Atomic Spectroscopy

Atomic spectroscopy measures the spectra of elements in their atomic/ionized states.

Atomic spectrometry, exploits quantized electronic transitions characteristic of each individual element in their atomic or ionic state.

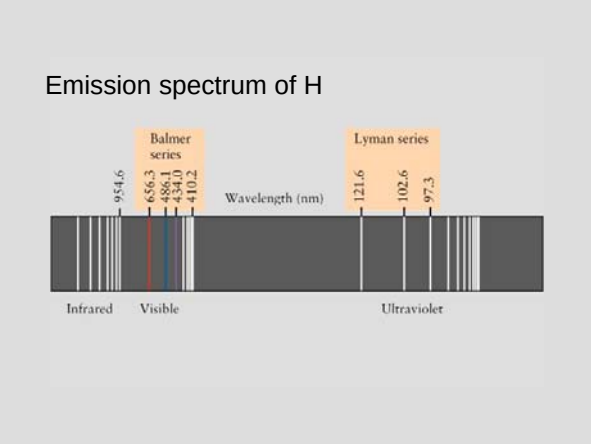
Transitions occur in the UV, VIS and NIR regions of the electromagnetic spectrum.

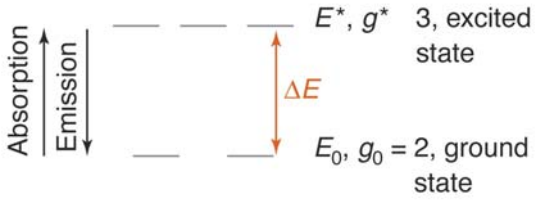
It is valence electronic transitions of atoms/ions that is being exploited.

This requires each atom to be isolated from all others, so the transitions are not perturbed by neighboring atoms or by bonding effects.

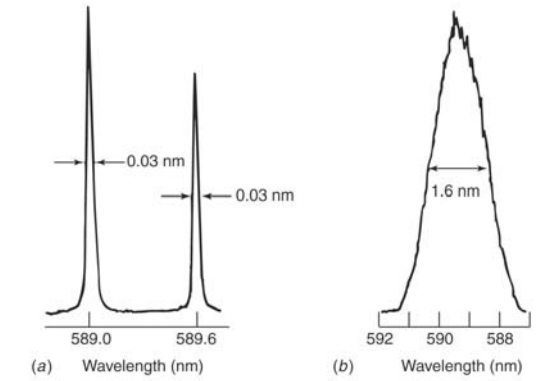
Otherwise the resulting spectra are representative more of molecules or molecular fragments than of atoms themselves.

Atomic spectral profiles are very narrow.

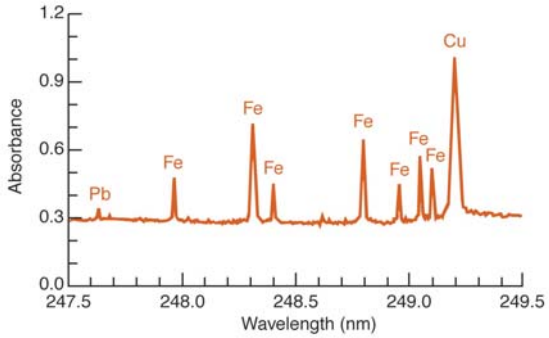


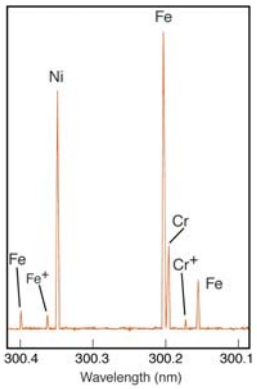


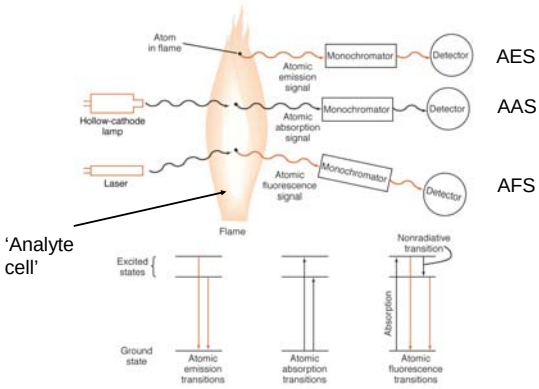
No vibrational or rotational quantization in atoms or their ions. Therefore lines from individual atomic species rarely overlap with one another. Thus broadening due to overlap of adjacent transitions do not exist.



