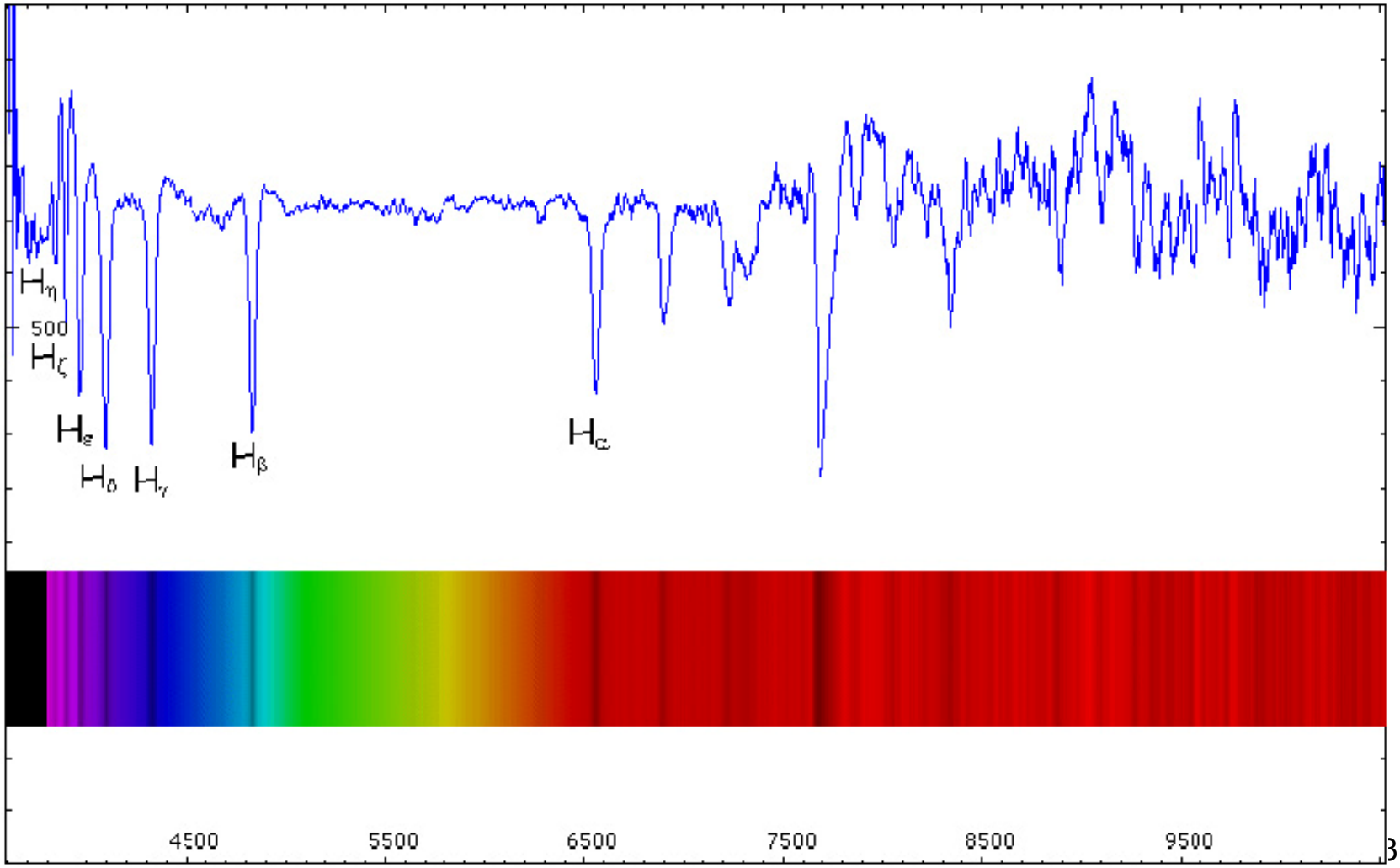
ATOMIC ABSORPTION SPECTROMETRY

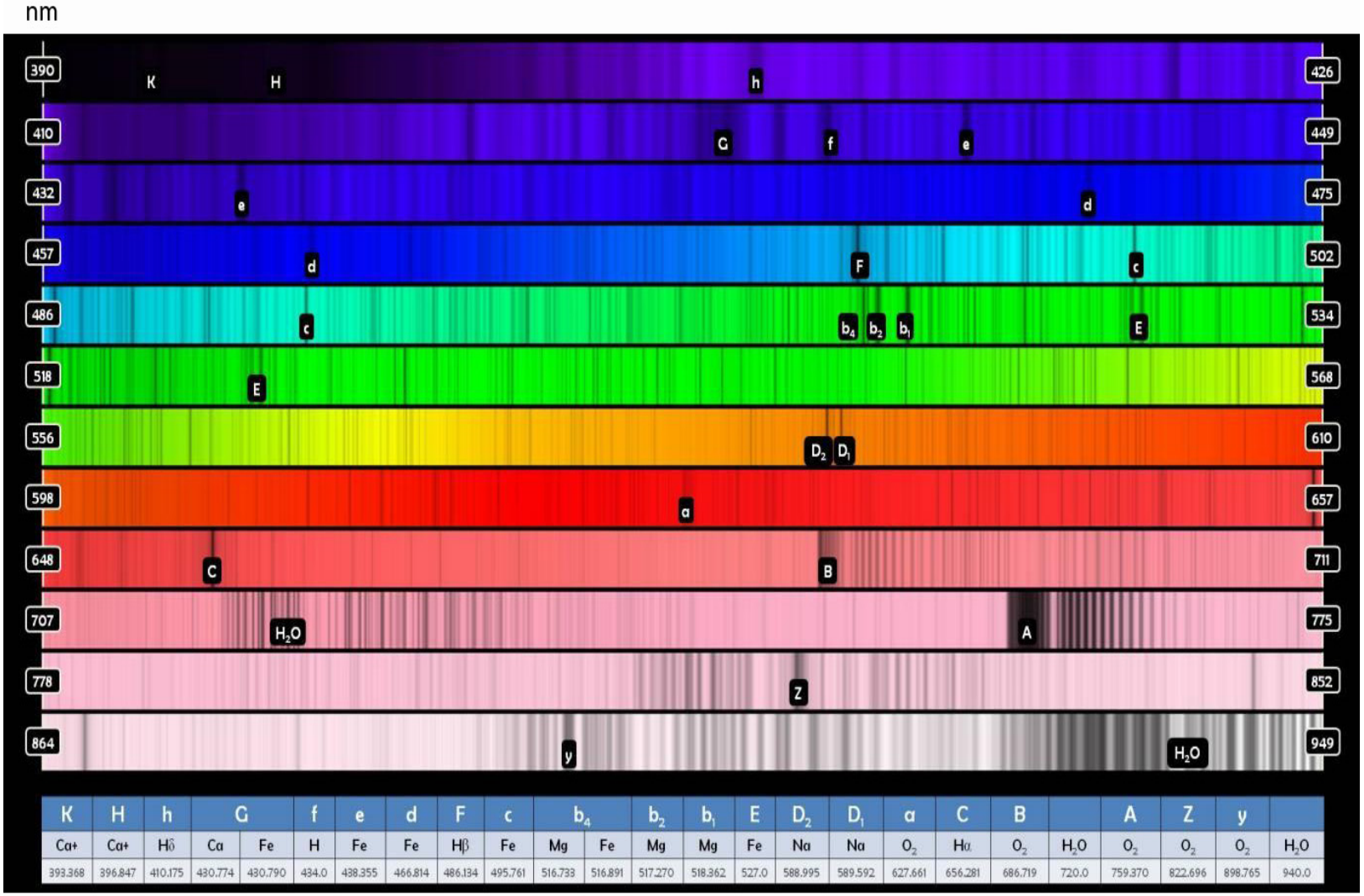
The phenomenon of atomic absorption was first discovered by Woolaston in 1802 in the spectrum of sunlight. Till then thought to be a continuous spectrum, Woolaston made a remarkable observation that the solar spectrum was in fact interrupted by "dark lines" which was later confirmed by Fraunhofer in 1814. However, Brewster put forward the idea that these dark lines denoted till then by alphabetical markers are in fact due to the presence of vapors of certain elements in the sun's atmosphere. Therefore, it follows that substances emitting specific radiations are also capable of absorbing the same, causing the spectrum of dark lines in the bright background.

This phenomenon generally known as Kirchoff's law was used to deduce the presence of oxygen, hydrogen, sodium, iron, calcium etc., in the solar spectrum. The experimental confirmation for this came from electric arc or spark, when the spectral source surrounded by atomic vapors also showed dark lines because of absorption of the emitted radiations. Foucalt in France also demonstrated the reversal of spectral lines.

FRAUNHOFFER LINES



FRAUNHOFFER LINES



K	H	h	G		f	e	d	F	c	b_4		b_2	b_1	E	D_2	D_1	α	C	B		A	Z	y	
Ca+	Ca+	Hδ	Ca	Fe	H	Fe	Fe	Hβ	Fe	Mg	Fe	Mg	Mg	Fe	Na	Na	O_2	Hα	O_2	H_2O	O_2	O_2	O_2	H_2O
393.368	396.847	410.175	430.774	430.790	434.0	438.355	466.814	486.134	495.761	516.733	516.891	517.270	518.362	527.0	588.995	589.592	627.661	656.281	686.719	720.0	759.370	822.696	898.765	940.0

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In 1902, Wood repeated the experiments of Kirchoff and Foucalt and proved conclusively that by introducing sodium vapor in the optical path of sodium emission lines (589.0 and 589.6 nm), a reduction in the intensity of radiation occurs. By analogy with acoustic resonance lines, he also showed the possibility of using these resonance effects to detect traces of mercury. The potential of this technique was not recognized by analytical chemists and spectroscopists till 1924.

Angerer and Joose published the atomic spectra of iron group metals, followed by Frayne and Smita for indium, aluminum, gallium and tantalum. Muller and Pringshiem in 1930 published the first atomic absorption method of measuring the mercury content in air. Even this did not evoke interest in the analytical chemists for the determination of other elements.

Walsh, in 1955 developed the first real application of atomic absorption to chemical analysis. In the same year Alkamade and Miatz described a double beam method of spectral selection with two flames, the first being the source and the second as atomizer. Since then the atomic absorption spectrometry is in the forefront of chemical analysis. The first commercial atomic absorption instruments appeared in 1960s.

Spectacular advances in instrumentation, electronics, automation and computers over the years have made atomic absorption spectrometry, one of the most reliable analytical techniques of modern times perhaps equalled only by atomic emission spectrometry in terms of simplicity, sensitivity, specificity and speed of operation.

The development of electrothermal atomization by L'vov and Massmann pushed the detection limits of atomic absorption technique to nanogram and picogram and sometimes even up to femtogram levels.

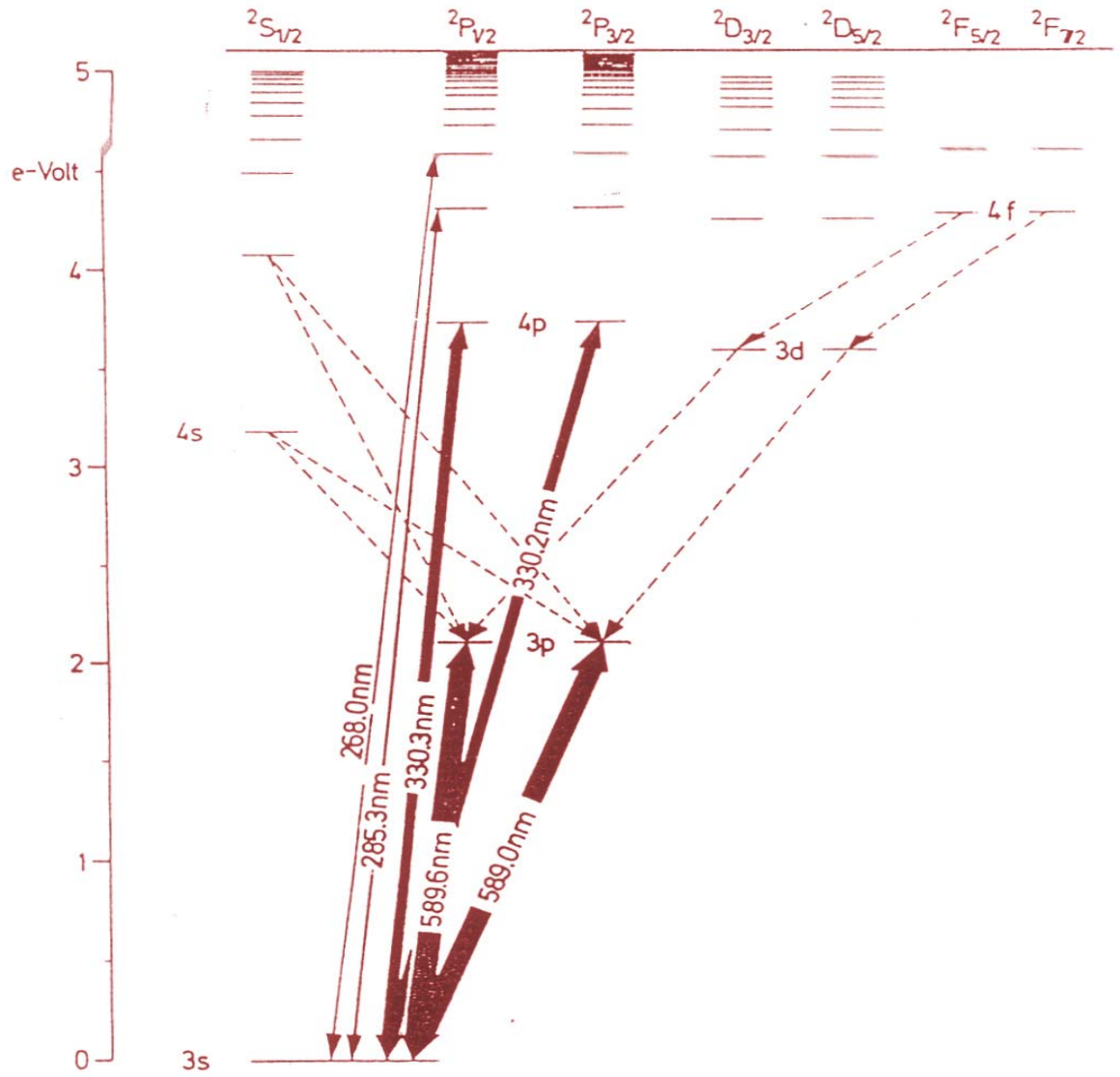
Hydride generation atomic absorption spectrometry for arsenic, antimony, bismuth, selenium, tellurium, germanium, lead and cold vapor mercury determination have proved attractive accessories for atomic absorption technique to make it the first choice of analytical chemists throughout the world.

