Atomic absorption and atomic emission spectrometry

Atomic absorption spectrometry

Method is based on measurement of light absorbance of a certain wavelength by analyte atoms

Atoms are formed during preliminary atomization

Used for determination of elements (mainly metals) in samples

More than 70 metals can be analyzed by this method

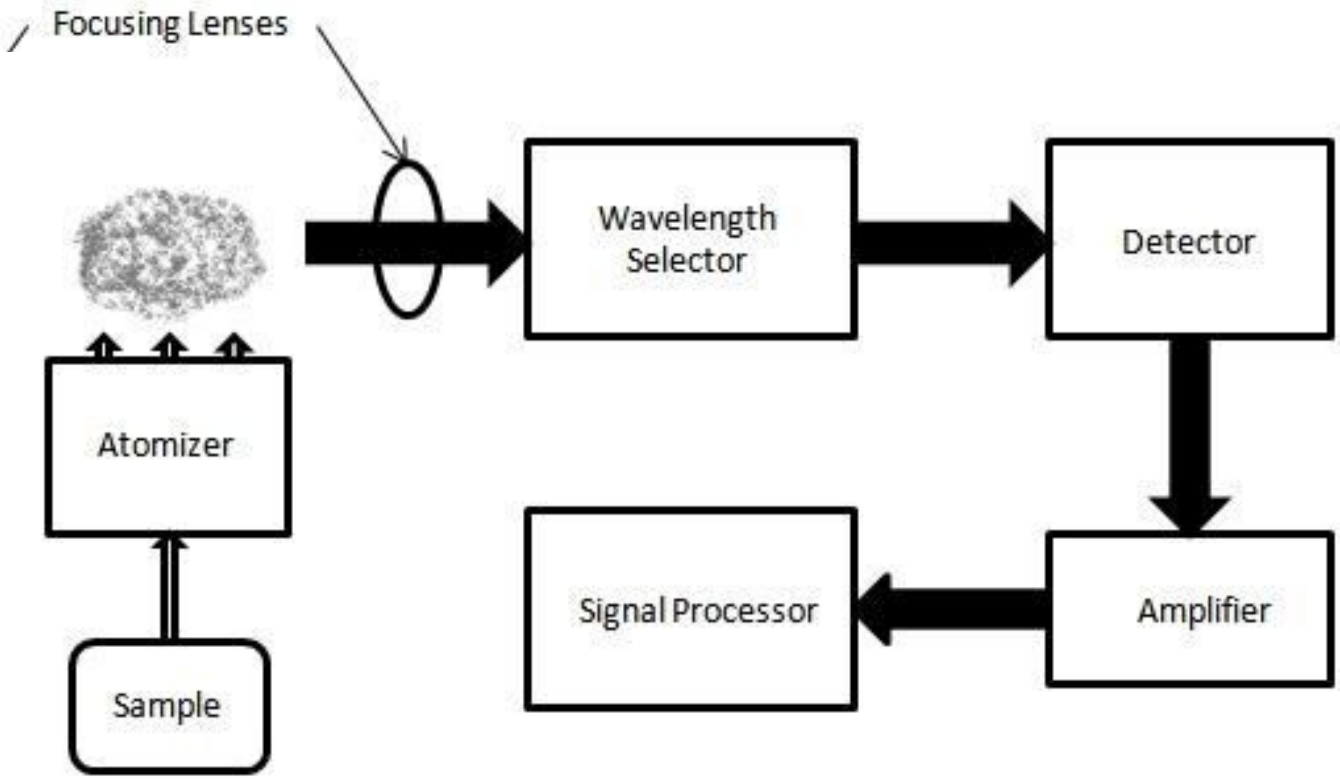
Atomic emission spectrometry

Method is based on a measurement of intensity of emission of atoms of elements in excited state formed due to atomization