In AA absorption and emission spectral profiles are very narrow.

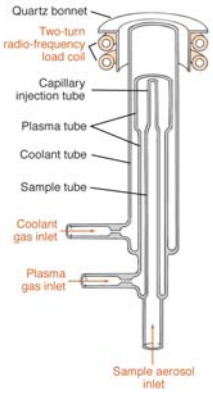


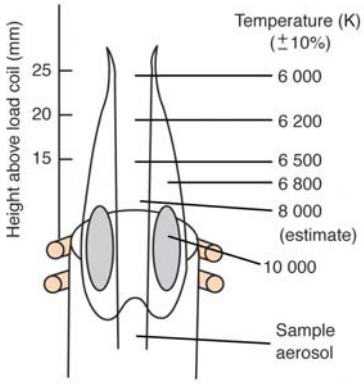




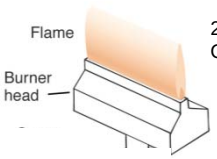
'Analyte cell'

Origins of AS traced to 'flame test'.





Conventional sample cell - flame.

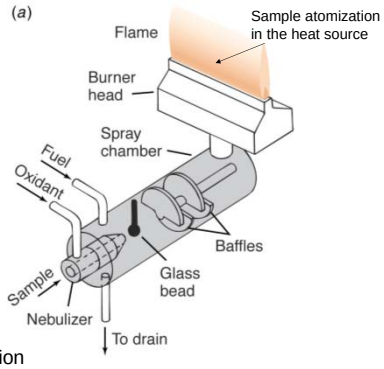


2300-2600°C
O_2-C_2H_2 flame

Sample: salts- element existing as ions or compounds where the element of interest is bonded.

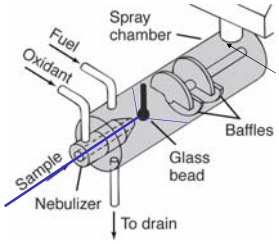
Sample must be decomposed to the greatest extent possible into its constituent atoms/ions. Ideally, this ***atomization*** step should be quantitative; there should be no residual bonding in the gas-phase 'atomic' cloud.

Atomization of analytes start with the sample nebulization (spraying) process.



aspiration

The suction caused by high flow rates of oxidant gas - Venturi effect.



Larger drops

Solution impinging on the bead aerosolizes the sample.

Once formed, droplets in the nebulized spray are sent into a high-temperature environment such as a (chemical) flame or flowing rare-gas plasma - ICP.

Nebulization serves to increase the surface area of the solution sample, so solvent evaporation (desolvation) can proceed more rapidly and so the resulting dried solute particles can be volatilized better. (flame atomic absorption, flame emission, and plasma emission spectrometry).

In the flame; de-solvation and solute-particle vaporization takes place, the resulting vapor converted more or less efficiently into free atoms.

$$M^{+}(g) + e(g) = M(g)$$
$$M^{+2}(g) + e(g) = M^{+}(g)$$
..

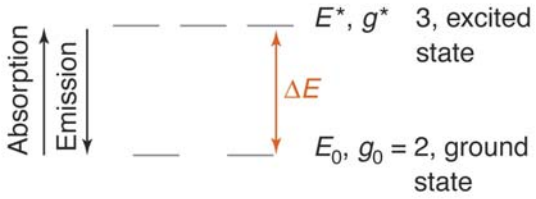
The environment in the 'flames' often hot enough that many of the atoms that are formed exist as positive ions.