The popularity of the atomic absorption spectrometry can be gauged by the fact that more than 100 books, 10,000 publications and 5000 symposia and conferences till date have appeared with applications in biological, chemical, nuclear, industrial products, soils, environment etc.,

THEORETICAL CONCEPTS OF ATOMIC ABSORPTION

The simplest concept of atomic structure is that of the positively charged nucleus containing protons and neutrons surrounded by an equal number of electrons orbiting in space in the electric field created by the protons. According to quantum mechanics, such a system can exist in a stable state only if its energy is quantized even at the lowest energy level or ground state. All other levels are excited levels, which can be induced by mechanical or electromagnetic means. The energies associated with these atomic states are in the range of a few electron volts represented by Grotian diagram. Such a diagram for sodium is shown in the next slide.

ENERGY LEVEL DIAGRAM FOR SODIUM



Emission of light occurs when an atom reverts to a state of lower energy. Bohr's equation expresses the conservation of energy by the relation:

$$\nu = E_1 - E_2 / h \qquad (1)$$

$$\text{or } \lambda = c / \nu = hc / E_1 - E_2$$

where c is the velocity of light (2.99793 x 108 m/s), h is the Plank's constant (6.62 x 10^{-34} in SI Units), v is the frequency, λ is the wavelength and E_1, E_2 are the energy levels of excited and ground states.

Inserting the numerical values, we get:

$$\lambda = 1.23978 / \Delta E$$

Thus a transition from the resonance level of sodium (2.102 electron volts) to ground state would correspond to the emission of:

$$\lambda = 1.23972 / 2.102 = 0.5986\ \mu m \text{ or } 589.6\ nm$$

When a photon of frequency ν interacts with an atom of energy E_2, the atom may be able to absorb the photon thus raising it s energy to $E_2 + h\nu$, provided the new energy level is equal to one of the excited energy levels of that atom, Then we can write:

$$\nu = E_1 - E_2 / h \qquad (2)$$

Comparison of equations 1 and 2 shows that "An atom can only absorb the radiations that it is able to emit". This forms the basis of spectrometry.

The fundamental difference between emission spectrometry and absorption spectrometry may be defined as:

(i) For emission to occur, a number of atoms must be in the excited state.

(ii) For atomic absorption to occur, a number of atoms must be in the ground state.

The second condition is easily attained compared to the former in that, free atoms in the ground state can be easily generated in flame compared to the excited state, by flame emission.

The characteristic absorption wavelengths for an atom can be calculated once the energy levels are experimentally determined. But several wavelengths are never observed which proves that some sort of selection rules be developed. These rules were evolved empirically at first, and subsequently confirmed by applying quantum mechanical principles to the concept of transition probabilities.

The probability of a spontaneous emission by transition between energy levels E_1 and E_2 is defined as the fraction of number of atoms that drop to lower level per unit time.

Mathematically,

$$dN_{1\rightarrow 2} = AN_1\, dt \qquad (3)$$

where A is the coefficient of proportionality termed as **Einstein emission coefficient.** Higher the probability of transition, the greater is the intensity of emission. The strongest emission lines correspond to values of A in the range of 10^8 to 10^9 / sec.

Similarly if N_2 atoms in the lower transition state are irradiated by a radiation of frequency ν derived from equation (1) and the volume flux density $\rho(\nu)$, the number of d $N_{2\text{-}1}$ of atoms that will absorb the radiation in time dt is proportional to N_2, $\rho(\nu)$ and dt. Hence,

$$dN_{2\rightarrow 1} = B_{2\text{-}1} \, , N_2 \, \rho \, (\nu) \, dt \qquad (4)$$

The term $B_{2\rightarrow1}$ is known as Einstein's absorption coefficient. Now a days, the term oscillator strength is being used to denote the relationship between B and the total number of electrons.

$$B_{2\rightarrow1} = \pi e^2 \lambda / m h c f_{2,1} \qquad (5)$$

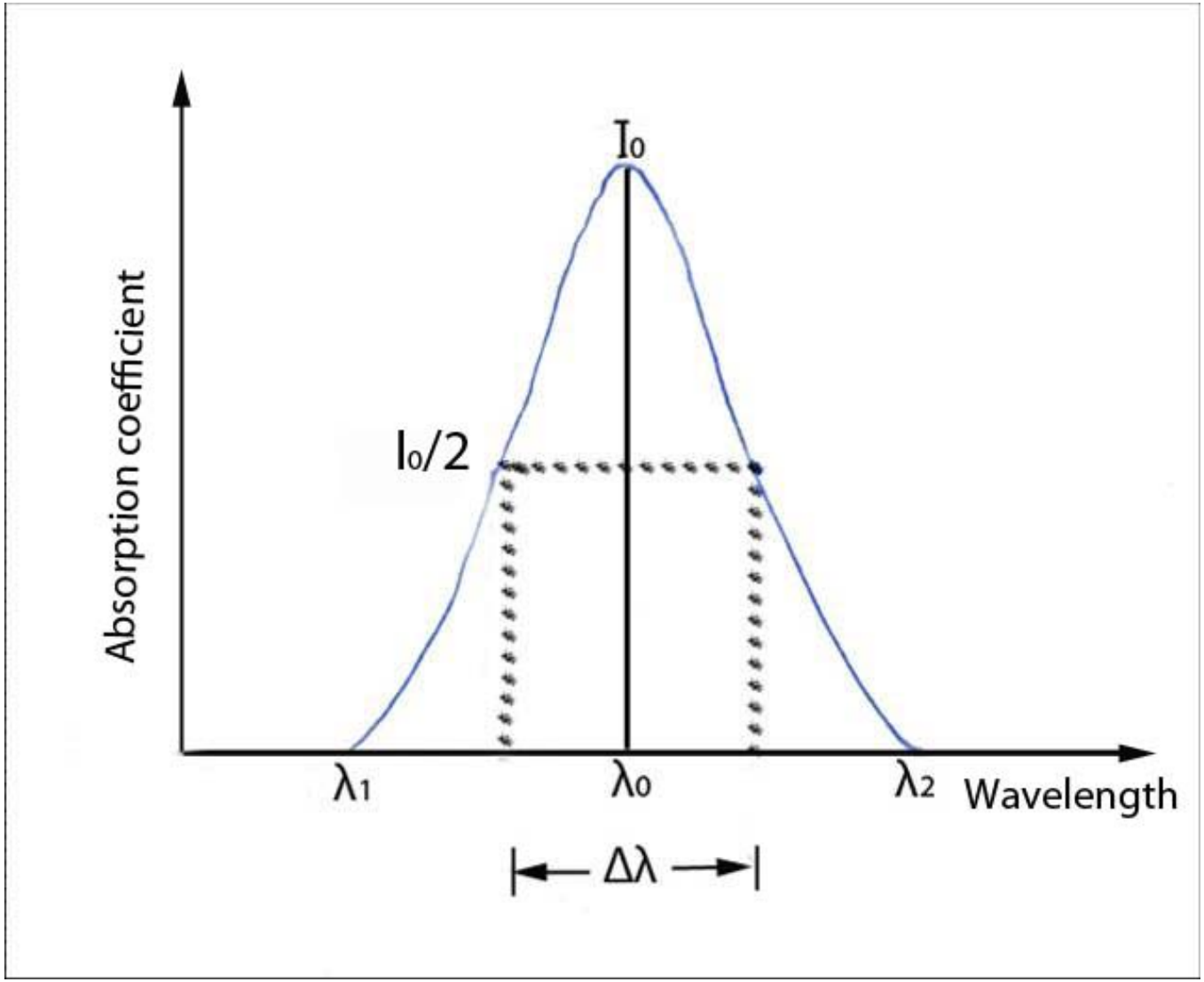
where, e and m are the electronic charge and mass. Thus for sodium D lines, oscillator strength is 0.23 and 0.47 and for potassium they are 0.35 and 0.70.

The emission lifetime of any transition is approximately 10^{-8} sec. However, if there are sufficient numbers of atoms, steady state emission or absorption phenomena can be observed within the experimental time frame. For atomic absorption to occur , intense emission of the desired element must be generated first. The radiations generated from electric dipole, magnetic dipole, electric quadrupole interactions give rise to such lines among which electric dipole are most important. Both Einstein emission (A) and absorption coefficients (β) are non-zero, only if the levels involved are of opposite parity and if $\Delta J = \pm 1$.

Using these selection rules, resonance level of an atom may be defined as that of lowest excited energy level that can interact with the ground state by a transition of electric dipole type. The corresponding wavelength is known as the resonance line. Therefore, it follows that for a particular atom the resonance line is the most intense of highest oscillator strengths and only this line is useful for analysis provided the wavelengths are in the 200-600 nm range.

In practice, it is impossible to get a truly monochromatic line, but the energy is distributed symmetrically over a narrow waveband. The width of a spectral line is defined as the value of $\Delta\lambda$ where the intensity is 50 percent of the total. This is called as **half width.** The shape and size of an absorption or emission band is affected by several factors such as natural broadening, Doppler broadening, pressure broadening and electric or magnetic field broadening etc.,

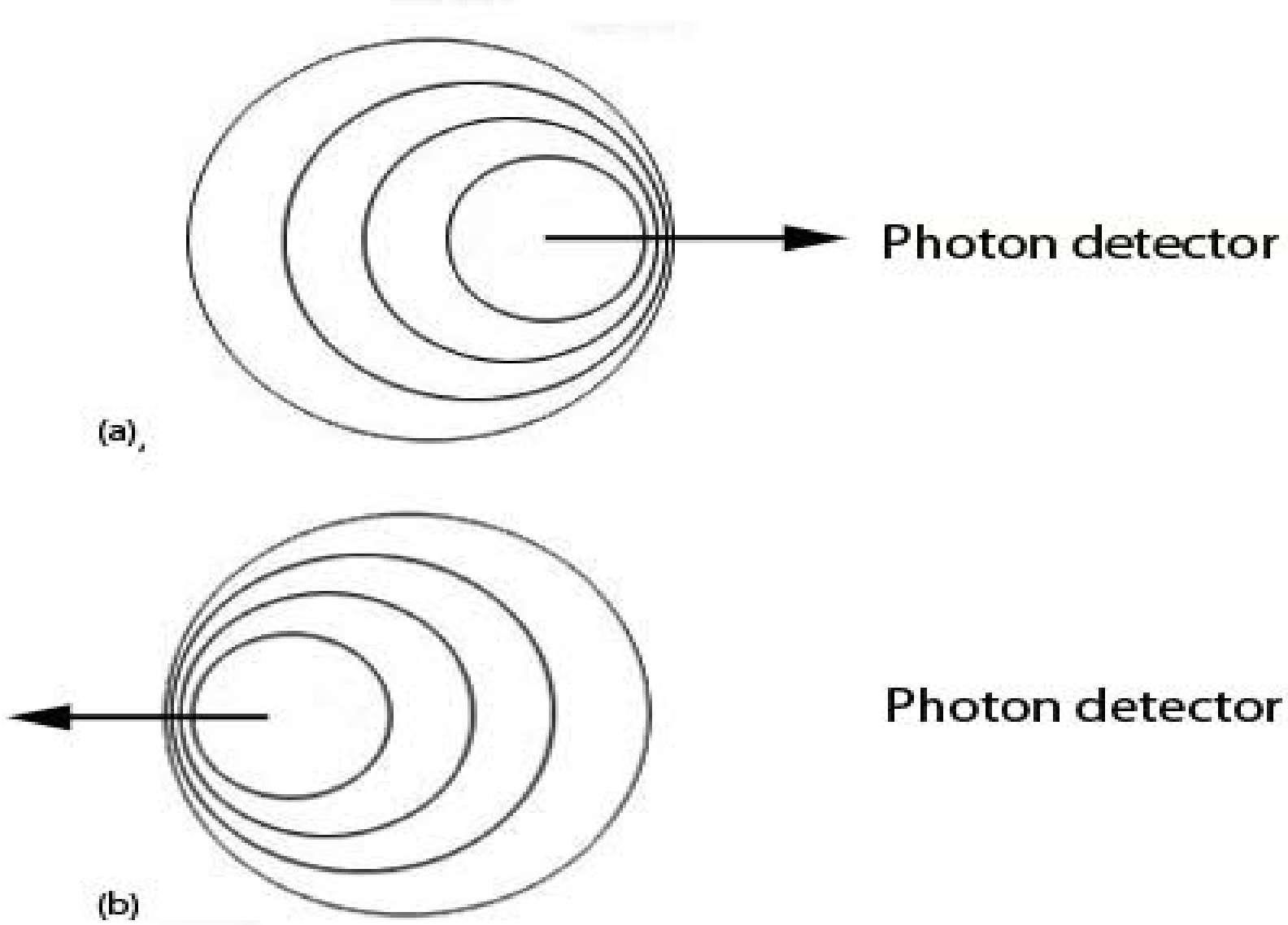
PROFILE OF A RESONANCE LINE



NATURAL BROADENING

Due to the short lifetime of energy states, Heisenberg's uncertainty principle is applicable for all transitions. Thus a small broadening effect of the order of a few millionth of a nanometer at 250 nm occurs rising to about 10^{-4} nm at 1μm. This natural width is influenced further by a variety of factors, chief among them being the disordered thermal motion of the atoms and various types of collisions of atoms.

DOPPLER BROADENING



If an atom emitting a radiation λ_0 moves with a velocity v relative to the observer, the observed wavelength λ is given by,

$$\lambda = \lambda_0 + \lambda_0 v / c \qquad (6)$$

where c is the velocity of light in the vacuum. Further, if the atoms are in thermal equilibrium at temperature T, their velocities will have a Maxwellian distribution.

The monochromatic absorption coefficient K as a function of λ may be expressed as:

$$K(\lambda) = K_0 \exp \{ [-(\lambda - \lambda_0) / \Delta\lambda_d \, 2 (\ln 2)^{½}]^2 \} \qquad (7)$$

where $\Delta\lambda_d$ is the Doppler halfwidth related to T and the atomic mass M by the equation:

$$\Delta\lambda_d = 7.16 \times 10^7 \, \lambda_0 \, (T/M)^{1/2} \qquad (8)$$

The line is thus shown to have a Gaussian profile. It is possible to calculate the values of $\Delta\lambda_d$ at 2000, 2500 and 3000 K and the line widths for these temperatures are of the order of 30-50 mÅ.

PRESSURE BROADENING

Since the atoms in the vapour state are in a perpetual state of motion, collision of atoms is inevitable causing radiation quanta of slightly differing frequencies to be absorbed or emitted. Several types of particles may be involved in the collisions. Interaction of electrically charged particles causes line broadening known as 'Stark effect'. Collisions with uncharged atoms lead to van Der waal's effect. Collisions between atoms of the same type leading to resonance broadening effect is referred as 'Holtsmark' effect. Since it is difficult to differentiate between these three effects they are collectively referred as 'Lorentz' broadening.

