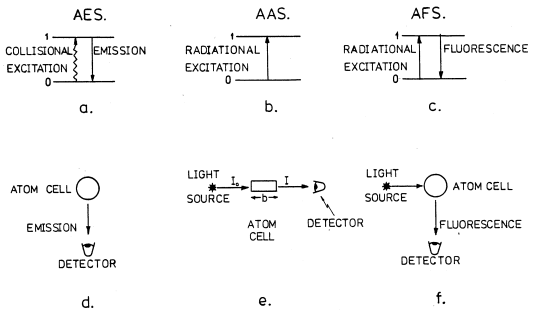
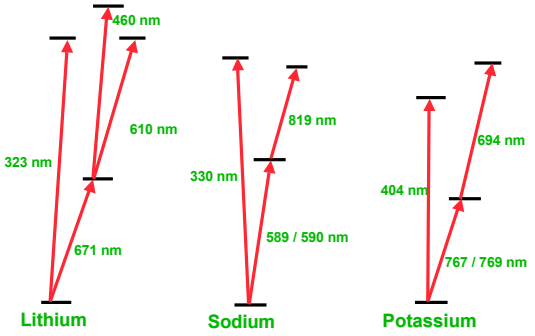
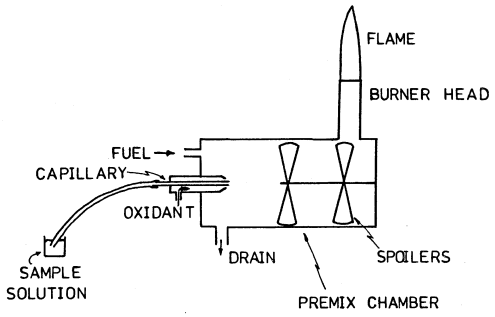
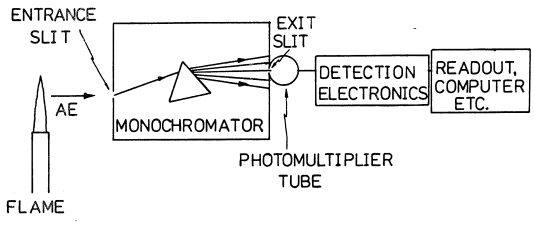


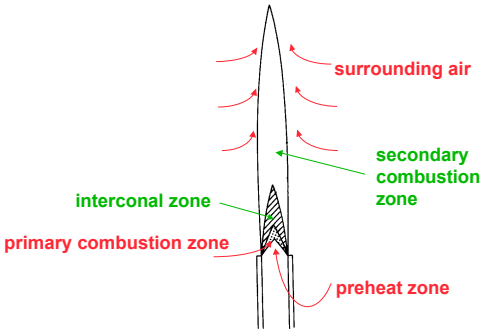
Partial Energy Level Diagrams







Gas Mixtures	Maximum Temperatures, °C
Air-Coal Gas	1825
Air-Propane	1725
Air-Hydrogen	2045
Air-Acetylene	2250
Oxygen-Hydrogen	2677
Oxygen-Acetylene	3060
Nitrous Oxide-Acetylene	2955
Argon-Hydrogen-Entrained Air	1577



Maxwell-Boltzmann Equation:

$$\frac{N_1}{N_0} = \frac{g_1}{g_0} e^{-(E_1 - E_0)/kT}$$

	(nm)	Energy (eV)	g_1/g_0	N_1/N_0 2000 K	3000 K	4000 K
Cs	852.1	1.46	2	4.44×10^{-4}	7.24×10^{-3}	2.98×10^{-2}
Na	589.0	2.11	2	9.86×10^{-6}	5.88×10^{-4}	4.44×10^{-3}
Ca	422.7	2.93	3	1.21×10^{-7}	3.69×10^{-5}	6.04×10^{-4}
Zn	213.8	5.80	3	7.29×10^{-15}	5.38×10^{-10}	1.48×10^{-6}

The 228.8 nm line of Cadmium corresponds to the $^1S_0$ - $^1S_1$ transition.