Also, the environment in these atomization sources is energetic to yield sufficient population in the exited state, strong emission from either the free atoms or their ionic counterparts.

For each atomic/ionic species the population distribution can be calculated using the Boltzmann's Law, n_u, n_l excited and ground state populations, respectively:

$$\frac{n_u}{n_l} = \frac{g_u}{g_l} e^{\frac{-\Delta E}{RT}}$$

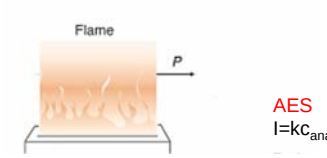
Statistical weighings



$$\frac{n_u}{n_l} = \frac{g_u}{g_l} e^{\frac{-\Delta E}{RT}}$$

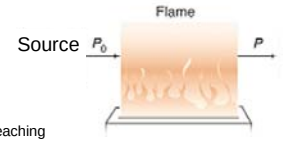
Large flame T makes power of the exponential term →0, despite high ΔE; makes n_u (excited state) significant making AES possible, from the radiative decay of the excited states.

Flame AA implementation



AES
$I=kc_{analyte}$

AAS AES

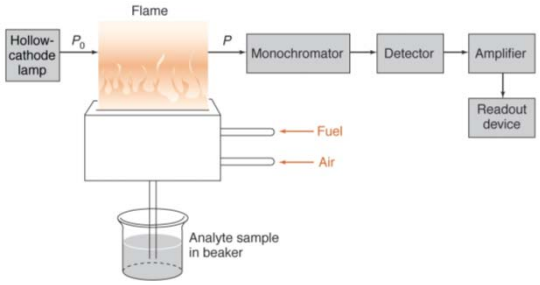


AAS
Lambert-Beer Law

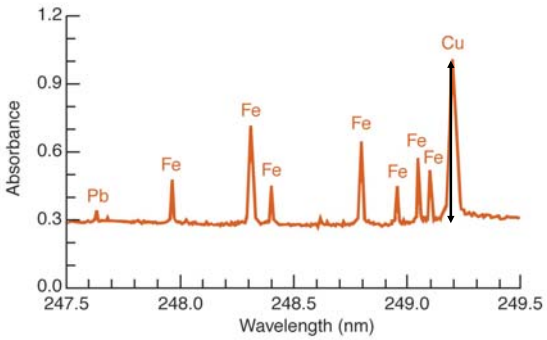
$A=\log(P_0/P)$
$=k'c$

In reality P_0 is the intensity of light reaching with the 'blank'.

Flame AA block diagram



Atomic Spectral lines are sharp (narrow).



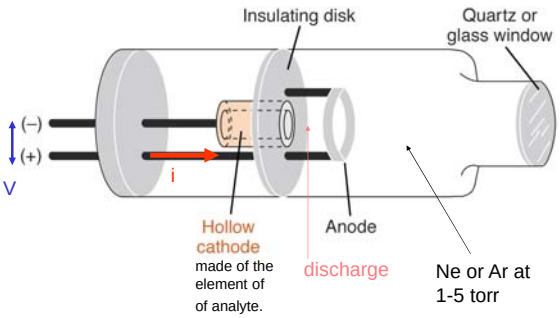
AAS mode:

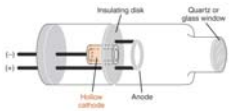
The source is unique. The narrow band width of the spectral absorption/(emission) lines precludes the employment of broad band source-monochromator combination to irradiate the sample.

The irradiating beam must be comparable or narrower band-width to that of the absorption profile.

The strategy is to use the emission lines of high intensity from the element of interest. This is accomplished in HCLs.

Hollow Cathode Lamp (HCL)



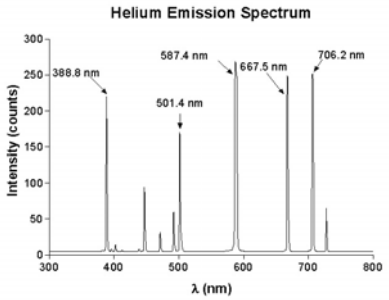


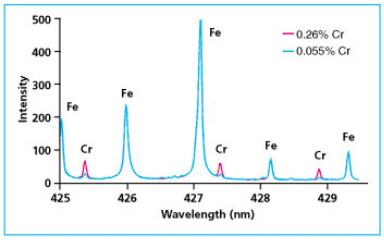
At low pressure and applied high voltage a discharge is created.