The broadening of spectral lines reduces the lifetime of the excited state of the atoms. It also increases the line profile of the radiation. The monochromatic absorption coefficient of the em radiation at a wavelength λ is given by:

$$K(\lambda) = K_0 / 1 + [2 (\lambda - \lambda_0) \Delta L]^2 \qquad (9)$$

where K_0 is the maximum absorption coefficient and ΔL is the half width. The profile of this distribution is flatter than Doppler broadening but both are almost of the same order. The half width ΔL is thus a fraction of the frequency of collision (Z), which in turn is a function of the temperature and the effective cross section defined by:

$$\Delta \lambda = Z \lambda_0^2 / \pi C \qquad (10)$$

It may be noted that both Doppler and Lorenz broadening occur simultaneously resulting in a similar but broader profile known as Voigt profile (Kλ) which may be mathematically expressed as:

$$K(\lambda) = K_o \, a / \pi \int_{-\infty}^{+\infty} e^{-y2} / a^2 + (w - y)^2 \, dy \qquad \textbf{(11)}$$

Where $a = \Delta\lambda_L / \Delta\lambda_D (\ln 2)^{1/2}$,

$w = \lambda - \lambda_0 / \Delta\lambda_D \, 2 (\ln 2)^{1/2}$,

$y = 2\delta / \Delta\lambda_D (\ln 2)^{1/2}$ and

δ = distance to the point λ at which K(λ) and K_0 are the calculated and the maximum value of the coefficient.

The curves are symmetrical with a maximum at λ_0. Apart from Doppler and Lorenz effects, line broadening also occurs due to hyperfine structure exhibited by many resonance lines due to nuclear spin. Isotope shift of the resonance lines also contributes additionally to the line broadening. These effects are also significant but not as prominent.

In essence, the sum total of all these line broadening effect is of the order of 0.0005-0.005nm, which increases with increasing temperature and pressure. The significance of peak width at half the peak height has a profound effect on the emission characteristics of radiation sources, (especially hollow cathode lamps) which will be discussed later.

MEASUREMENT OF ABSORPTION

Based on quantum physical description given earlier, rigorous mathematical expressions have been derived to determine the absorption coefficient, its variation with N.f.l, effect of monochromator band width and also of optical density. However, for practical analytical purposes a physical understanding of these phenomena is more relevant which may be Interpreted as follows.

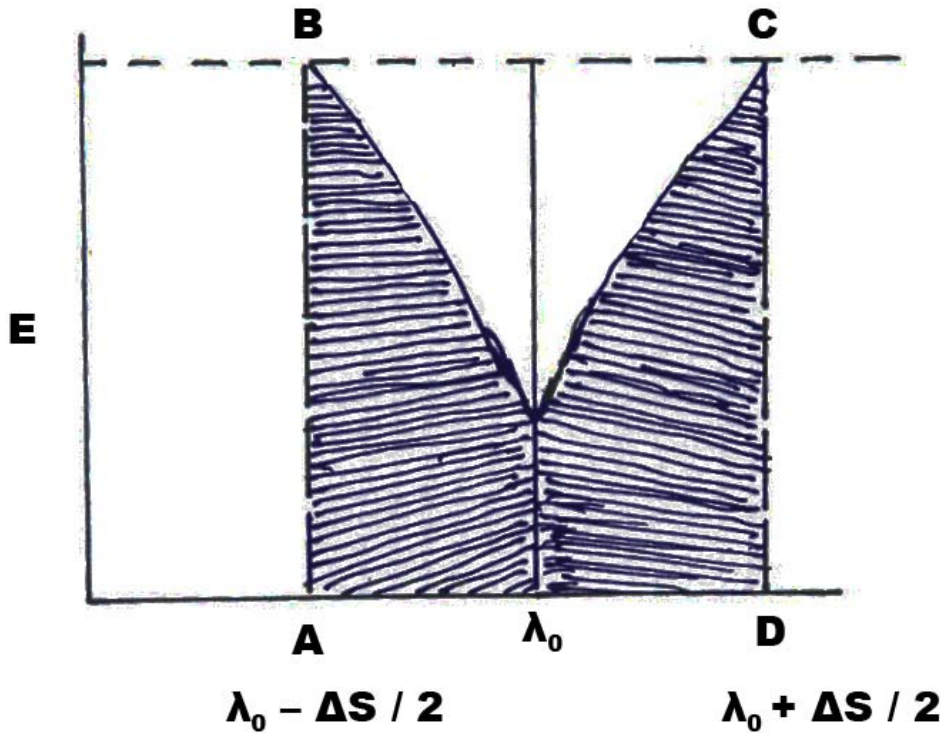
A very narrow frequency interval is essential for the absorption of resonance radiation. However, it is impossible to isolate and obtain high intensity of illumination in the range of 0.0005 – 0.005 nm from continuum radiation sources. It would be too weak to be of any practical use. To overcome this difficulty, Walsh recommended that the radiation source should be made of the analyte element only. Therefore only the resonance line need to be separated from other spectral lines by a monochromator.

Assuming that a monochromator isolates a spectral band ΔS covering the absorption line λ_0 (resonance line), the total spectral energy received by the detector is :

$$I_0 = \int_{\lambda_0 - \Delta S/2}^{\lambda_0 + \Delta S/2} \mathrm{I}_0 \mathrm{d}\lambda \qquad \textbf{(13)}$$

$$= \mathbf{I_0\ \Delta\ \lambda_S} \qquad \textbf{(14)}$$

= Area of the rectangle ABCD



Now if a homogeneous gas having an absorption K(λ) is interposed in a length of the radiation beam, the energy within the band λ will decrease by the same amount but the spectral profile will have the same shape.

Instead of considering the radiation per unit volume, if the total radiant flux (Φ) is considered, then it may be proved that the absorption factor and hence optical density is proportional to the concentration of the free atoms and to the path length in the absorbing medium provided that the concentration is low and the spectral bandwidth is narrow. This is nothing but Beer – Lambert's law which can be expressed as:

$$\Phi_{tr} = \Phi_0 \, e^{-x_v \, N \, l} \qquad (16)$$

Where Φ_0 and Φ_{tr} are the radiant fluxes before and after absorption in the path length l, x_v is the spectral absorption coefficient and N is the number of atoms.

This expression may be rearranged in the familiar form,

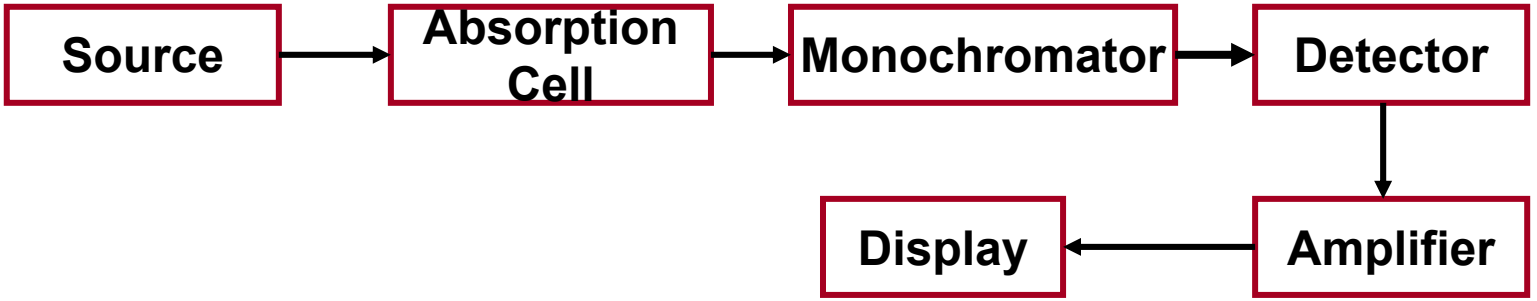
$$\text{Absorbance} = A = \text{Log}\ \Phi_0 / \Phi_{tr} = 2.303\ x_v\ N\ L \qquad (17)$$

The total number of free atoms in optical path cannot be determined but it is not necessary for routine applications, as atomic absorption is a relative technique like any other spectroscopic techniques.

The physical conditions for highest sensitivity may be summarized as follows:

- **The absorption line should have lowest energy state and highest population of the atoms in the ground state.**
- **If several resonance lines are there, the one with highest oscillator strength has to be chosen.**
- **Employing a source of radiation, that emits a line of the same wavelength but with lower half width.**
- **Path length may be increased within practical limits in the absorbing medium since B-L law states that the absorption also increases according to the path length.**

Employing these conditions, we can in principle, construct an atomic absorption spectrometer using a hollow cathode lamp made of the same element as the analyte, an atomizer to produce a population of ground state atoms, a monochromator with an entrance and exit slit for collection, dispersion and selection of resonance line, a detector for the measurement of radiation intensity followed by an amplifier and a read out device. A schematic diagram of such a system is shown here.



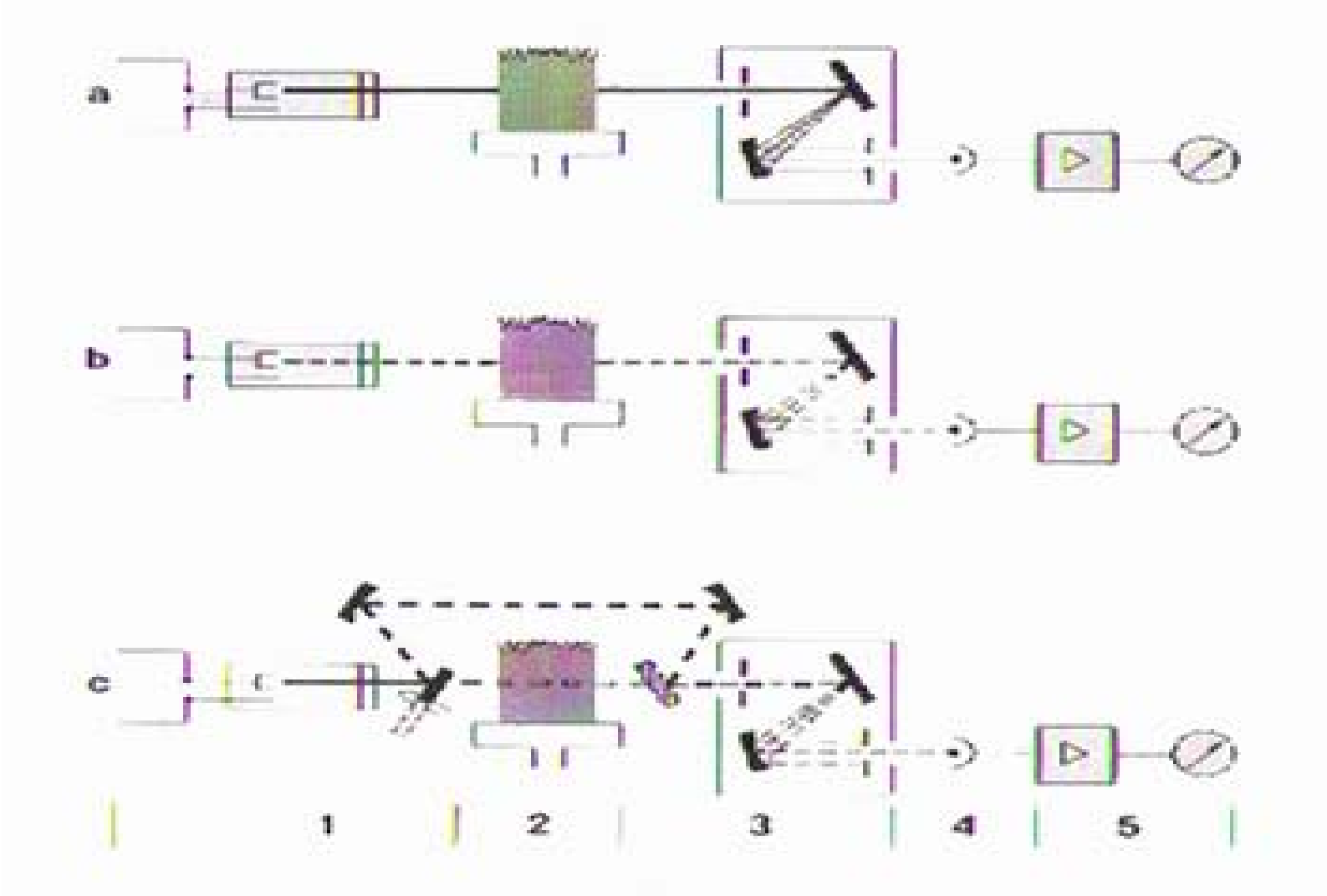
Depending upon the choice of the components and method of operations several variants of atomic absorption spectrometers result, which are enumerated below,

1) Single beam DC instrument – This is the simplest arrangement. The earliest AAS instruments were of this type.

2) Single beam AC instrument – By applying the pulsed current to the radiation source or by mechanically chopping the radiation before it enters the absorption cell.

3) Double beam AC instrument – By using a rotating mirror/chopper arrangement, the radiation is passed alternately through the flame and around the flame. Then it is possible to construct a double beam instrument. Both beams are recombined by a semitransparent mirror placed behind the flame. The electronics of the system is designed to yield directly the ratio of the transmitted radiation flux to that of the incident radiation. The stability is also better.

SCHEMATICS OF ATOMIC ABSORPTION SPECTROMETERS



4) Multi element Simultaneous AAS – Use of radiation sources containing resonance lines of several elements focused in to the absorption cell permits simultaneous determination of several elements. However the optics and electronics need to be suitably modified to handle various signals readout and printouts.

5) Electrothermal AAS – By substituting the absorption cell (i.e flame) with an electrically heated graphite furnace, very efficient means of producing atomic vapor can be achieved. This technique has gained wide popularity since last 15 years permitting the quantitative determination in ppb levels (10^{-9} g).

6) Hydride Generation AAS – Arsenic, antimony, bismuth, selenium, tellurium, germanium, lead etc, are capable of forming their respective hydrides in acidic medium. These compounds easily dissociate into their metallic and non-metallic components which, when introduced into the flame (absorption cell), permit not only their separation but also estimation in ppb levels (10^{-9} g).

7) Mercury cold vapor AAS – Mercury has a unique property of being reduced to metallic form directly from its combined state and also has a significant vapor pressure which permits its determination at room temperature. It only needs to be transported to the absorption cell. This technique is known as cold vapor technique.

Over the years atomic absorption spectrometry as an analytical technique has been accepted as a standard method of analysis all over the world. An enormous amount of literature on the instrumentation, radiation, sources, atomization techniques, optics, signal handling and data presentation has been developed. The advent of computers has made it possible for maximum use of automation, instrument control and statistical data evaluation. On an average, more than 500 research papers are being published on the application of AAS to various matrices every year.

Now we shall discuss the detailed aspects of atomic absorption spectroscopy.

AAS is the measurement of the absorption of em radiation by the atoms in the gaseous state.

Free atoms do not undergo vibrational & rotational transitions but only electronic transitions. Such excited electron may return to ground state by atomic emission, atomic fluorescence or atomic absorption phenomena.

The various energy states of an atom are described by n,l and inner quantum number J.
Selection rules permit L = ±1 and n = any number.