Calculate the ratio of $\frac{N_1}{N_0}$ in air/C_2H_2

The temperature is 2250 °C or 2523 K

Degeneracy ratio of the two levels is:

g_1/g_0 = [2(1)+1]/[2(0)+1] =3/1

$$\frac{N_1}{N_0} = \frac{g_1}{g_0} e^{-(E_1 - E_0)/kT}$$

First find the frequency of light at 228 nm so that the energy difference can be calculated from E = hν

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{10}\, cm\ \text{sec}^{-1}}{2.288 \times 10^{-5}\, cm}$$

$$= 1.310 \times 10^{15}\ \text{sec}^{-1}$$

$$\frac{N_1}{N_0} = \frac{g_1}{g_0} e^{-(E_1 - E_0)/kT}$$

Find the energy difference between the levels:

$$E_1 - E_0 = h\nu$$

$$= (6.626 \times 10^{-27}\ erg\text{-}\sec)(1.310 \times 10^{15}\ \sec^{-1})$$

$$= 8.682 \times 10^{-12}\ erg$$

Find the ratio:

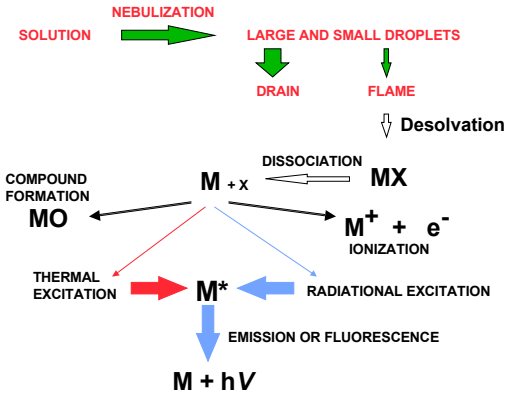
$$\frac{N_1}{N_0} = \frac{g_1}{g_0} e^{-(E_1 - E_0)/kT}$$

$$= \frac{3}{1} e^{\left[\frac{8.682 \times 10^{-12}\ erg}{(1.3805 \times 10^{-16}\ erg\ K^{-1})(2523\ K)}\right]}$$

$$= 3e^{-24.93} = 4.5 \times 10^{-11}$$

SI Units

$$1\ Joule = 10^7\ ergs$$



Types of Interferences

- chemical
- ionization
- spectral
- background
- excitation

- **chemical** - formation of stable compounds
  - hotter flame, releasing agent, separation
- **ionization** - ionization suppressant
- **spectral** - atomic and molecular
  - improve spectral resolution of spectrometer
- **background** - flame gas or matrix emission
  -matrix match, resolve spectrally, modulation
- **excitation**- temp. change by matrix or solvent
  - standard addition, matrix match