Discharge ionizes the inert atoms, ionized particles accelerated toward electrodes. High energy particles sputter atoms and ions into gas phase.

Ions and atoms are exited by high energy particle impact.

As they relax, they produce radiation of the same frequency of analyte of interest.





LIBS spectra obtained from steel showing Fe and Cr emission lines

Spectral Line widths (absorption or emission)

The AA line profile is broadened due to three factors:

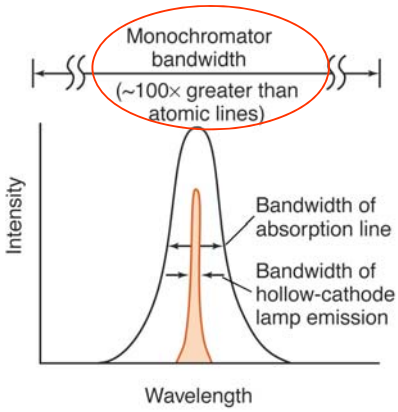
1. Natural Decay leads to natural broadening
2. Doppler effect leads to Doppler broadening

   Where T is temperature and M is atomic mass.

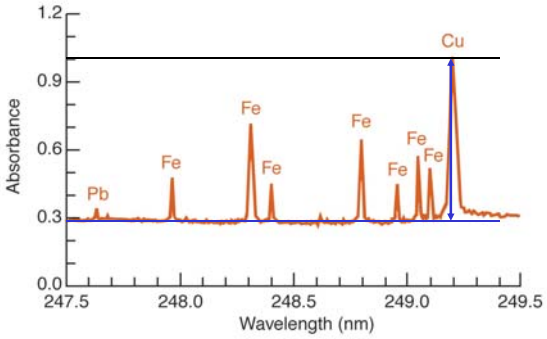
$$\Delta\nu(\text{Hz}) \approx (7.0\times10^{-7})\nu\sqrt{\frac{T}{M}}$$

3. Pressure broadening due to collisions. Collisions lowers the excited state life time thus broadens the spectral line.

The sample is at a higher temperature than the HCL. Therefore they will have two different profiles due to different broadening.



Background in Atomic Spectroscopy is significant.
Background signal should be accounted for in analysis.



The significant background makes the usefulness of the pure absorbance value for calculations erroneous.

The background arises due to;

1. scattering of the HCL light beam, mainly from the sample matrix; tends to reduce the power of the beam reaching the detector (false absorbance, P).
2. emissions from sample molecular species and from the fuel component emissions, generally broad spectral emissions; tends to increase the power reaching the detector (false P_0) .

Correction for the background emission is an essential feature in atomic spectroscopy.

Background correction methods:

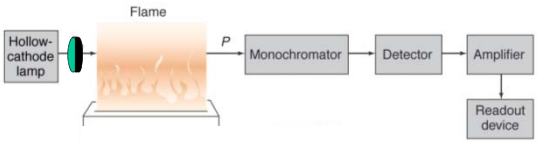
Beam chopping: Simple method to produce alternate current.

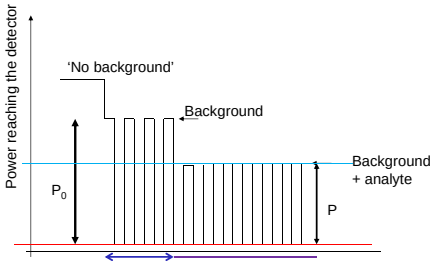
Deuterium lamp: Use D_2 lamp to simulate the background intensity.