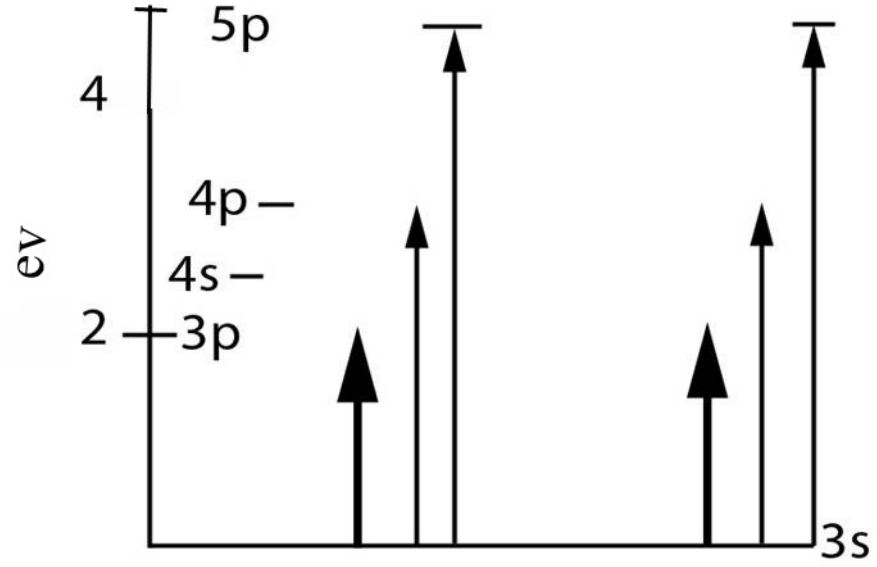
For sodium atom the most loosely bound electron is designated by,

$3s^2\ S^{1/2} \rightarrow 3\ p^2\ p^{1/2,3/2}$ **589.593 nm / 588.996 nm**

$4\ p^2\ p^{1/2,3/2}$ **330.294 nm / 330.234 nm**

$n\ p^2\ p^{1/2,3/2}$

In emission spectrum all possible lines are obtained.



Since all elements can be excited to their next higher energy level ,in theory any element can be determined by atomic absorption spectrometry.

However, below 200 nm, analysis of As, Se, I, S , P etc., is difficult owing to the incipient absorption by oxygen and hot flame gases. Cerium ,Thorium and other refractive elements also present difficulty. Artificial and radioactive elements can not be analyzed by atomic absorption spectrometry.

THERMAL EXCITATION

It must be appreciated that for atomic absorption to occur , we have to produce a population of atoms in the ground state. This can be achieved by exposing a sample of the analyte to high temperatures. At high temperatures prevailing in the flames, compounds decompose into ions, which in turn pick up electrons to produce atoms.

The ratio of number of atoms N_j in an excited state j to the number of atoms in the ground state N_0 is given by,

$$\frac{N_j}{N_0} = \frac{P_j}{P_0} \cdot e^{-Ej/KT}$$

where P_j & P_0 are the statistical weights of the excited and ground states , k is the boltzmann's constant and T is the absolute temperature .

Since this equation is inversely proportional to the absolute temperature, increase in N_j/N_0 with T is exponential. However N_j is always small compared to N_o. Therefore N_j can be neglected and we can assume that the number of atoms in the ground state is independent of the energy of the excitation E_j and nominal temperature of the flame.

Example : let us calculate the number of atoms in the cadmium excited state.

For $nS_{1/2} \rightarrow n P_{3/2}$ transition occurs at 228.8nm.

$P_j / P_o = 3$

$$\nu = c / \lambda = \frac{2.998 \times 10^{10} \text{ cm /sec}}{2.288 \times 10^{-5} \text{ cm}} = 1.310 \times 10^{15} \text{ sec}^{-1}$$

$$E_j - E_o = h\nu = 6.626 \times 10^{-27} \text{ erg.sec} \times 1.310 \times 10^{15} \text{ sec}$$

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

$$N_j / N_o = 3 \exp \left(\frac{-8.682 \times 10^{-12} \text{ erg}}{1.3805 \times 10^{-16} \text{ erg k}^{-1} \quad (2730) \text{ k}} \right)$$

$$= 4.5 \times 10^{-11}$$

At the hottest flame temperature of ~ 4000 k, the population of the excited state atoms is very small. Given below are the alkali and alkaline earth metal characteristics at different temperatures.

Element	Resonance line	ev	2000 k	3000 k	4000 k
Cs	8521(nm)	1.46	4.44×10^{-4}	7.24×10^{-3}	2.98×10^{-2}
Na	5890	2.11	9.86×10^{-6}	5.88×10^{-4}	4.44×10^{-3}
Ca	4227	2.93	1.21×10^{-7}	3.69×10^{-5}	6.04×10^{-4}
Fe	3720	3.33	2.29×10^{-9}	1.31×10^{-6}	
Cu	3248	3.82	4.82×10^{-10}	6.65×10^{-7}	
Mg	2852	4.35	3.35×10^{-11}	1.50×10^{-7}	
Zn	2139	5.80	7.29×10^{-15}	5.38×10^{-10}	1.48×10^{-6}

In emission, one measures the difference between zero signal and the sample signal. The limit of detection is governed by electrical noise.

In AAS, the difference between the noise level of the blank & finite signal is measured. Hence sensitivity is governed by noise level of the signals.

Free atoms do not undergo vibrational and rotational transitions. They undergo electronic transitions only. The excited electrons may return to the ground state by atomic emission, or by atomic fluorescence or by atomic absorption.

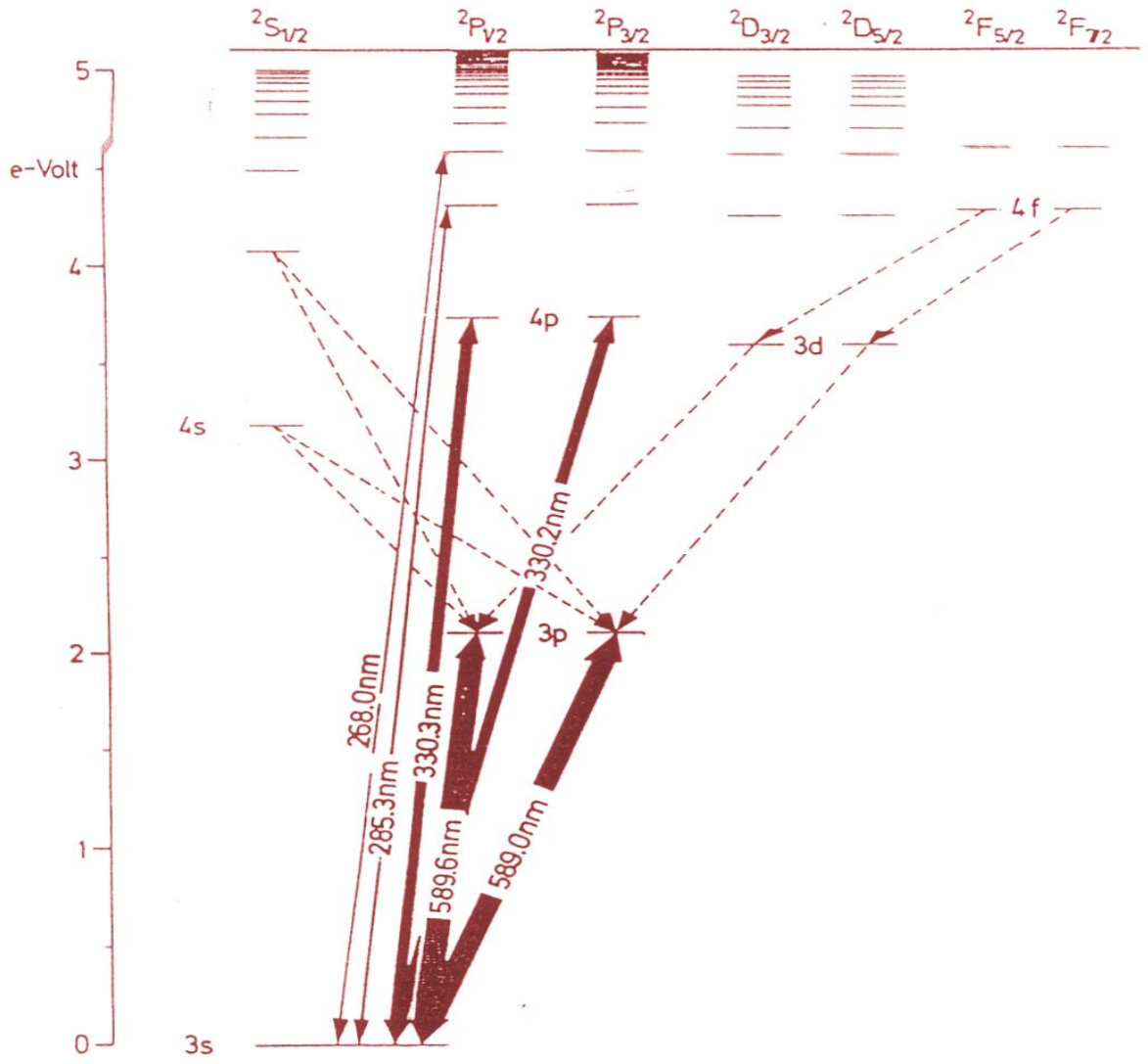
Atomic absorption spectrometry involves the measurement of the absorption of electromagnetic radiation by the atoms in the gaseous state.

If the excitation is by optical radiation the atoms absorb the radiation of definite frequency. The absorbed energy is subsequently in the form of heat.

The absorption spectrum of an element consists of a number of lines which appear closer and closer together and decrease regularly in intensity until the lines merge together and only continuous absorption is observed.

In the spectrum of sodium so far 57 absorption lines have been observed. In contrast, emission lines are more numerous and do not exhibit the same regularity of the absorption spectrum.

SPECTROSCOPIC CONSIDERATIONS



The energy level diagram for sodium is shown here.

Each line represents an energy level.

If the sodium vapour is excited thermally using a hot flame or electrically terms with arbitrary n and l can be attained and the emission spectrum can contain all the emission spectrum can contain all the lines starting from $3s^2S^{1/2}$. Similarly complex emission spectrum can be obtained for all other elements.

The energy level diagram of sodium indicates that atomic absorption can occur only for those lines which originate from the ground term of the neutral atom. These lines are called as resonance lines since they can come into resonance with optical radiation of suitable frequency. The most intense and easily excited line should be of least energy and hence lowest frequency. This is a very simple and clear cut situation applicable only to very simple atoms. For transition elements the exact resonance line is more complex and usually determined by experiment.

In order to analyze a spectrum it is necessary to know which spectral term corresponds to the spectral lines. This information is provided by the selection rules of LS coupling(J) where ΔJ value has to change by 1 unit and n, the value of the principle quantum number can alter by any amount.

Let us recapitulate our knowledge about the energy states of an electron in an atom. They are defined by four quantum numbers n, l , m and s.

The state of an electron in an atom is described by L,S and J.

The orbitals of an electron in any atom have shapes of s,p,d,f and g albeit with variance in their energy levels.

The magnetic quantum number m_l can assume 2l+1 integer values from –l to +l. the magnitude of the angular momentum vector is given by $\sqrt{l(l+1)}.h/2\pi$

Spin angular momentum (s) is also quantized according to

$$s = \sqrt{s(s+1)}\, h/2\pi$$

The quantization law for spin momentum is that the S_z can have half integral multiples of h/2π so that S_z have values of +1/2 or -1/2 only ($S_z = \pm 1/2$).

Total angular momentum (j) of one electron is the vector sum of l & s. Thus

$$j = l + s$$

The total angular momentum quantum number is given by,

$$j = \sqrt{j(j+1)}\ h/2\pi$$

j can have z components defined as

$j_z = \pm j , \pm (j-1) , \pm (j+2) \ldots..1/2$

when l = 1 and s = ½, j can have values 3/2 or 1/2

Since $j_z = l_z + s_z$ the summation of z components yields,

j_z = 1+1/2 , 1-1/2, 0+1/2, 0-1/2, -1+1/2 and -1-1/2

= 3/2 , 1/2, 1/2, 1/2 , -1/2 , -1/2 and -3/2

Thus for p electron (l = 1), the orbital and spin momenta combine to give a total momentum of j = 1/2 $\sqrt{15}$ (when l & s reinforce) or 1/2 $\sqrt{3}$ when l and s oppose each other. These states split into doublet with slightly deferring energies and represented as $^2P_{3/2}$ or $^2P_{1/2}$. Similarly for l= 2,3,4 we get doublets ($^2D_{5/2,3/2}$) ($^2F_{7/2}$, $^2F_{5/2}$),($^2G_{9/2}$, $^2G_{7/2}$) etc.

The total orbital angular momentum of an atom is the vector sum of all quantized angular momenta of individual electrons. These states are also quantized. The orbital angular momentum can interact with the magnetic moment due to spin. This is termed as Russel Saunders coupling(RS) or simply LS coupling. The LS interaction gives multiple splitting of each term. The coupling scheme for heavy atoms is called jj coupling.

LS COUPLING FOR S AND P ELECTRONS

	L =0(s)	L = 1(p)	L = 2(d)	L=3(f)
n=1	$1s\ ^2S^{1/2}$			
n=2	$2s\ ^2S^{1/2}$	$2p\ ^2P^{1/2};^2P^{3/2}$		
n=3	$3s\ ^2S^{1/2}$	$3p\ ^2P^{1/2};^2P^{3/2}$	$3d\ ^2D^{3/2};\ ^2D^{5/2}$	
n=4	$4s\ ^2S^{1/2}$	$4p\ ^2P^{1/2};\ ^2P^{3/2}$	$4d\ ^2D^{3/2};\ ^2D^{5/2}$	$4f\ ^2F^{5/2};^2F^{7/2}$
n	$ns\ ^2S^{1/2}$	$np\ ^2P^{1/2};\ ^2P^{3/2}$	$nd\ ^2D^{3/2};\ ^2D^{5/2}$	$nf\ ^2F^{5/2};\ ^2F^{7/2}$

TERM SYMBOLS

1. ll coupling : Orbital angular momentum of electrons are added vectorially and the resulting L values are designated as S,P,D,F and G.

2. ss coupling : Spin angular momentum of individual electrons are added vectorially to give total s.

   $S = (s_1+s_2), (s_1+s_2-1), \ldots\ldots\ldots |s_1-s_2|$

   The multiplicity of the term is then(2S+1)

3. LS coupling

$J = (L+S)\ ,\ (L+S-1)\ldots\ldots \left| L-S \right|$

The J value is subscripted to the left of the term symbol.

4. The term symbol for a particular atomic state is expressed as $^{2S+1}L_J$

Example : Derive the term symbols for carbon atoms (p^2)

Solution : C $1s^2$, $2s^2$, $2p^2$

For two equivalent electrons $l_1 = l_2 = 1$ and $s_1 = s_2 = 1/2$

Hence,

L = 2,1,0 and S = 1,0

Terms corresponding to these values are calculated by spin multiplicity (2s + 1).