analyte, aluminum ionizes in flame

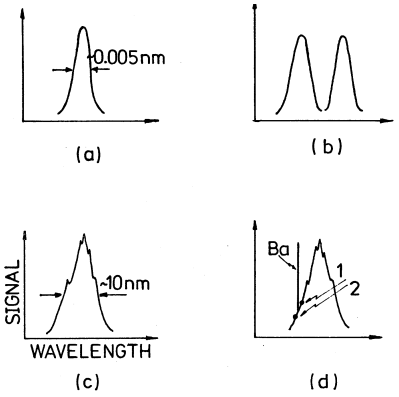
$$Al \Leftrightarrow Al^{+} + e^{-}$$

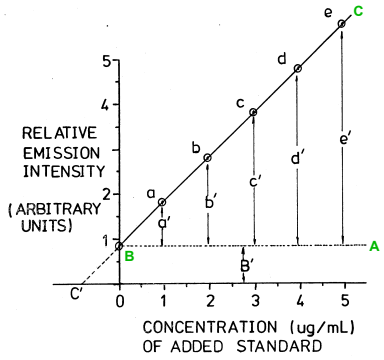
ionization suppressant sodium

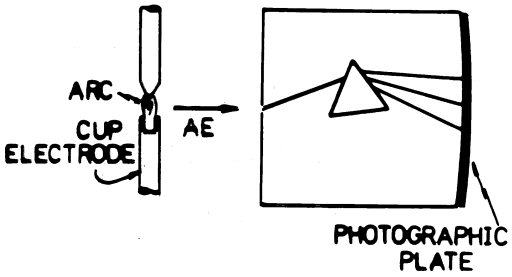
at 100 - 1000 $\mu g\ l^{-1}$

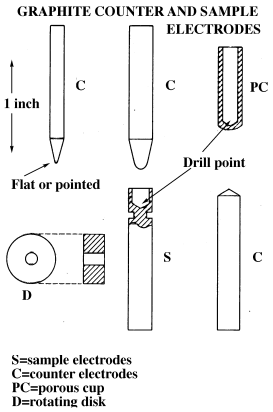
$$Na \Leftrightarrow Na^{+} + e^{-}$$

forces equilibrium of Al to left

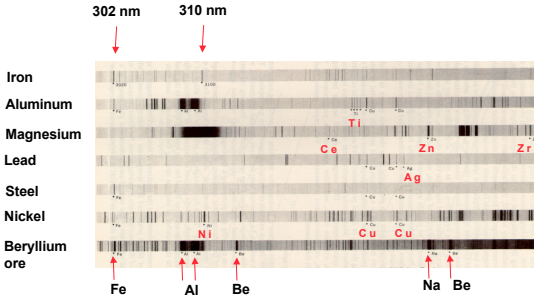


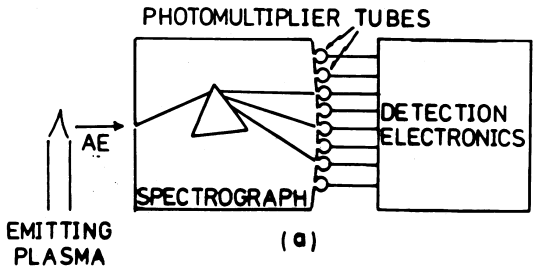






Photographic plate -UV spectrum





$$Emission = \left(\frac{c\Phi\varepsilon\beta}{e_f Q}\right) L \left[h\nu_0 A_{21} \left(\frac{g_1}{g_2}\right) e^{\frac{-E_{21}}{kT}} \right] f(\theta,\lambda) g(\lambda)$$

c = concentration, L = path length

$h\nu_0$ = energy of photon

A_{21} = Einstein coefficient

Φ = rate of sample introduction

ε = efficiency of sample introduction

β = efficiency of atomization

$$Emission = \left(\frac{c\Phi\varepsilon\beta}{e_f Q}\right) L \left[h\nu_0 A_{21} \left(\frac{g_1}{g_2}\right) e^{\frac{-E_{21}}{kT}} \right] f(\theta,\lambda) g(\lambda)$$

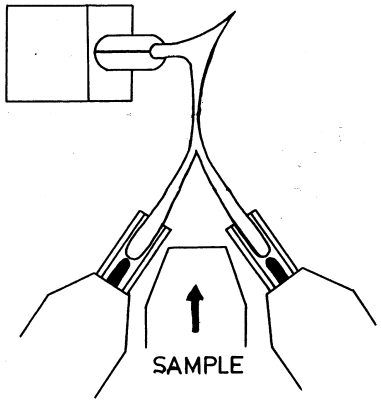
Q = flow rate of flame gases

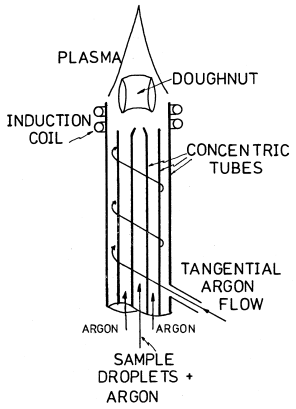
e_f = increased volume on combustion

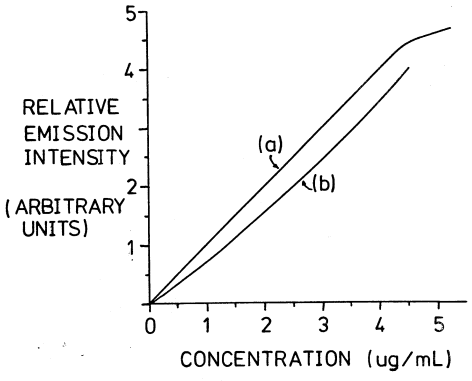
θ = solid angle of light collection

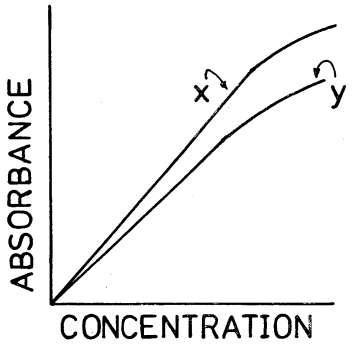
λ = wavelength

g = efficiency of detector

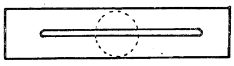

SAMPLE


PLASMA
DOUGHNUT
INDUCTION COIL
CONCENTRIC TUBES
TANGENTIAL ARGON FLOW
ARGON
ARGON
SAMPLE DROPLETS + ARGON


5
4
2
1
RELATIVE EMISSION INTENSITY
(ARBITRARY UNITS)
(a)
(b)
0
1
2
3
4
5
CONCENTRATION (ug/mL)