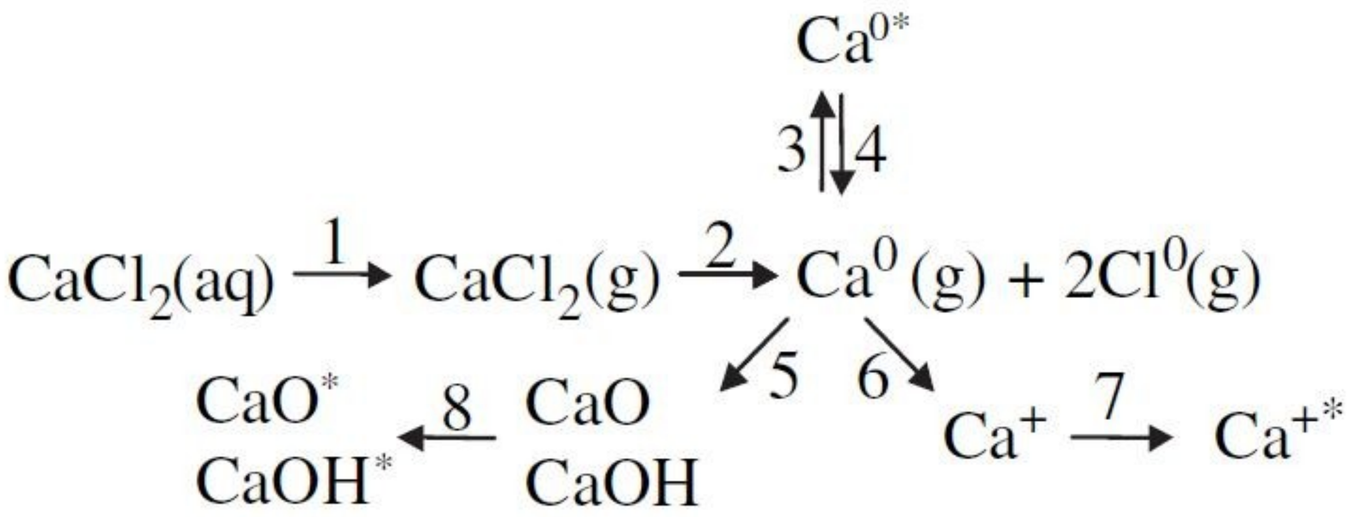
Method does not require light source

Allows identification of elements in samples

Atomic emission spectrometry - principle



Processes running at atomization



1 = Desolation
2 = Dissociation
3 = Excitation
4 = Emission

5 = Oxide & hydroxide formation
6 = Ionization of atom
7 = Excitation of ion
8 = Excitation of oxide & hydroxide

Absorption and emission

Emission

$$M^* \rightarrow M + h\nu$$

Methods of atomization

Flame – sample is injected into a flame, the type of which is chosen depending of the nature of analyte

Graphite furnace (flameless) – atomization goes under the effect of high temperature