For S = 1, spin multiplicity is 3 (triplet)

S = 0, spin multiplicity is 1 singlet

Hence we get 6 states defined by ^3D, ^3P, ^3S and ^1D, ^1P and ^1S

Corresponding J values will be:

3D with J values of 3,2,1; give rise to $^3D_3$, $^3D_2$ and $^3D_1$

3P with J values of 2, 1, 0; gives rise to $^3P_2$, $^3P_1$ and $^3P_0$

3S with J =1 ; gives rise to $^3S_1$

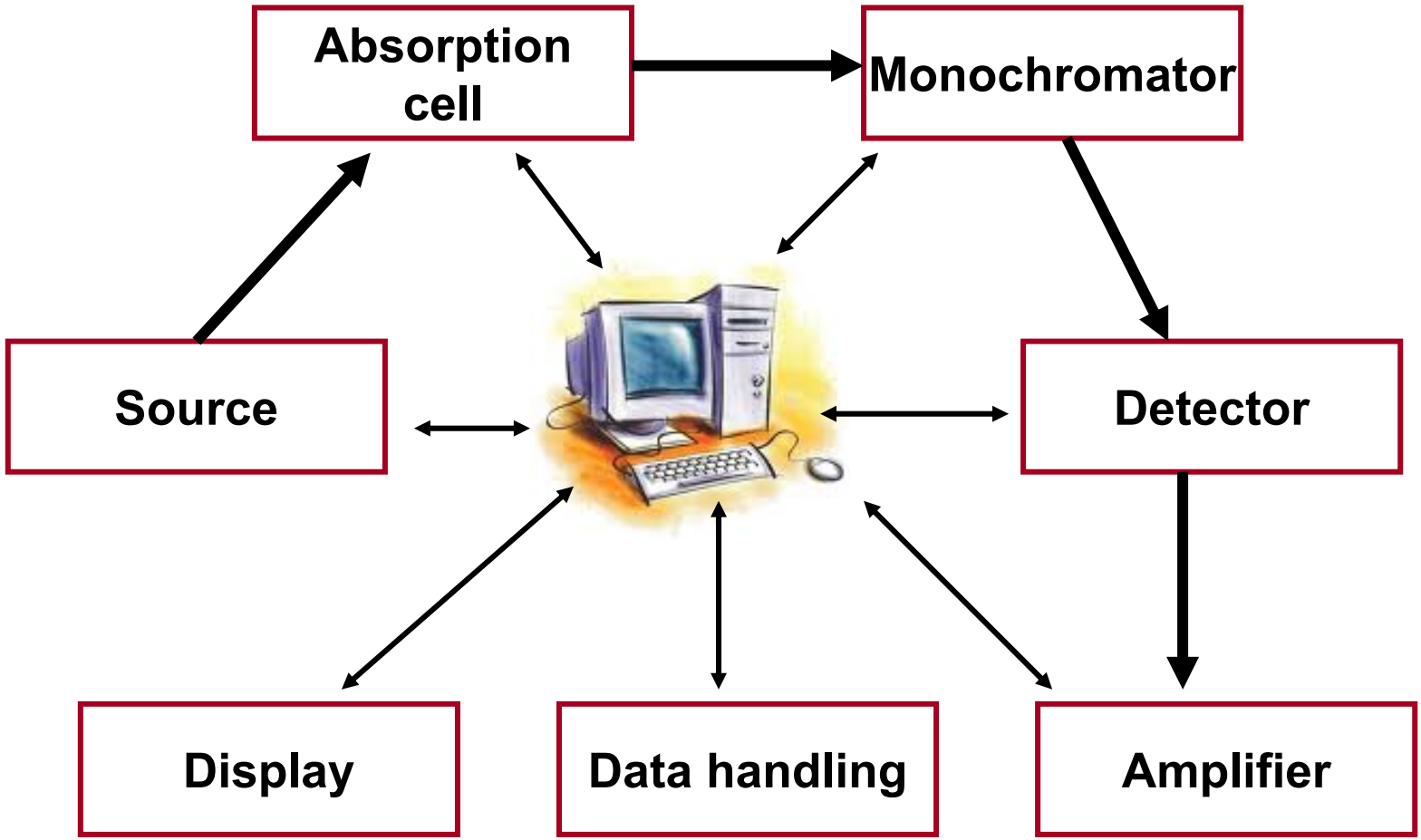
1D with J = 2 ; gives rise to $^1D_2$

1P with J = 1 ; gives rise to $^1P_1$

1S with J = 1 ; gives rise to $^1S_0$

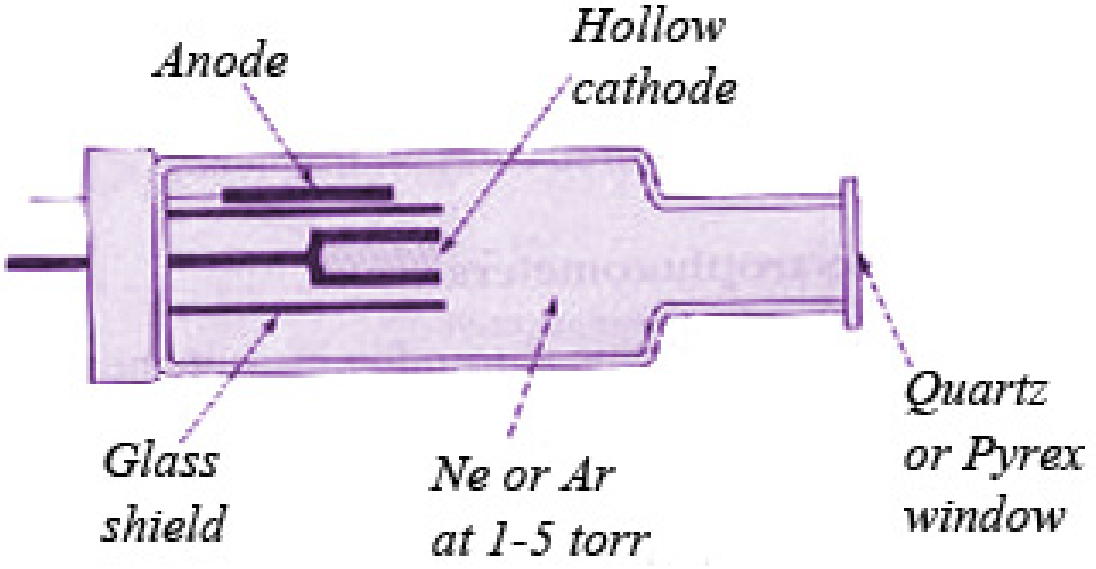
The corresponding energy level diagram of sodium can be shown to contain 56 transition lines for sodium, 106 for lithium, 124 for potassium and 294 for rubidium etc.

SCHEMATIC DIAGRAM OF ATOMIC ABSORPTION SPECTROMETER



1. RADIATION SOURCES

1.1 HOLLOW CATHODE LAMPS



A hollow cathode lamp (HCL) consists of a glass cylinder filled with an inert gas (neon or argon) under a pressure of 1-5 torrs into which an anode and a cathode are fused. The cathode is made of the analyte element in the form of a cylinder and the anode is a thick wire usually made of tungsten or nickel.

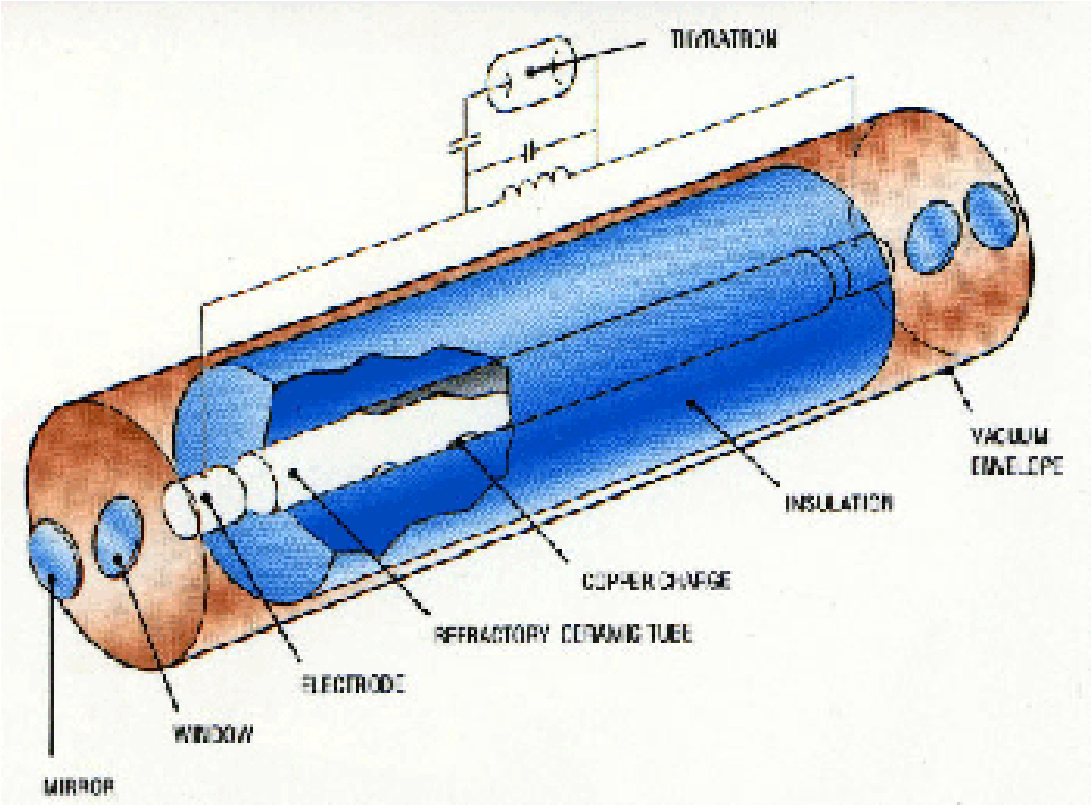
A voltage of several hundred volts is required to light the lamp. The applied voltage generates 5 -15mA current and sets up a glow discharge of the carrier gas. A stream of positive ions strikes the cathode and releases the atoms of the cathode material by collisions. This process is known as sputtering. These atoms contain atoms in the excited states which emit their characteristic radiation as they return to the ground state. Eventually the metal atoms diffuse back on to the cathode surface or redeposited on the glass walls of the tube.

The cylindrical configuration of the cathode concentrates the emitted radiation and enhances the possibility of reposition of the atoms on to the cathode rather than the glass walls.

The efficiency of the HCL depends upon the geometry and operating voltage. Higher the voltage, higher the current and greater is the intensity. This advantage is some what offset by an increase in Doppler broadening of the emitted radiation. Further increased number of unexcited atoms in the gas cloud in turn are capable of absorbing the same excited radiation. This process is known as 'self reversal' and lowers the intensity of the emitted radiation.

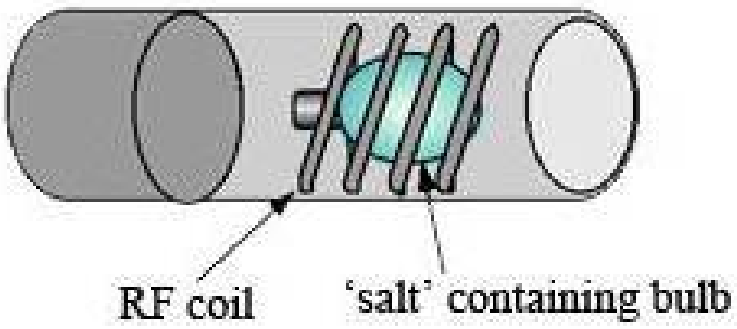
A variety of hollow cathode lamps for most of the elements are available commercially. By using an alloy of 2-5 metals as cathodes more multi element determination is possible.

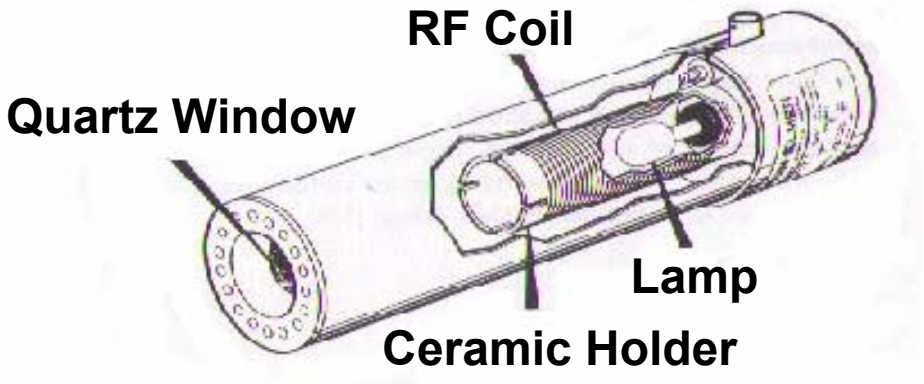
1.2 VAPOUR DISCHARGE LAMP



Very volatile materials like mercury, thallium, zinc, alkali metals can be determined using low pressure vapour discharge lamps. They can low cost and give high radiant intensity. They emit strongly broadened lines owing to self absorption and self reversal. Therefore VDLs must be operated as highly reduced currents. However this leads to instability of the lamp.

1.3 ELECTRODELESS DISCHARGE LAMP





Electrodeless discharge lamps (EDLs) exhibit highest radiant intensity and narrowest line widths compared to HCLs. They consist of a sealed quartz tube of 5-10 mm dia and 4-5 cm length, filled with a few milligrams of the analyte element or its salt. The tube is filled with argon.

The lamp contains no electrode but it is energized by an intense field of radio frequency. The tube is mounted within the coil of a high frequency generator 2400 (MHz) and excited by an output of about 200 watts. Ionization of argon takes place.

EDLs are ideal for elements whose resonance lines are below 200 nm. Such elements include As, Se, P. EDLs are now available for most of the volatile elements including Cs, Rb. The detection limits with EDLs are 2-3 times lower than HCLs. They are also very stable during operation and have long life times. HCL and EDLs are complementary to each other.

1.4 CONTINUUM SOURCES

Continuum spectrum of hydrogen , xenon and halogen lamps offer good stability. They are cost effective and exhibit multielement capability. However owing to the low intensity of the chosen wavelength, high demands on the monochromator to produce 0.002 nm wavelength accuracy, risk of spectral interferences etc., they have not become popular.