Smith-Hieftje: Run HCL at high and low currents to produce different emission profiles of the lamp. First run lamp at low current measure absorbance of analyte and background. Then lamp is pulsed with a high current. During the pulse, the analyte absorbance is reduced but not to zero. Most of absorbance is due to background.

Zeeman Background Correction: A magnetic field is used to split the degenerate energy levels. Under the field the species absorb polarized light only. This difference is exploited.

Beam chopping

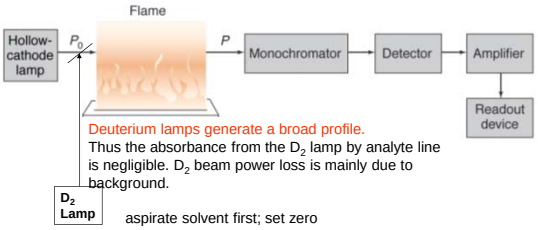




$$A = \log\left(\frac{P_0}{P}\right) = kc$$

D_2 Lamp correction

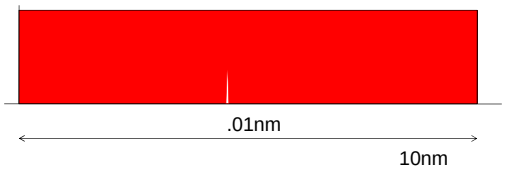
Measure the A for HCL and D_2 lamps, alternatively.



Deuterium lamps generate a broad profile.
Thus the absorbance from the D_2 lamp by analyte line is negligible. D_2 beam power loss is mainly due to background.

aspirate solvent first; set zero
aspirate sample; measure A_{D2}
aspirate sample; measure A_{HCL}

$A_{D2}=A_{background}$
$A_{HCL}=A_{background}+A_{analyte}$
$A_{HCL}-A_{D2}=A_{analyte}$



A_{D2} for all practical purposes is due to background.

$A_{D2}=A_{background}$
$A_{HCL}=A_{background}+A_{analyte}$
$A_{HCL}-A_{D2}=A_{analyte}$

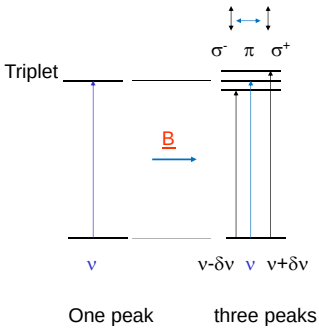
Smith-Hieftje Background correction: Conceptually similar to D_2 correction (which uses a broad spectral band). Broad band is generated from the HCL itself.

HCL at high currents produce a wide emission spectral line.

Thus alternating the current density through the HCl (modulation), to account for the background (absorbance at high current density) and measure line absorbance and background (absorbance at low current density) makes the correction possible

$A_{high}=A_{background}$
$A_{lowL}=A_{background}+A_{analyte}$
$A_{low}-A_{high}=A_{analyte}$

Zeeman Background Correction



One peak three peaks

Polarization w.r.t. B

Interaction with polarized light:

π absorbs light if polarized parallel to the B.

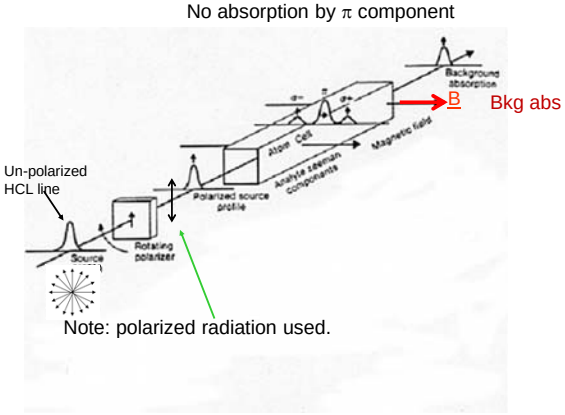
σ absorbs light if polarized normal to the B.

When atoms are subjected to a B, the light component polarized parallel to B is absorbed by the atoms, but the light component polarized normal to B is hardly absorbed.