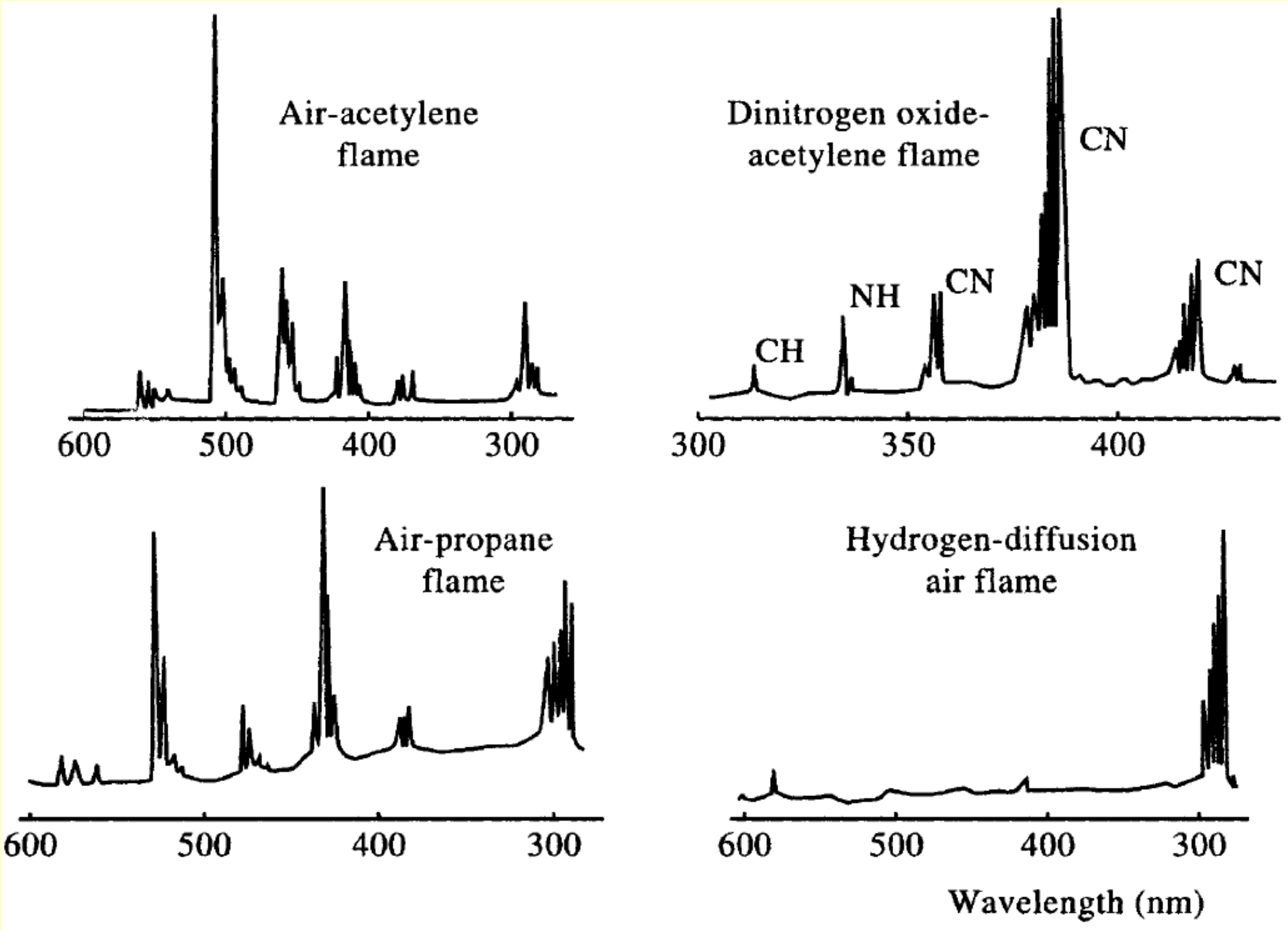
In the first case, just 0.1% of the total element content in solution is atomized, while the flameless atomization allows 100% atomization rate leading to a 3 order of magnitude higher sensitivity

Selection of a flame

Table 7 *Characteristics of some common flames*

Flame	*Flow rate* ($l\ min^{-1}$)		*Temperature (K)*	*Burning velocity* ($cm\ min^{-1}$)
	Fuel gas	*Oxidant*		
Air-propane	0.3–0.45	8	2200	45
Air-acetylene	1.2–2.2	8	2450	160
Air-hydrogen	6	8	2300	320
N_2O-propane	4	10	2900	250
N_2O-acetylene	3.5–4.5	10	3200	285
N_2O-hydrogen	10	10	2900	380