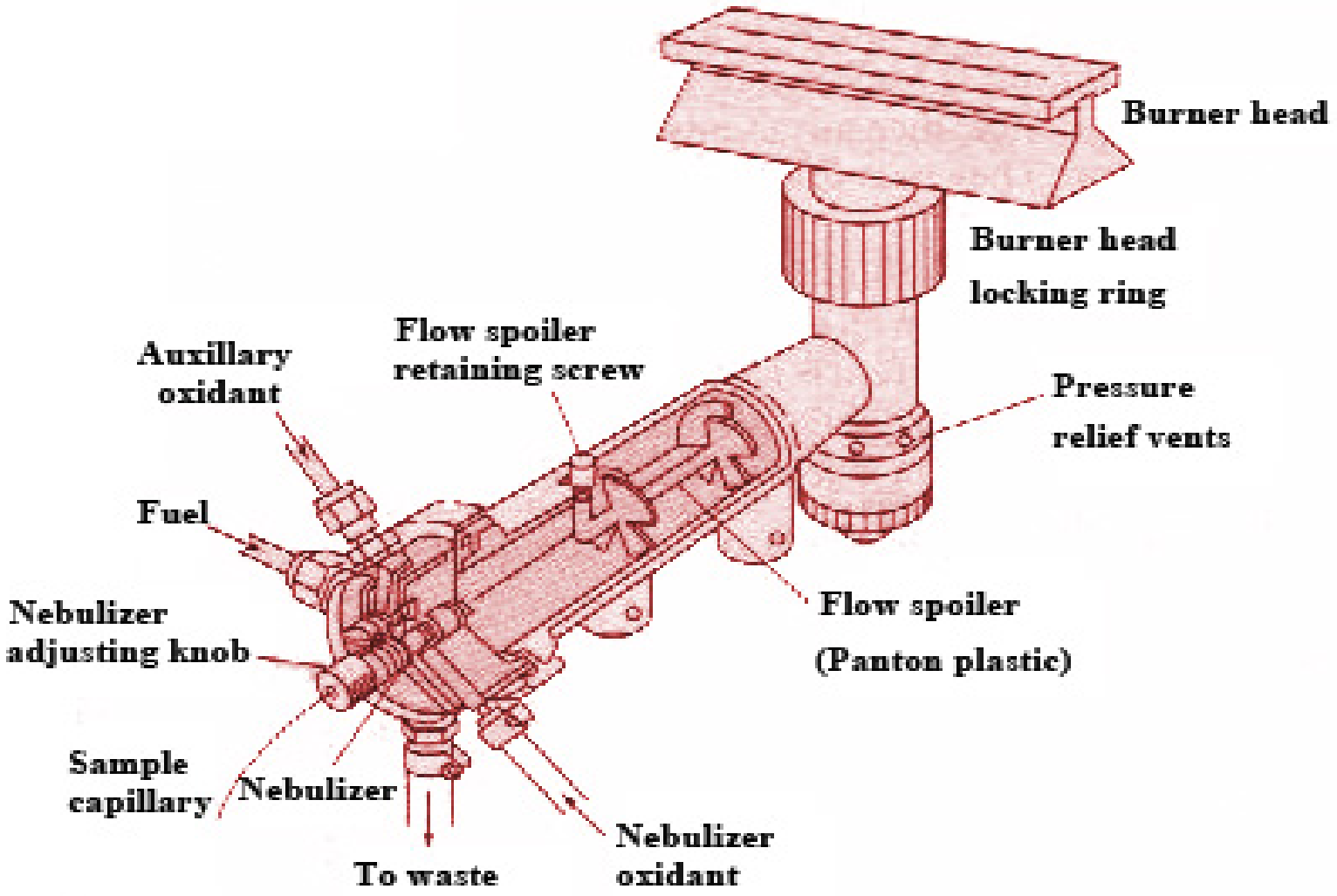
2. ATOMIZERS

Atomizers transform a liquid sample into atoms. This is easily accomplished by spraying the analyte solution into a flame where the ions or molecules are converted into atoms. Other techniques of atomization include electro thermal evaporation, hydride technique and cold vapour technique which will be discussed later. The success or failure of AAS determination is virtually dependent upon the efficiency of atomization i.e the total number of atoms that are formed.

Numatic nebulizer is very useful to spray the sample into a flame in a continuous manner to maintain a steady supply of atoms. Usually nebulizers are connected to the flame burner which can be considered as a single unit even though, both parts are detachable and serviced independently and reconnected. Typical design of a Laminar flow burner is shown here.

Laminar flow burner uses a concentric tube nebulizer in which oxidizer and the fuel gas combine to produce an aerosol of the sample. The sample passes through a number of baffles and flow spoilers. Only the fine mist and mixture of gases are led into a slotted burner of 5 cm width. The flame height is approximately 5 – 10 cm.

NEBULIZER AND BURNER



Both the fuel and the oxidant flows are independently and accurately controlled and combined in stoichiometric proportions. Flow rates are usually controlled by double diaphragm pressure regulators followed by needle valves. Rotameters are used to adjust the gas flows to the desired volumes.

The nebulizer - flame combination is of two types:
Pre-mix burner and total combustion burner.

COMPARISION OF PRE-MIX AND TOTAL COMBUSTION BURNERS

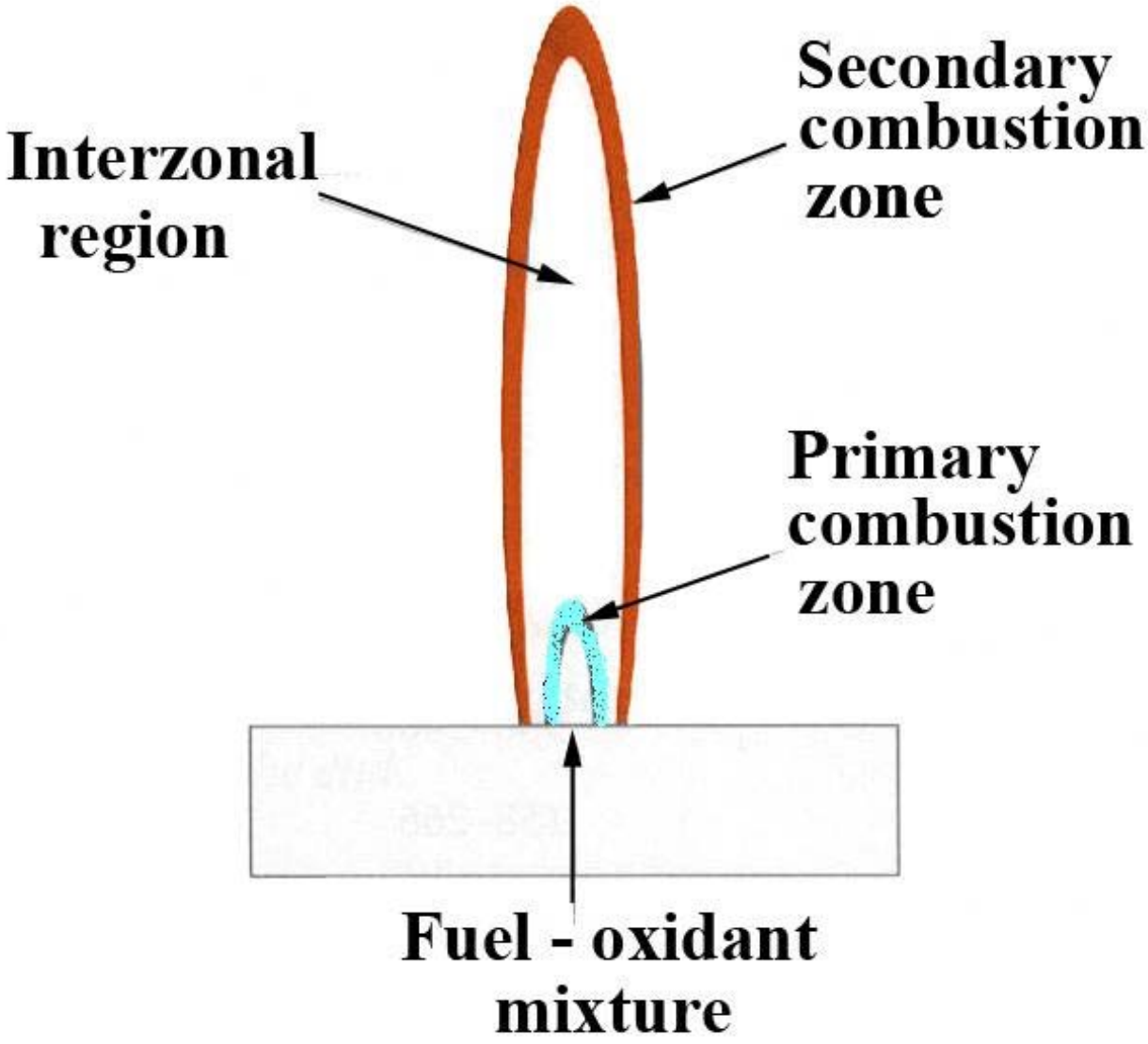
Pre-mix burner	Total combustion burner
Laminar flow, controlled.	Entire sample is aspirated.
Uniform droplets.	Oxidant – Fuel gas ratio is fixed.
Low turbulence and less electrical noise.	Cooling and loss of droplets.
High solids clog the burner.	Noisy flames.
Explosion hazard.	Flow rate is 1ml/min.
Flow rate is 3 – 10 ml/min.	High solids can be handled.
Atomization efficiency 10 -15%.	Low S/N ratio.

TYPES OF FLAMES

Common fuels and oxidants used in AAS are listed below.

Fuel	Oxidant	Temperatures, °C	Maximum Burning Velocity (cm s^{-1})
Natural gas	Air	1700–1900	39–43
Natural gas	Oxygen	2700–2800	370–390
Hydrogen	Air	2000–2100	300–440
Hydrogen	Oxygen	2550–2700	900–1400
Acetylene	Air	2100–2400	158–266
Acetylene	Oxygen	3050–3150	1100–2480
Acetylene	Nitrous oxide	2600–2800	285

FLAME STRUCTURE

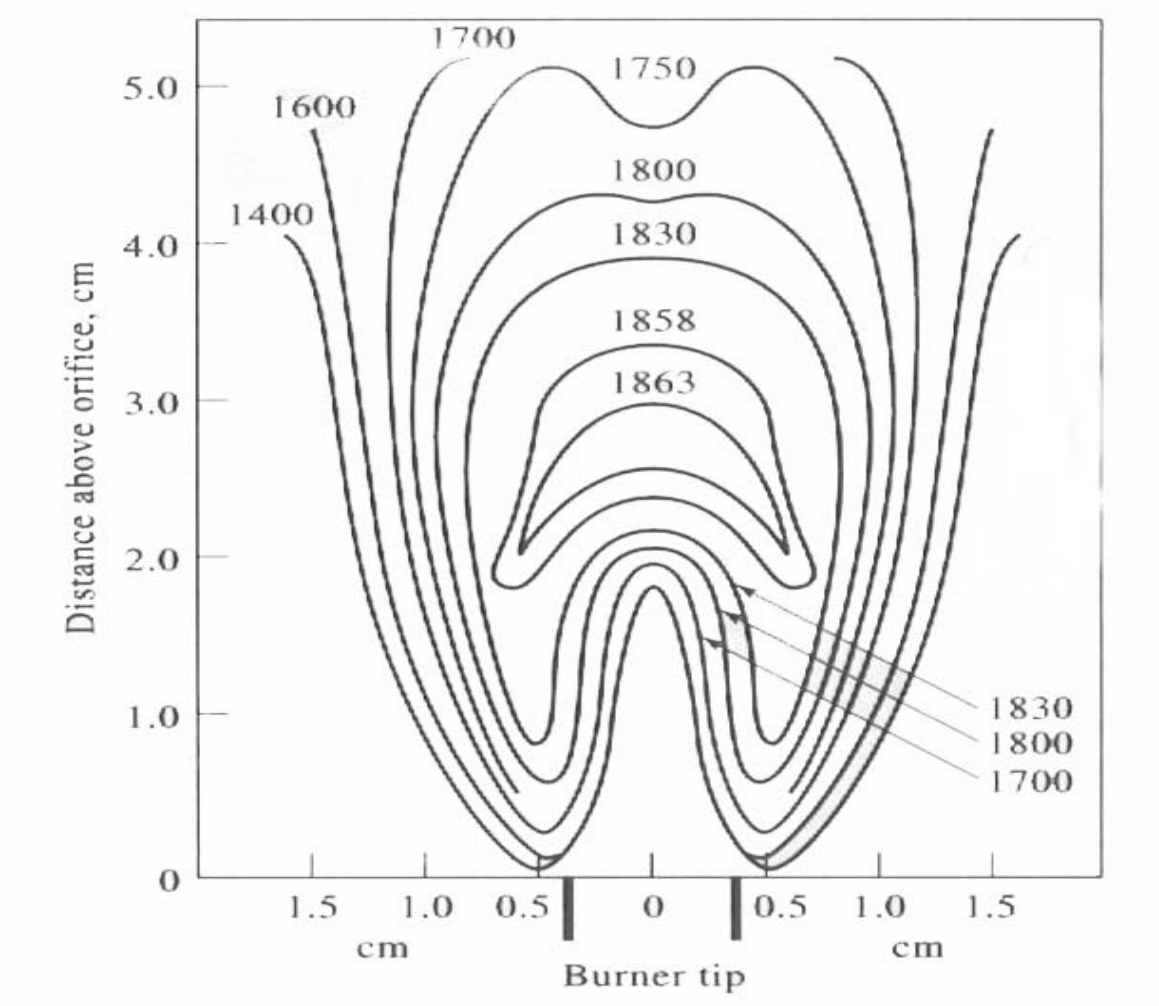


A typical flame structure contains a primary combustion zone, inter zonal region and the secondary combustion zone. The primary combustion zone is blue in colour due to the band emission of C_2, CH and other radicals. This region is not of analytical interest because thermal equilibrium conditions are not obtained here.

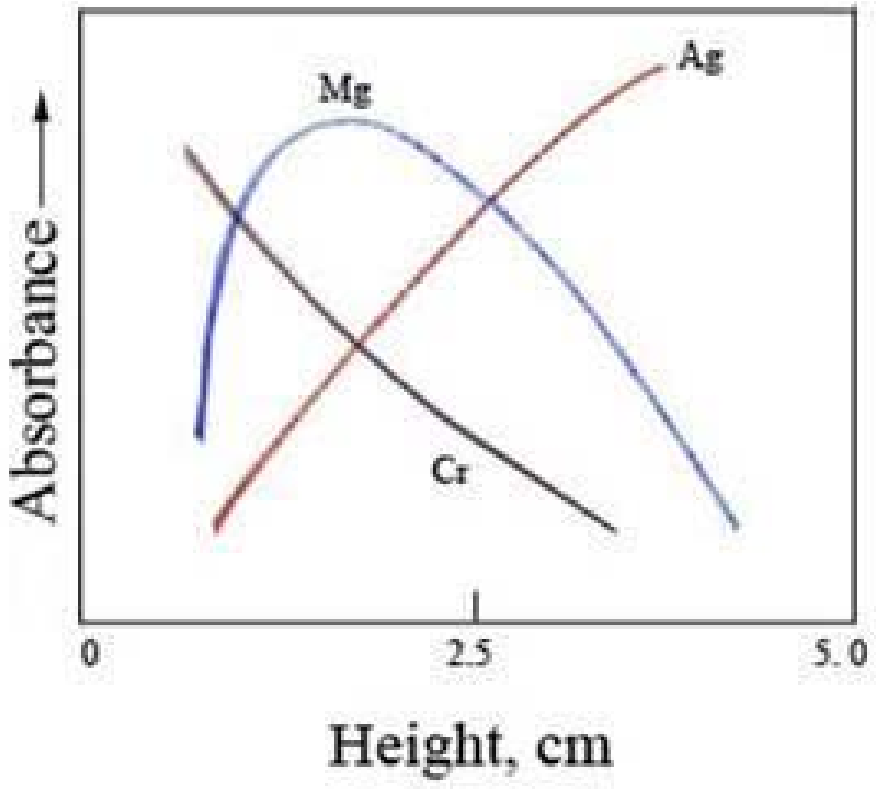
The interzonal area has a height of several centimeters. It contains free atoms and stable molecular oxides.