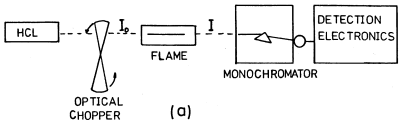


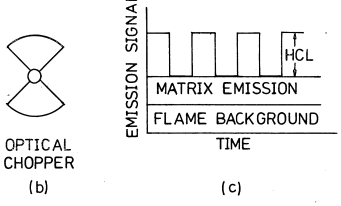
BURNER HEADS

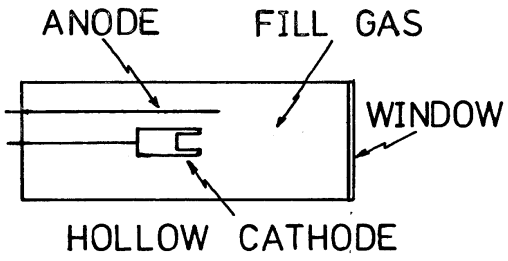


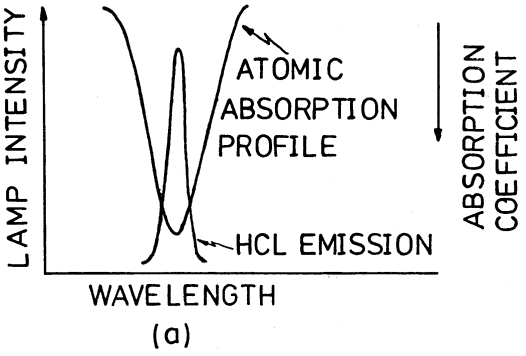
ATOMIC ABSORPTION

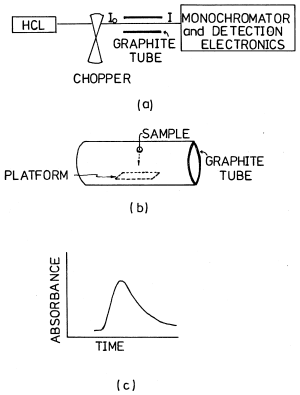
EMISSION OR FLUORESCENCE






ANODE
FILL GAS
WINDOW
HOLLOW CATHODE


LAMP INTENSITY
ATOMIC
ABSORPTION
PROFILE
HCL EMISSION
ABSORPTION
COEFFICIENT
WAVELENGTH
(a)

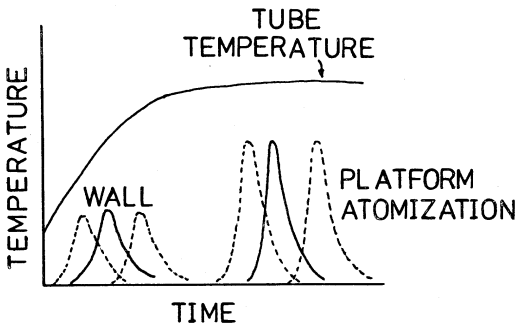

HCL
I_o
I
MONOCHROMATOR
and DETECTION
ELECTRONICS
GRAPHITE
TUBE
CHOPPER
(a)
SAMPLE
PLATFORM
GRAPHITE
TUBE
(b)
ABSORBANCE
TIME
(c)

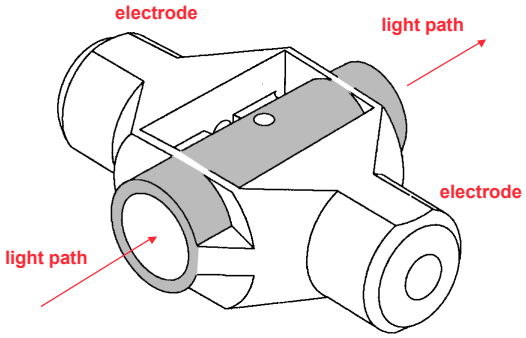
Advantages of graphite furnace

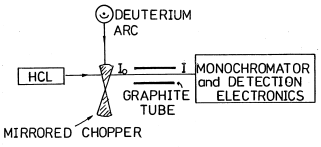
- long residence time compared to flame
- micro samples
- electrically heated