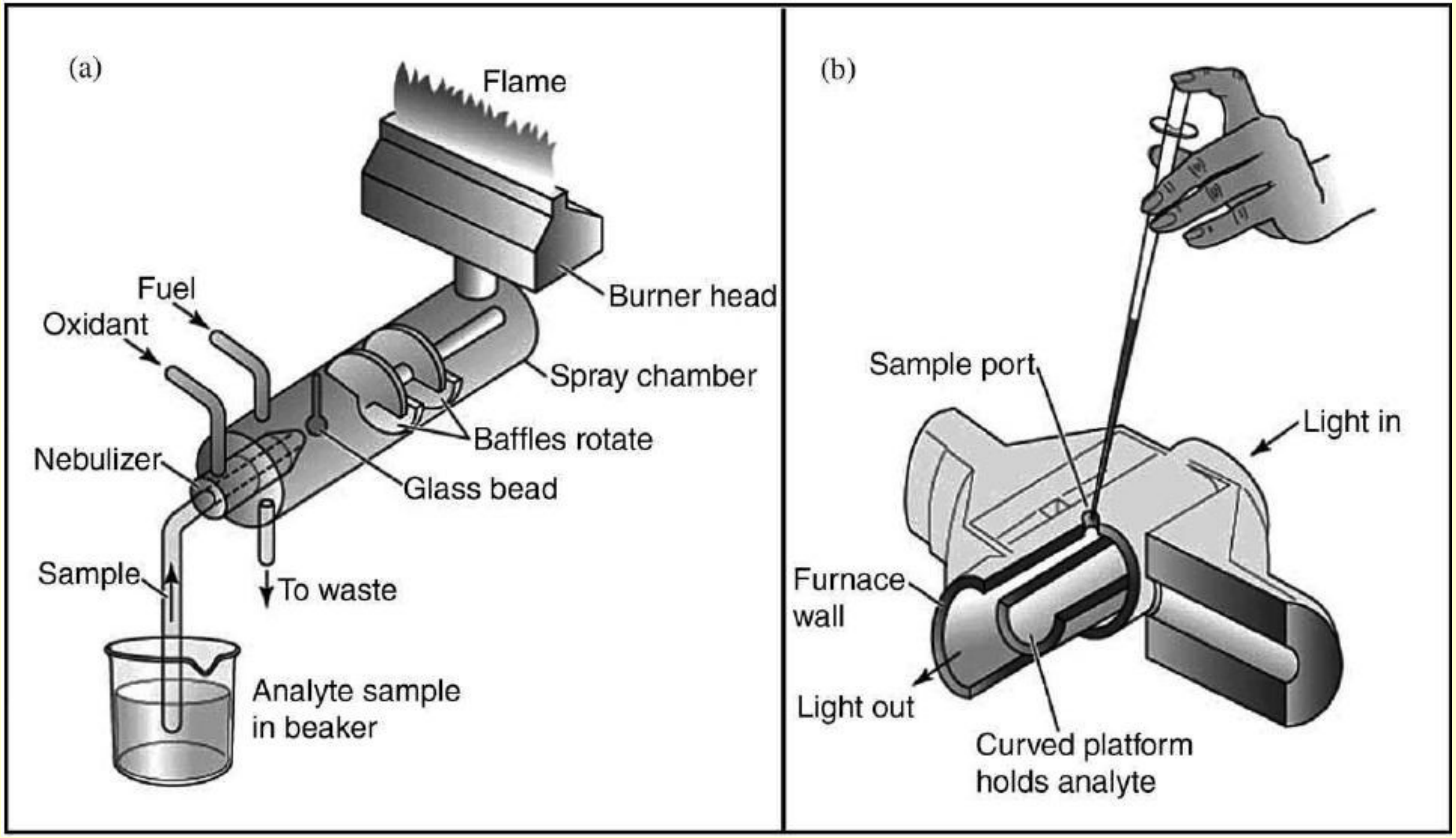
Selection of a flame – emission spectra of different flames



Spectral overlaps in AAS

Source[a]	Emission wavelength (nm)	Analyte	Absorption line (nm)	Separation (nm)
Al	308.215	V	308.211	0.004
Sb	217.023	Pb	216.999	0.024
Sb	217.919	Cu	217.894	0.025
Sb	213.147*	Ni	231.095	0.052
Sb	323.252	Li	323.261	0.009
As	228.812	Cd	228.802	0.010
Cu	324.754*	Eu	324.753	0.001
Ga	403.298*	Mn	403.307	0.009
Ge	422.657	Ca	422.673	0.016
I	206.163	Bi	206.170	0.007
Fe	271.903*	Pt	271.904	0.001
Fe	279.470	Mn	279.482	0.012
Fe	285.213	Mg	285.213	<0.001
Fe	287.417*	Ga	287.424	0.007
Fe	324.728	Cu	324.754	0.026
Fe	327.445	Cu	327.396	0.049
Fe	338.241	Ag	338.289	0.048
Fe	352.424	Ni	352.454	0.030
Fe	396.114	Al	396.153	0.039
Fe	460.765	Sr	460.733	0.032
Pb	241.173	Co	241.162	0.011
Pb	247.638	Pd	247.643	0.005
Mn	403.307*	Ga	403.298	0.009
Hg	253.652*	Co	253.649	0.003
Hg	285.242	Mg	285.213	0.029
Hg	359.348	Cr	359.349	0.001
Ne	359.352	Cr	359.349	0.003
Si	250.690*	V	250.690	<0.001
Zn	213.856*	Fe	213.859	0.003