In the secondary combustion zone, the products of interzonal area are dispersed into the surroundings.

TEMPERATURE ZONES IN A FLAME



FLAME ABSORPTION PROFILE



Air – acetylene flame is the most common flame used in AAS. This flame is completely transparent above 230 nm but shows about 65% absorption around 193.7nm. Normal temperatures of 1100^0C – 2400^0C are obtained which is quite sufficient for the atomization of most elements except refractory samples. Alkali metals do ionize to an appreciable extent at these temperatures. This flame is operated under stoichiometric or weakly oxidizing conditions (excess of air) for Au, Ir, Pd, Pl, rh. Alkaline earth metals are determined in a slightly reducing flame (excess of fuel gas – green or blue flame).

An important development in AAS is the introduction of nitrous oxide/ acetylene flame operated with a slight excess of fuel gas. This flame has a 2 - 4 mm high blue – white primary reaction zone above which 5 – 50 mm red reducing zone is present. The red reducing zone is suitable for the analysis of refracting elements such as Mo, W, V and rare earth elements. It is largely free of interferences. The burning fuel produces a carbon monoxide environment according to the reaction,

$$3N_2O + C_2H_2 \rightarrow 2CO + 3N_2 + H_2O$$

Nitrous oxide – acetylene flame has two disadvantages:

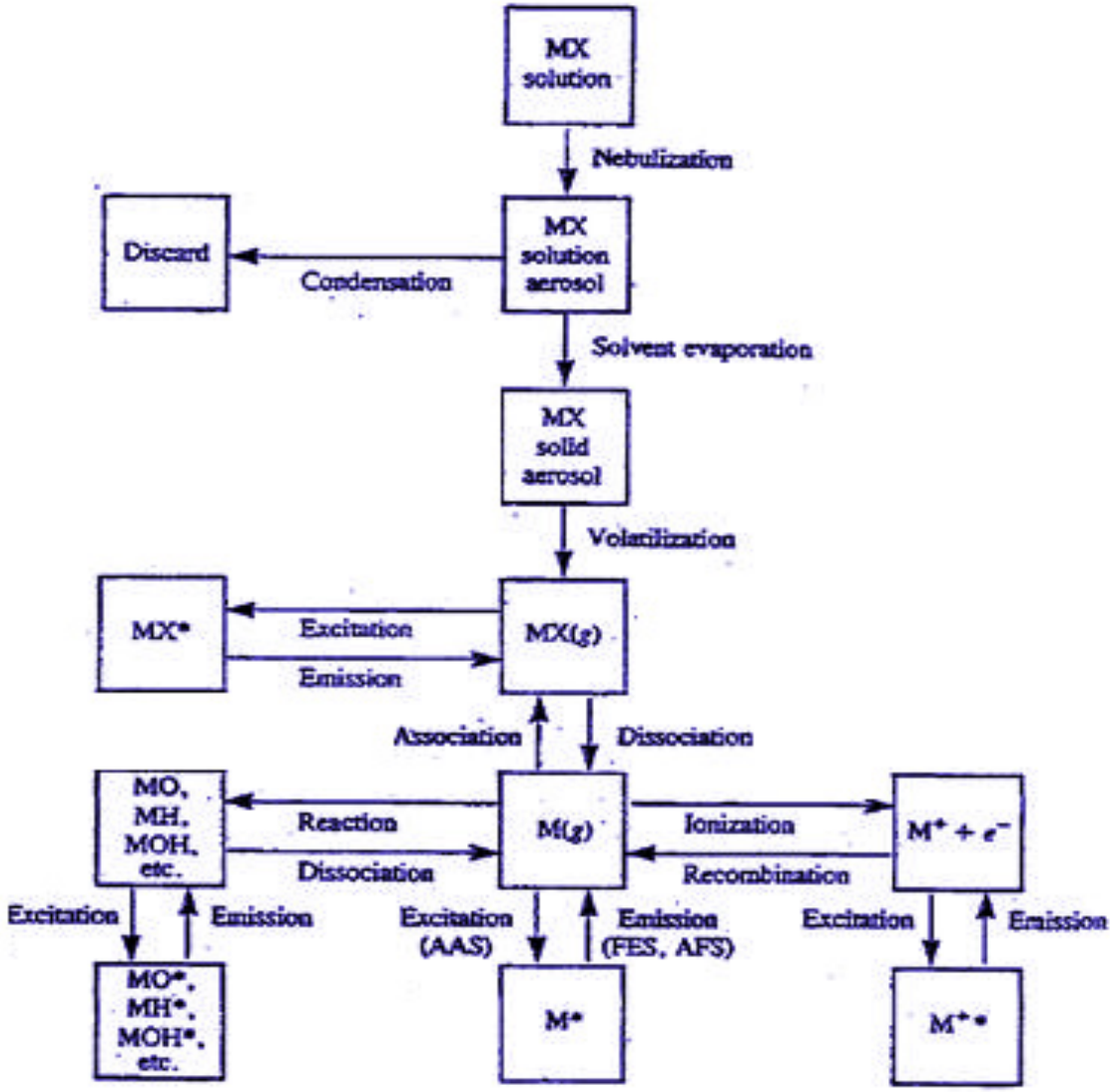
- **Due to high temperatures (2550 – 2800 ^{0}C) appreciable ionization occurs for many elements resulting in lowered sensitivity.**

- **The flame also emits strong broadband emissions of CN, CH, NH bands which can introduce errors due to their contribution at the analytical line. It also introduces "emission noise" which can affect the precision of the analysis.**

In addition to the composition of the gas mixtures, their burning velocities are also important. If the gas flow rate does not exceed the burning velocity, the flame propagates back into the burner giving a 'flashback'.

At high flow rates, the flame rises and eventually reaches a point where it blows off the burner. Therefore it is very important to adjust the flow rate of the fuel – oxidant mixture until it reaches a point above the burner where flow velocity and burning velocity are equal.

ATOMIZATION PROCESS



The atomization step converts the analyte within the aerosol into free ground state atoms. Various process occur during the conversion. These include:

Desolvation
Volatilization
Dissociation
Excitation

With so many processing occurring, it is not surprising that atomization is the most critical step in flame AAS which determines the sensitivity and precision of an analysis.

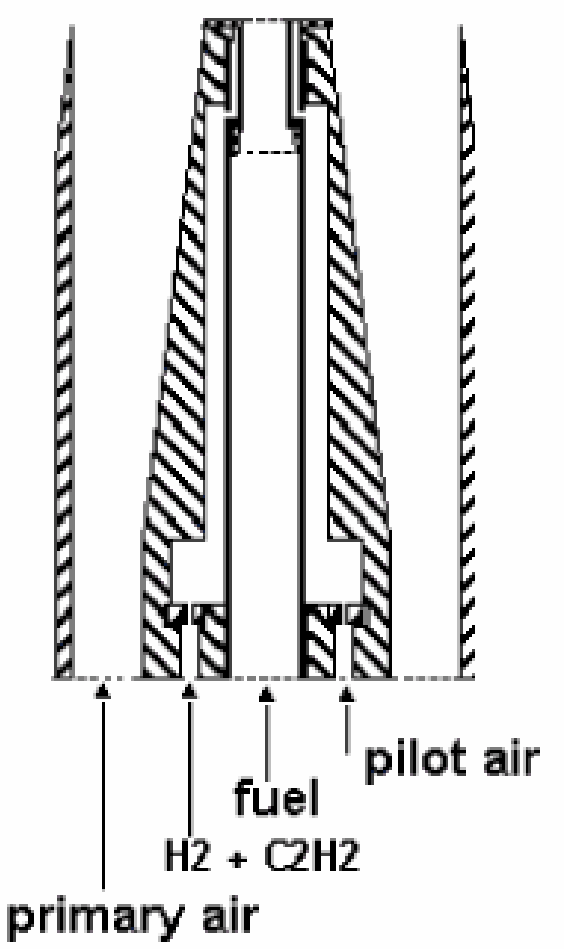
FLAME TYPES

1. Turbulent – Flow Burner

The characteristic of this type of burner is that the fuel gas and the combustion supporting gas are not mixed until the point at which they enter the flame and the solution to be sprayed is also introduced at this point. Thus the burner is actually a combination nebulizer burner. It is also known as ‘direct injection’ or ‘total consumption’ burner since all the aspirated liquid enters the flame and is converted into a spray at the point of entry. Several workers have used it for atomic absorption . The turbulent flow burner gives a tall narrow flame which provides a very short light path for atomic absorption.

A typical burner consists of a tube usually made of titanium or stainless steel or other chemically resistant and non – corrosive metal, containing either an array of holes or grooves as a slot in order to minimize salt deposition , as the underside of the burner surface and also to ensure stable absorption reading.

TURBULENT – FLOW BURNER



An ingenious way of utilizing the height of the flame to achieve long light-path and hence greatly improved sensitivity is to direct the flame into a tube, made of suitable heat resistant material such as quartz or ceramic.

The long tube technique is likely to be used for those metals which do not readily form oxides in the flame. Sensitivities of 10-100 times those obtainable in an ordinary flame have been reported for Cd, Zn and the noble metals.

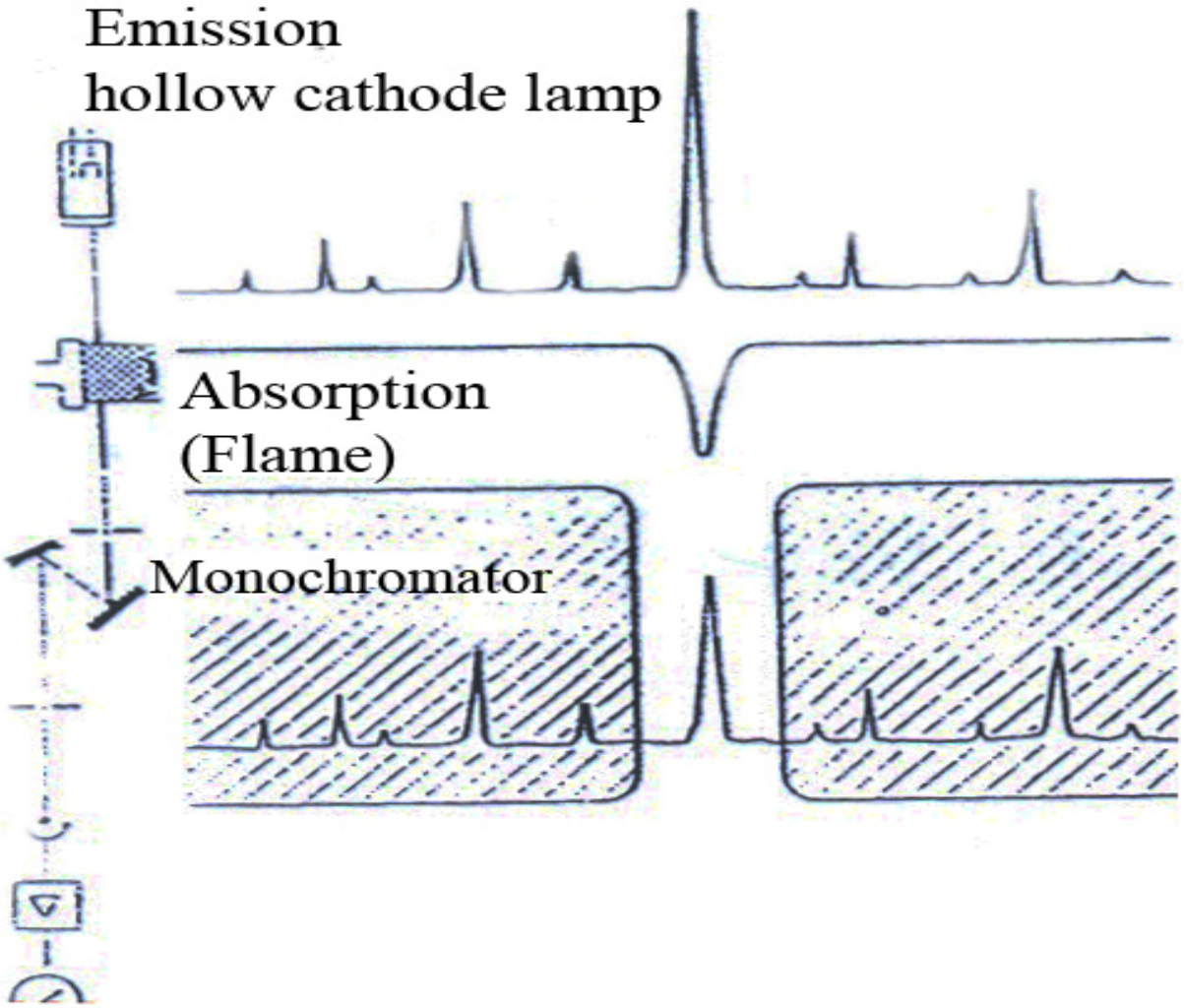
The requirement that the light beam must pass entirely through the flame, limits the geometry of the latter somewhat. Ideally, the light beam should be very narrow to allow the use of a flame burning at a long, narrow slot which will give highest sensitivity. The need for the monochromator to accept sufficient height to give a satisfactory signal–to–noise ratio usually means that a light beam of finite width is required and this needs a short wider flame.

The turbulent – flow burner gives a flame, which is tall and narrow. While ideal for AAS, it provides a much shorter light path and hence exhibits poorer sensitivity than a laminar- flow burner. The uptake of solution by the turbulent flow burner is usually less than that of the laminar flow system and since all the aspirated solution enters the flame, it should be a more efficient producer of atoms than the laminar - flow system. However, there is evidence that some of the aspirated liquid in the total consumption burner passes through the flame without being fully vaporized.

OPTICAL COMPONENTS

AAS covers the UV-visible wavelength range. It is necessary to employ proven monochromators in AAS, since atoms are only capable of absorbing radiation within a very narrow frequency interval. The sources are found to be weak if the interval of interest is considered. For this reason, some authors recommend that the radiation source used for absorption measurement should also emit the spectrum of the element to be determined. With such an arrangement the required resonance line merely has to be separated from other spectral lines of the same element by means of a monochromator.

ABSORPTION MECHANISM



The spectrum of the element under study is emitted from the HCL. In the flame, a portion of the resonance line, corresponding to the concentration of this element is absorbed. Lines that do not occur in absorption are not attenuated. After dispersion of the radiation in a monochromator, the resonance lines are separated by the exit slit and all other lines are masked.