Features of graphite furnace

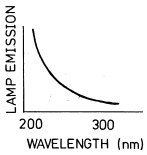
- matrix modifiers
- L'vov platform
- size: 20-30 mm x 6-8 mm
- blackbody radiation
- rapid heating
- absolute analysis



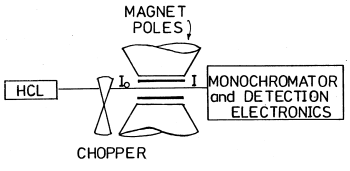

electrode
light path
electrode
light path


DEUTERIUM ARC
HCL
I_o
I
MONOCHROMATOR and DETECTION ELECTRONICS
GRAPHITE TUBE
MIRRORED CHOPPER

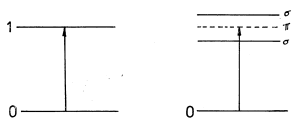
(a)


LAMP EMISSION
200
300
WAVELENGTH (nm)

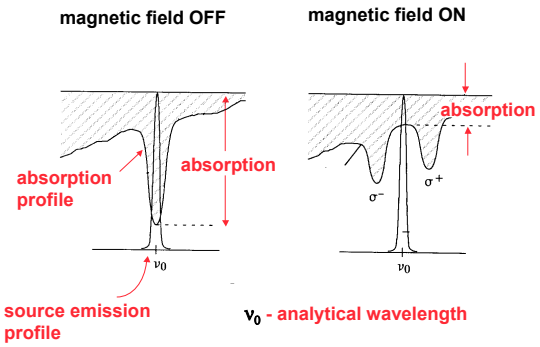
(b)

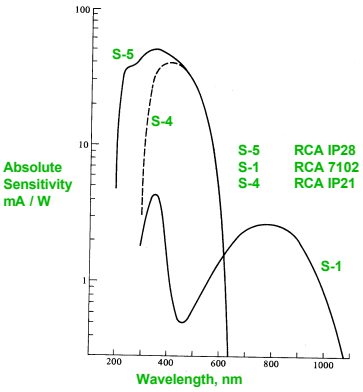

MAGNET POLES
HCL
I_o
I
MONOCHROMATOR and DETECTION ELECTRONICS
CHOPPER

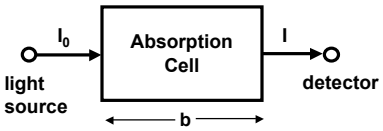
(a)


1
0
σ
π
σ
0

(b) (c)







$$\text{Transmittance } T = \frac{I}{I_0}$$

$$\%T = \frac{I}{I_0} \times 100$$

- Fraction of light transmitted decays exponentially with both
- path length:

$$T = \frac{I}{I_0} = 10^{-kb}$$

k is a constant

- and concentration:

$$T = \frac{I}{I_0} = 10^{-k'c}$$

- or:

$$\lg T = \lg \frac{I}{I_0} = -kb$$

- and:

$$\lg T = \lg \frac{I}{I_0} = -k'c$$

- combination of these two:

$$\lg T = \lg \frac{I}{I_0} = -abc$$

- define:

Absorbance, A = - lg T

- which results in Beer's law:

$$A = -\lg T = \lg \frac{I_0}{I} = abc$$

- and:

$$A = 2.00 - \log \%T$$

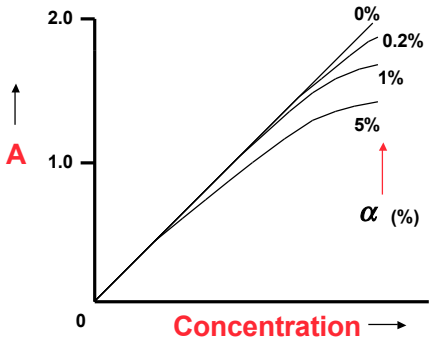
Instrumental Limitations of Beer's law

- Stray Light

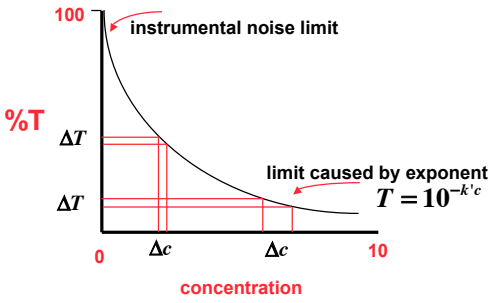
$$A = \lg \frac{I_0 + \alpha}{I + \alpha} = \lg \frac{1 + \alpha}{10^{-A_0} + \alpha}$$