Atomic absorption spectroscopy - analysis



Atomization (ionization in inductively coupled plasma

Plasma – ionized gas (argon) at high temperatures (more than 8000 K) and under strong magnetic field

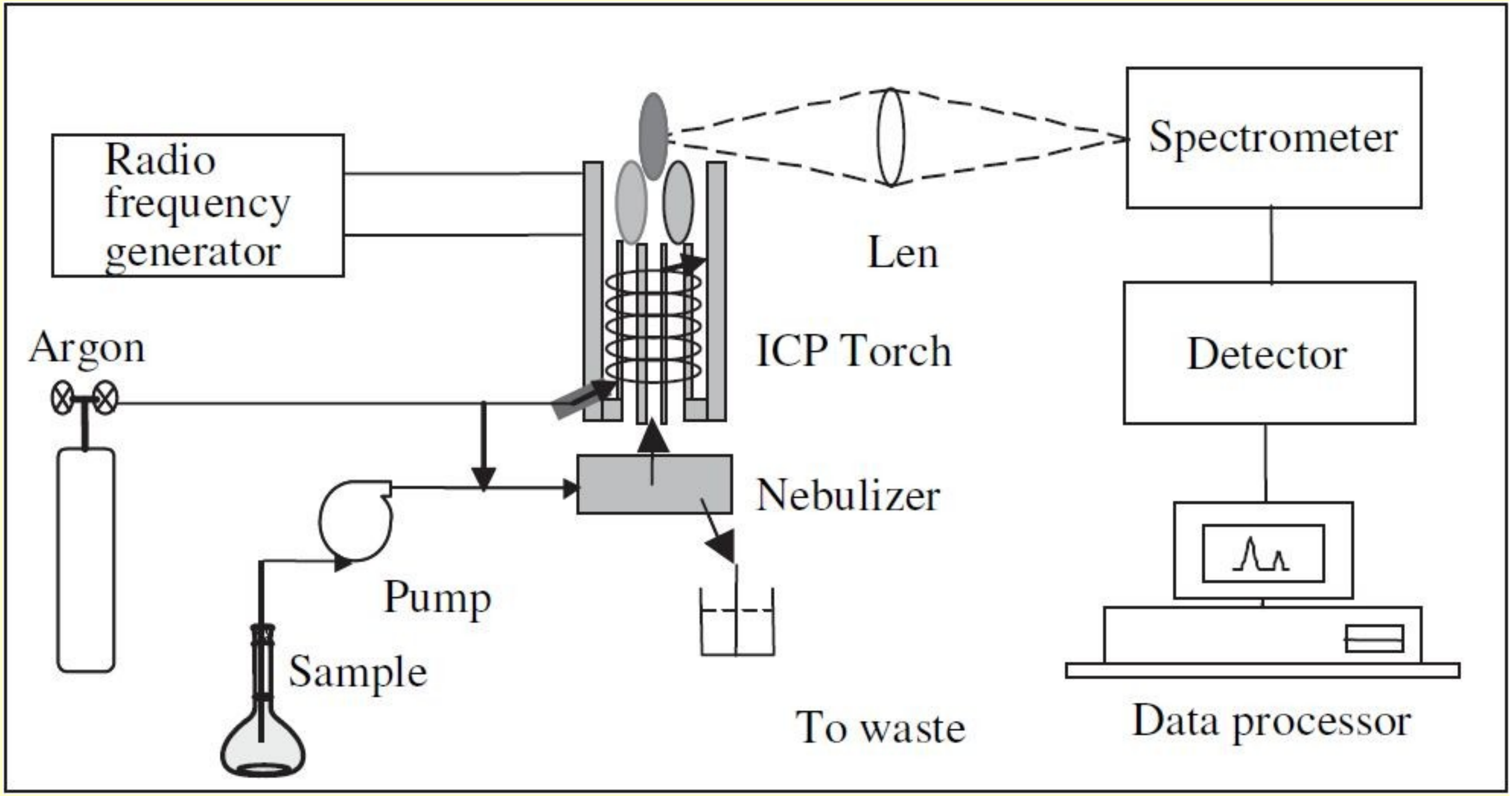
$$\mathrm{Ar} \rightarrow \mathrm{Ar}^{+} + \mathrm{e}^{-}$$