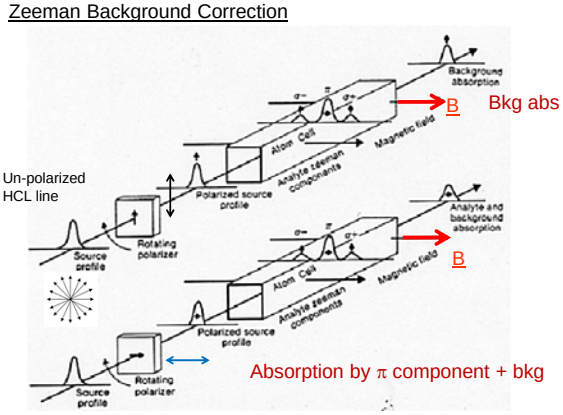
The background contribution to absorption of light remains unchanged, however, from the any polarized light.

Measuring the power of light parallel to B and normal to B measured at the same wave length the background absorption can be excluded; subtraction of signals of these two components the background component can be excluded.

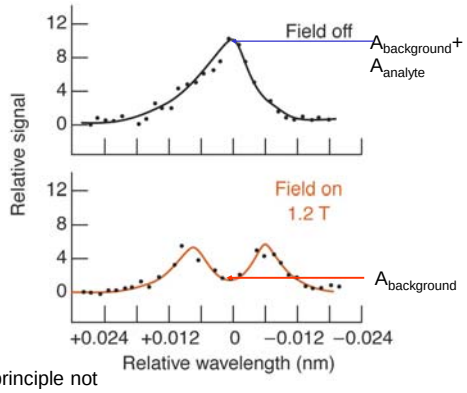
No absorption by π component



Zeeman Background Correction

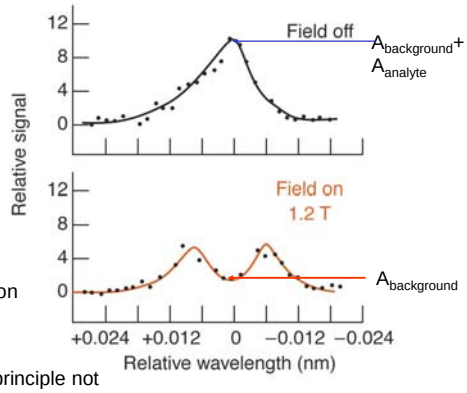


Variation



Better in principle not in practice.

Variation



Polarization ⊥ to B.

Better in principle not in practice.

Graphite Furnace AA

L'vov platform

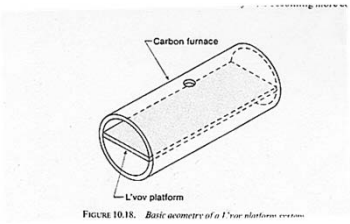
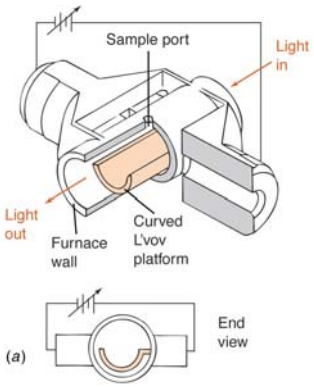
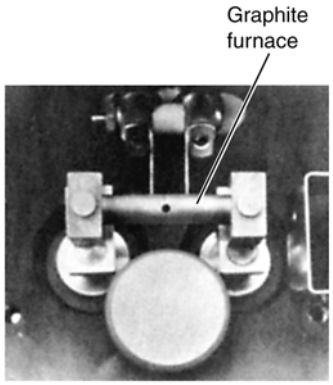
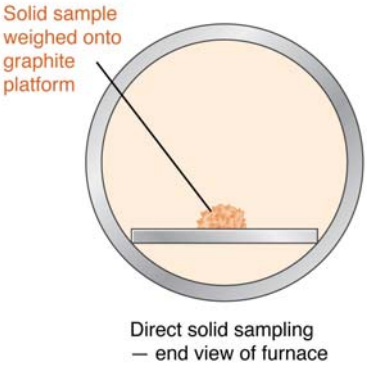