- α - fraction of light that is not absorbable
- A_0 - true or ideal absorbance

Deviations due to α



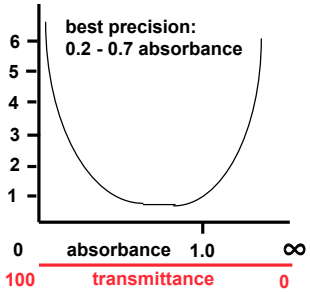
Effect of Instrumental noise on precision of analyses

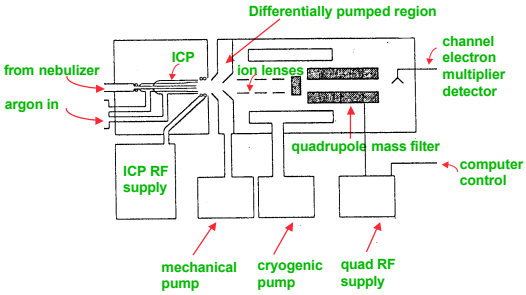


Effect of Instrumental noise on precision of analyses

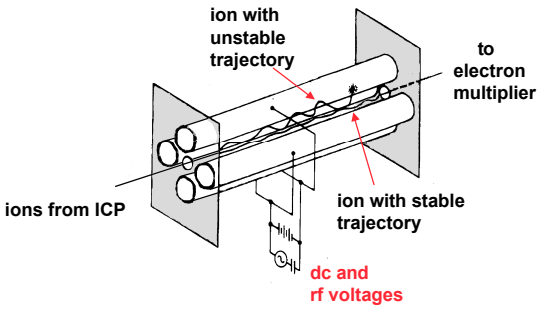
relative concentration uncertainty, %

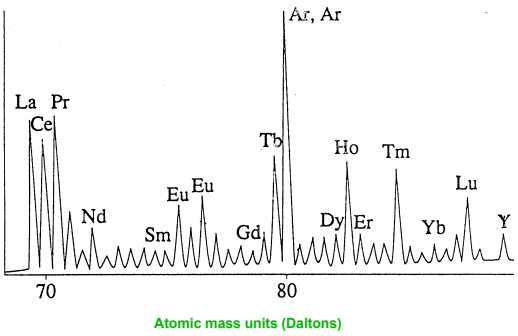
$$\frac{\Delta_c}{C} \times 100$$





Quadrupole Mass Spectromter





SPECTRAL INTERFERENCES in ICP-MS

- Polyatomic ions from mineral acids
- Diatomic ions from plasma and carrier gases
- Oxides of matrix elements

ICP-MS interferences

Acid	Ion	m/z	Overlap
HNO_3	N^+	14	
	ArN^+	54	$^{54}Fe^+$
			$^{54}Cr^+$
$HClO_4$	Cl^+	35.37	
	ClO^+	51	$^{51}V^+$
		53	$^{53}Cr^+$
H_2SO_4	S^+	32,33, 34	
	SO^+	48	$^{48}Ti^+$
		49	$^{49}Ti^+$
		50	$^{50}Cr^+$

ICP-MS interferences

plasma ion	m/z	Overlap
N_2^+	28	$^{28}Si^+$
NO^+	30	$^{30}Si^+$
O_2^+	32	$^{32}S^+$
	34	$^{34}S^+$
ArO^+	52	$^{52}Cr^+$
	54	$^{54}Cr^+$
	54	$^{54}Fe^+$
Ar_2^+	72	$^{72}Ge^+$
	74	$^{74}Se^+$

ICP-MS interferences

Analyte ion	m/z	Interferant
Ni^+	58	$^{42}Ca^{16}O$
	60	$^{44}Ca^{16}O$
	61	$^{44}Ca^{16}OH$
Cu^+	63	$^{46}Ca^{16}OH$
Co^+	59	$^{43}Ca^{16}O$
Zn^+	64	$^{48}Ca^{16}O$
Cd^+	111	$^{94}Zr^{16}OH$
Sb^+	123	$^{91}Zr^{16}O_2$