Average energy of argon ions is 15.76 eV that is sufficient for efficient ionization of most metals

Most ionized metals emit light in UV range which is registered by UV spectrometer

Theoretically this method allows simultaneous determination of all elements that makes it the most powerful method of element analysis

ICP/OES - equipment



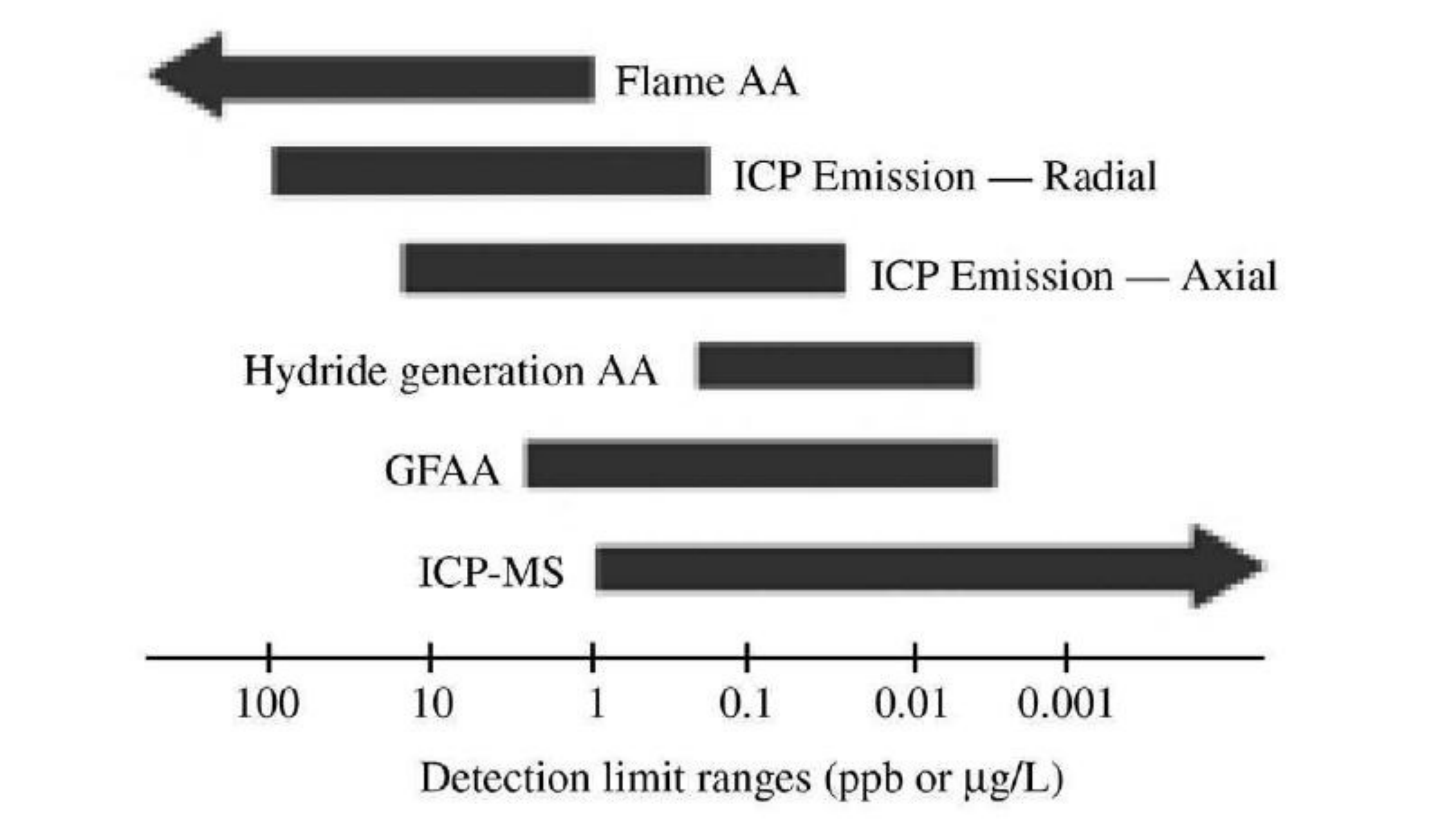
Target wavelengths and detection limits for selected elements by ICP/OES