FIGURE 10.18. *Basic geometry of a L'vov platform system.*

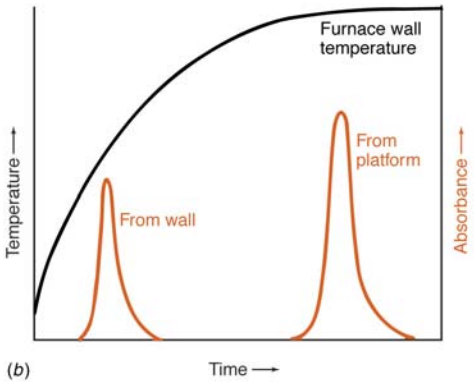






Introducing a sample also introduces a matrix that will form a partially burnt ashy material. Such material blocks the light path and interfere with absorption measurements.

To minimise such detrimental effects the temperature of The graphite tube increased starting at room temperature a in a stream of inert gas.



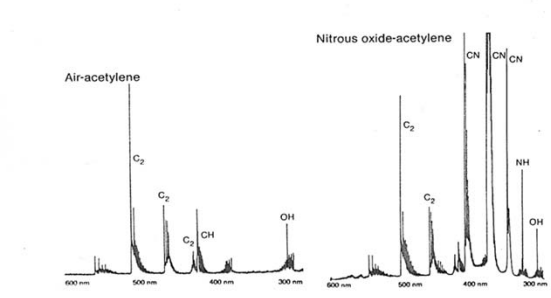
Oxidant-Fuel Combinations

Oxidant	Fuel	Maximum Temp C
Air	Acetylene	2250
Nitrous oxide	Acetylene	2955
Air	Coal gas	1825
Air	Propane	1725
Air	Hydrogen	2045
Entrained air/Ar	Hydrogen	1577
Oxygen	Natural gas	2740
Oxygen	Hydrogen	2677
Oxygen	Cyanogen	4500

Interferences:

Spectral interference: overlap of analyte signals from other elements. Select a different line to monitor.

Fuel Background:
Interference from partially oxidized fuel molecules



Emission from N_2O-C_2H_2 flame

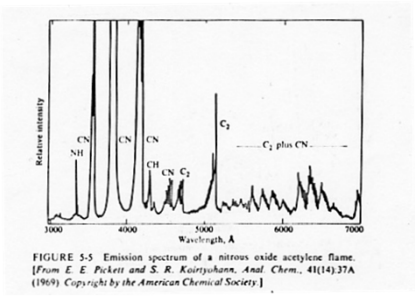
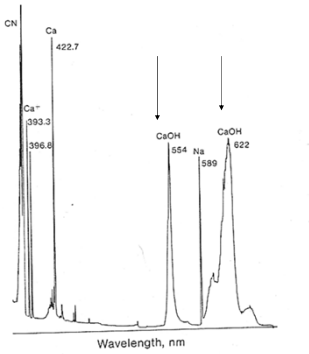


FIGURE 5-5 Emission spectrum of a nitrous oxide acetylene flame. [From E. E. Pickett and S. R. Koirtyohann, Anal. Chem., 41(14):37A (1969) Copyright by the American Chemical Society.]

Interference from the formation of molecular (refractory) species



Chemical interference:

Reduction of atomization because of the formation of non-volatile salts; in the presence of sulfates, phosphates.

Use a complexing agent (protecting agent, EDTA, 8HQ) to protect the ion.

Add La^{+3} (releasing agent) because $LaPO_4$ more stable, frees other atoms such as Ca^{2+} nonvolatile salts.

Use of fuel rich flame minimizes ionization, increase atom population.

High temperatures make ion population significant however, increase ion population.

Ionization Interference:

Often encountered with easily ionizable elements (alkali metals). Ionization very high, making atom population low.

