duplicate and with good precision in 1-2 minutes.
- Large linear dynamic working range.
- The effective combination of differing types of ICP-MS instruments coupled with the many varied types of sample introduction allow for customization of techniques for a specific sample type or form of analyte.

Disadvantages of ICP-MS

- The lower-cost ICP-MS systems utilize single-quadrupole mass analyzer systems, which are inherently sequential systems, and have relatively low mass resolution.
- Higher cost than ICP-AES, with a much lower body of knowledge and understanding available than the other technique.
- Elements such as Ca and Fe are difficult to determine by conventional Ar ICP-MS because of mass spectral interferences by argides.
- If Ni cones are used, can have as much as 5 ppt of nickel being detected as orifice ions. This can be alleviated by switching to more expensive Pt cones.
- Generally requires a clean room environment for ultra-low detection limits.

Disadvantages of ICP-MS

- An outstanding ICP-AES instrument offers a long-term RSD of less than 1% compared to less than 4% for most ICP-MS systems.
- The presence of oxides and doubly-charged ions in the plasma deteriorates the quantitative capability of ICP-MS in ultratrace analysis.
- ICP-MS instruments are more susceptible to instability than ICP-AES intruments when running samples with higher levels of total dissolved solids.
- The relatively cooler sampler and skimmer cones provide direct contact points for sample deposition from the plasma, and can become clogged over time when difficult matrices are analyzed.

Needed Improvements in ICP-MS

Compared to other methods of elemental analysis, ICP-MS comes closer to being the ideal method, but still requires much work in the following areas:

- Speciation approaches must be devised or refined.
- Matrix interferences must be better understood and controlled.
- Less expensive instruments for the elimination of spectral interferences must be developed.
- Alternative sources and mass spectrometers should be considered and evaluated.
- Sample-introduction efficiency must be improved.
- Sample-utilization efficiency ought to be raised.
- Precision must be increased.
- Instrumentation should be reduced in price and made simpler to use.

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