Detection Element	Wavelength[a] (nm)	Estimated IDL[b] (µg/L)
Aluminum	308.215	30
Antimony	206.833	21
Arsenic	193.696	35
Barium	455.403	0.87
Beryllium	313.042	0.18
Boron	249.678x2	3.8
Cadmium	226.502	2.3
Calcium	317.933	6.7
Chromium	267.716	4.7
Cobalt	228.616	4.7
Copper	324.754	3.6
Iron	259.940	4.1
Lead	220.353	28
Lithium	670.784	2.8
Magnesium	279.079	20
Manganese	257.610	0.93
Mercury	194.227x2	17
Molybdenum	202.030	5.3
Nickel	231.604x2	10
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	50
Silica (SiO_2)	251.611	17
Silver	328.068	4.7
Sodium	588.995	19
Strontium	407.771	0.28
Thallium	190.864	27
Tin	189.980x2	17
Titanium	334.941	5.0
Vanadium	292.402	5.0
Zinc	213.856x2	1.2

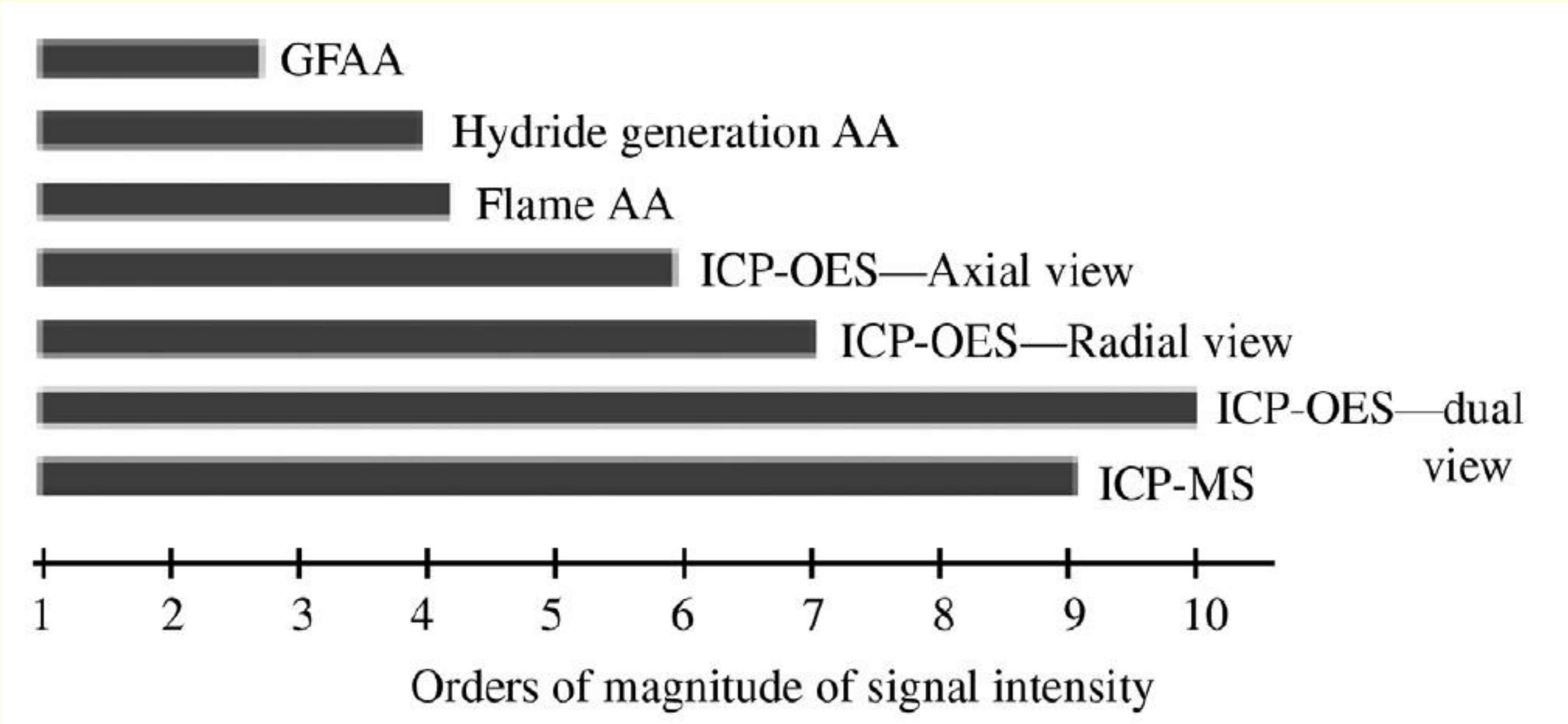
ICP/OES – spectral interferences

Analyte	Wavelength (nm)	Interferant[a,b] Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

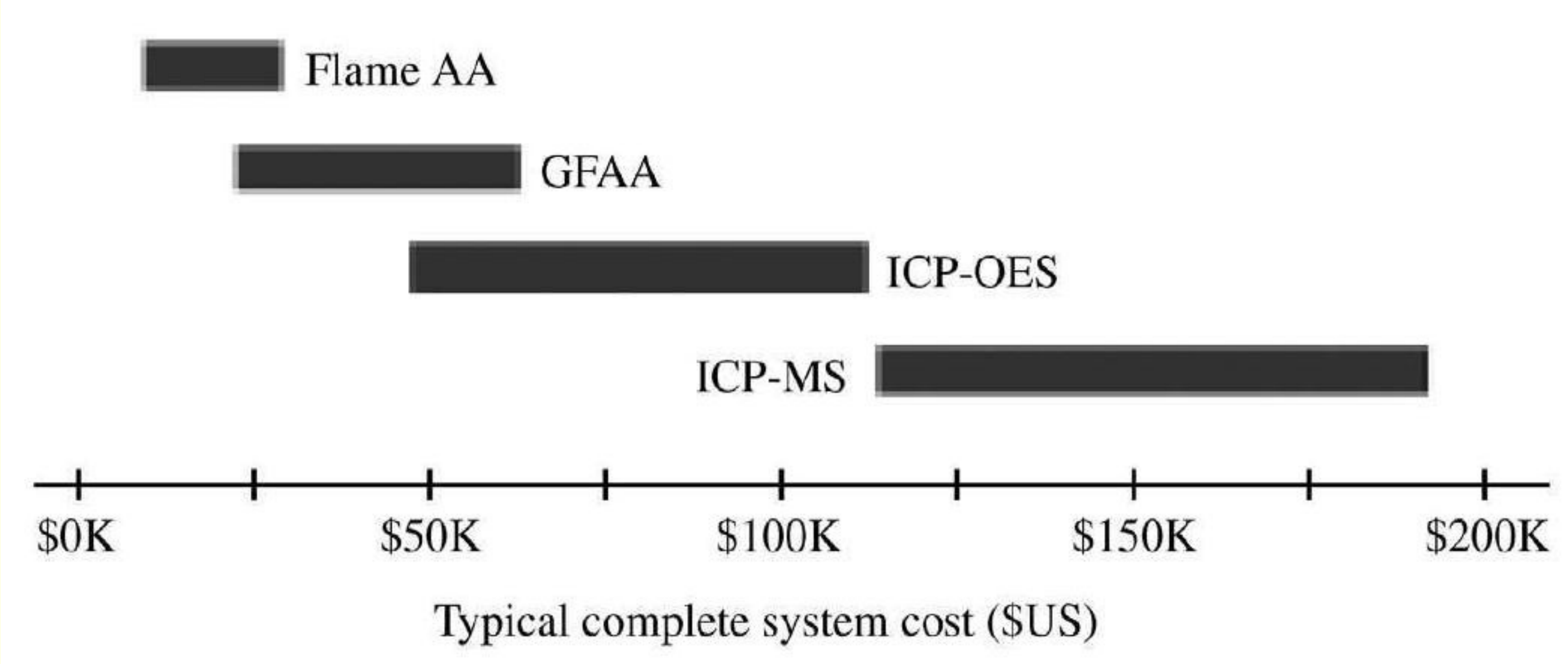
Method selection based on detection limits



Method selection based on analytical range width



Method selection based on system cost



Method selection based on speed and detection limit