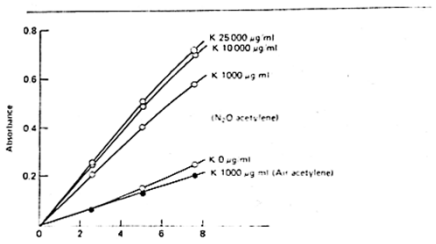
Reverse equilibrium by adding an ionization suppressor (buffer), e.g. CsCl (1000ppm).

$$M(g) = M^+(g) + e(g)$$

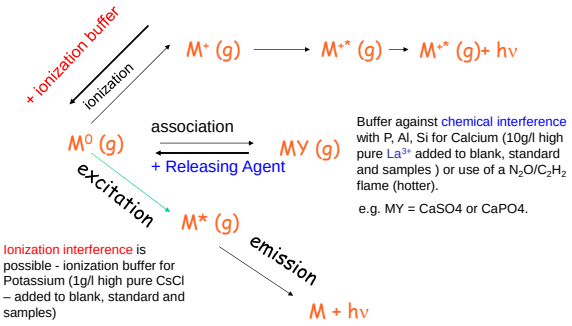
$$K = \frac{[M^+][e]}{[M]}$$

An ionization buffer is a salt of an alkali metal (easily ionizable). Ionization of alkali metals yields a higher electron density which would shift the ionization equilibrium of analyte M^+ to form atoms.

Effect of Ionization buffer on Atom population



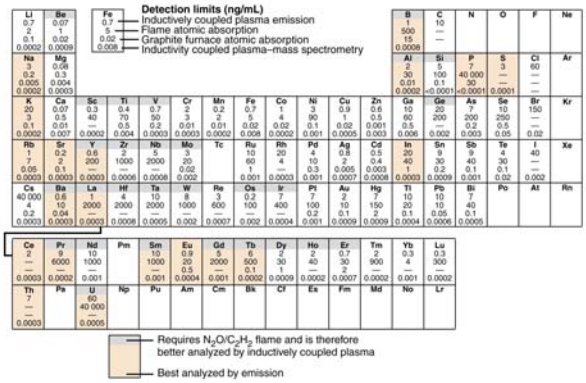
Improving excited state species



Buffer against chemical interference with P, Al, Si for Calcium (10g/l high pure La^{3+} added to blank, standard and samples) or use of a N_2O/C_2H_2 flame (hotter).

e.g. MY = CaSO4 or CaPO4.

Ionization interference is possible - ionization buffer for Potassium (1g/l high pure CsCl – added to blank, standard and samples)



Internal Standards (IS) in Quantitative Analysis:

An **internal standard** is a known amount of a compound, different from analyte, that is added to the 'unknown' sample.

Signal from analyte is compared with signal from the internal standard to find out how much analyte is present.

This method is especially useful for analyses where the quantity of sample and/or the instrument response varies slightly from run to run for reasons beyond control.

Because the concentration of internal standard known, the correct concentration of analyte can be determined.

Internal standards are widely used in chromatography, spectroscopy because the small quantity of sample solution injected into the chromatograph is not very reproducible in experiments.

In AA the flame instability creates situations of non-reproducibility.

In cases where detector response vary with time form a good situation to use IS.

Internal standards are also desirable when sample loss can occur during sample preparation steps prior to analysis.

If a known quantity of standard is added to the 'unknown' prior to any manipulations, the ***signal ratio*** of standard to analyte remains constant because the same fraction of each is lost in any operation

For a *known (concentration)* mixture(s) of an internal standard and analyte the measured the relative response of the detector to the two species, F;

$$\frac{\text{Analyte signal}}{\text{IS signal}} = F\frac{[\text{X}]}{[\text{S}]}$$

$$\frac{\text{A}_\text{X}}{\text{A}_\text{S}} = F\frac{[\text{X}]}{[\text{S}]}$$

$$\frac{\text{A}_\text{X}}{\text{A}_\text{S}} = F\frac{[\text{X}]}{[\text{S}]} + b$$

[X] and [S] are the concentrations of analyte and IS after they have been mixed together.

Once F is established, use the same relationship above for where an the unknown and the IS are present to calculate the concentration of the unknown.