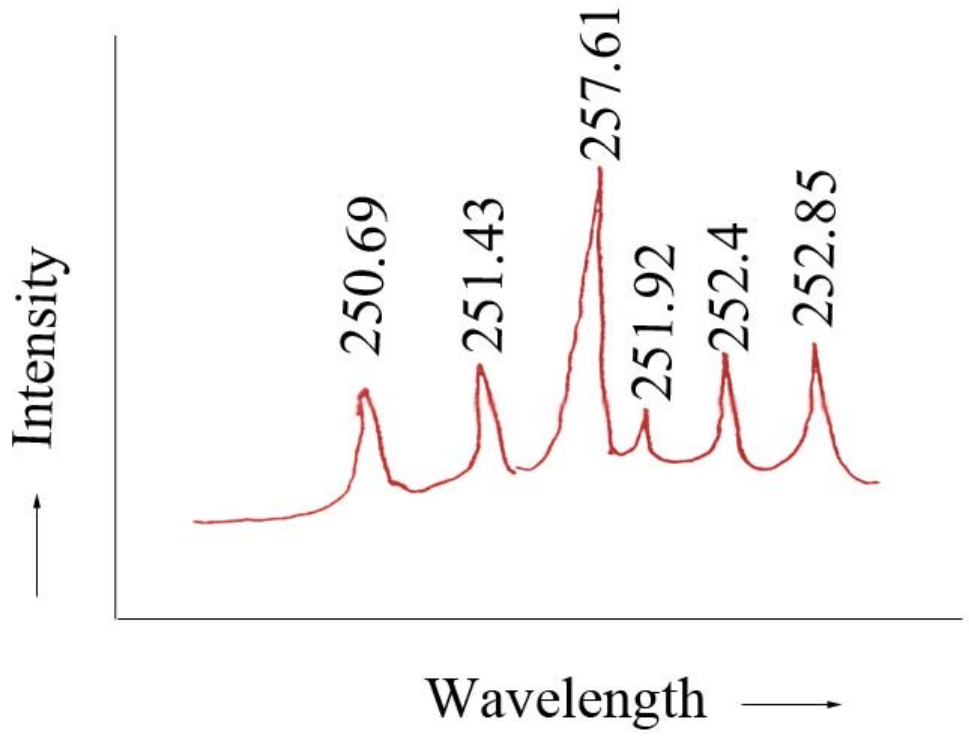
One of the greatest advantages of AAS namely its specificity is based on the use of specific radiation source that emits the spectrum of the analyte element in the form of very narrow spectral lines. The ability of AAS to differentiate between different elements is solely dependent on the half intensity widths of the emission lines (0.002-0.005nm). This range lies beyond the scope of the resolving power of normal monochromator.

When hollow cathode lamp is used as a source of radiation the monochromator in AAS has the important task of separating the resonance line of analyte element from other emission lines of the source. If slit widths are large in AAS, lower sensitivity and increasing non-resolved multiplets result (several resonance lines passing through the exit slit).

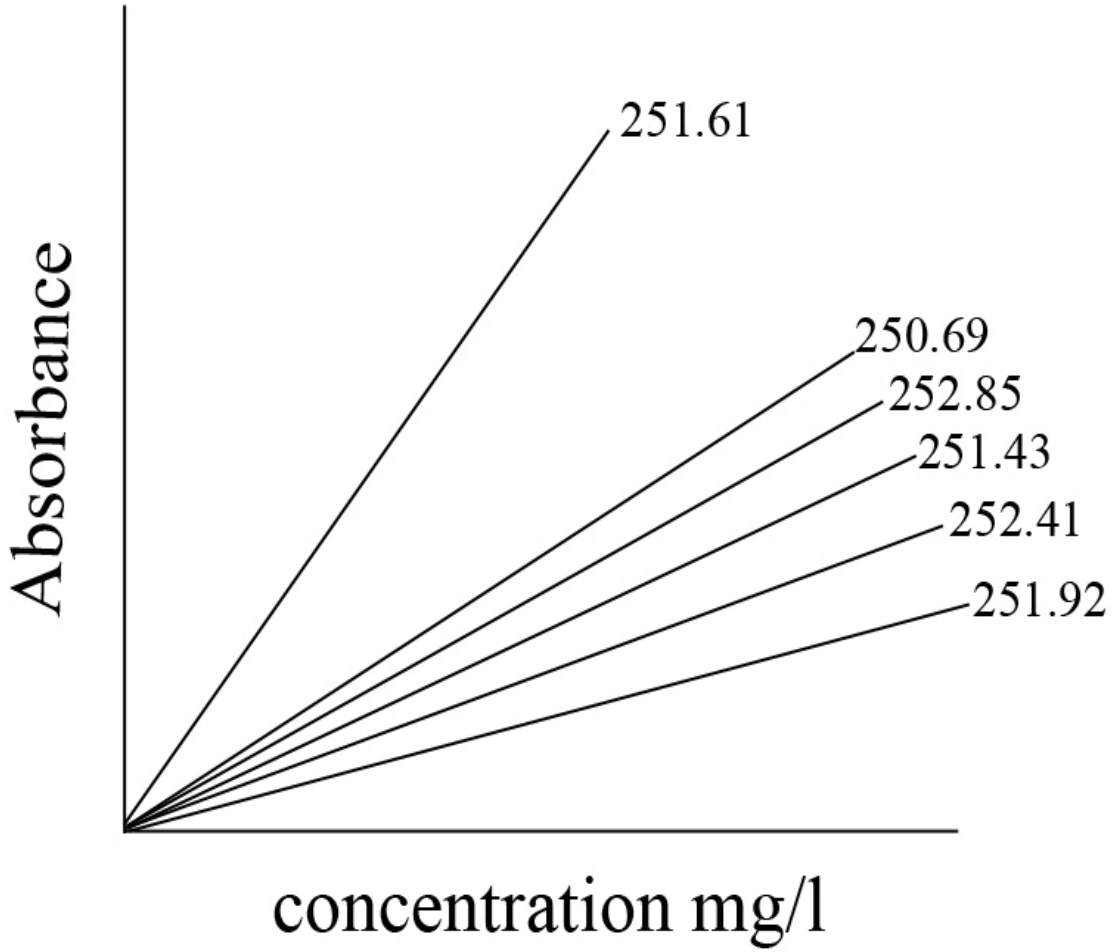
It is observed that for a number of elements a spectral band pass of 0.2 nm is necessary to obtain good sensitivity and linearity of analytical curve. For other elements the resonance line is more or less separated so that larger slit width can be used without disadvantage.

Following figures show the influence of the spectral band pass width on the sensitivity, signal-to-noise ratio and curvature of analytical curve. Resonance lines of silica lie between 250 – 253nm. With a sufficiently small slit width every resonance line gives a linear analytical curve within the observed range.

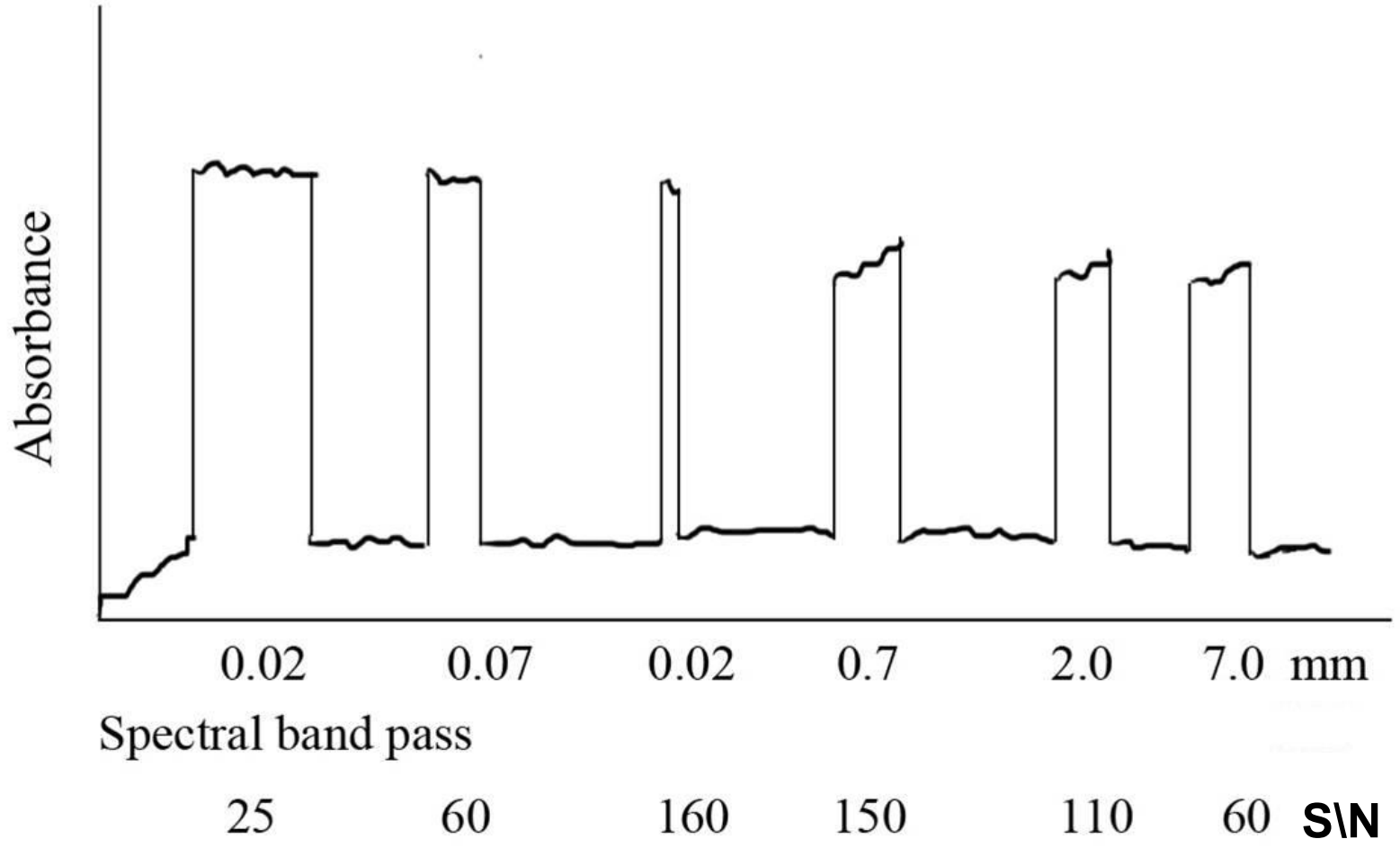
RESONANCE LINES OF SILICA



ANALYTICAL CURVE OF THE RESONANCE LINES

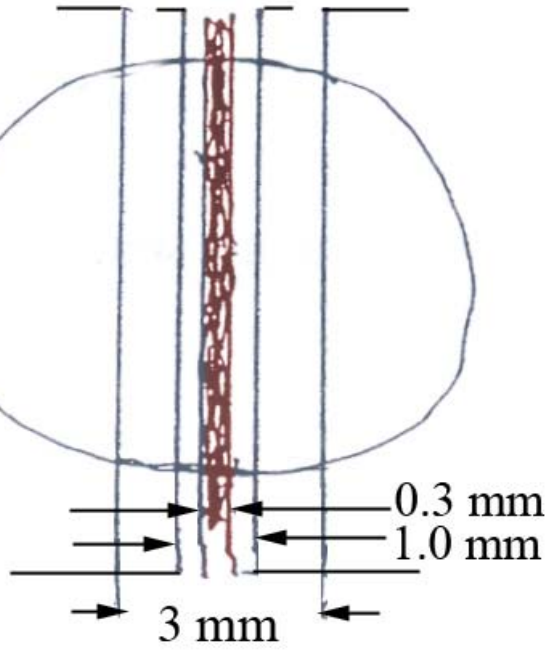


The signal to noise ratio is optimum at a spectral band pass of 0.2nm and clearly decreases on both sides as shown in figure,



Two requirements have been placed on the monochromator of an AAS. Firstly a spectral band pass of 0.2nm is required and secondly the entrance slit should have as wide a geometric width as possible. However, the entrance slit and exit slit of the monochromator must have the same mechanical dimensions. In AAS, the image of the radiation source is found at the entrance slit, (radiation beam of several nm falls on the slit). It can be seen from the figure that the geometric width of the entrance slit determines the amount of radiation that falls on the dispersing element and subsequently on the detector. This means that the noise always accompanying the signal is relatively small compared to the signal. At the same time lower amplification can be employed so that contribution to the noise are reduced. For the analyst, low noise means a stable signal and hence good precision and lower detection limit.

IMAGE OF THE RADIATION SOURCE ON THE ENTRANCE SLIT

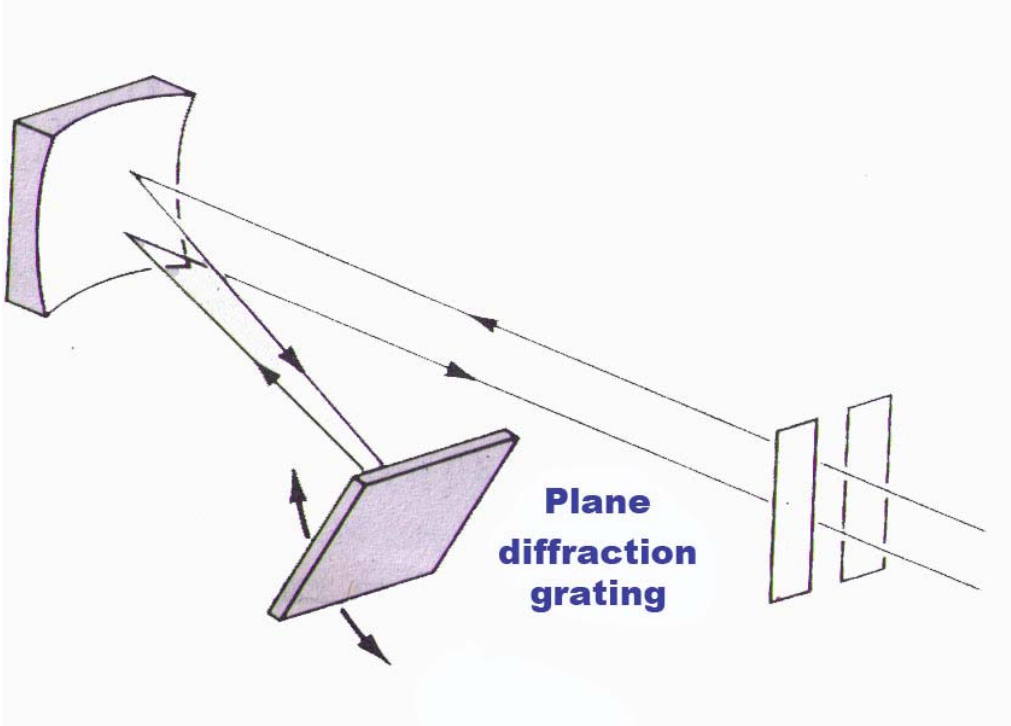


PRISMS AND GRATINGS

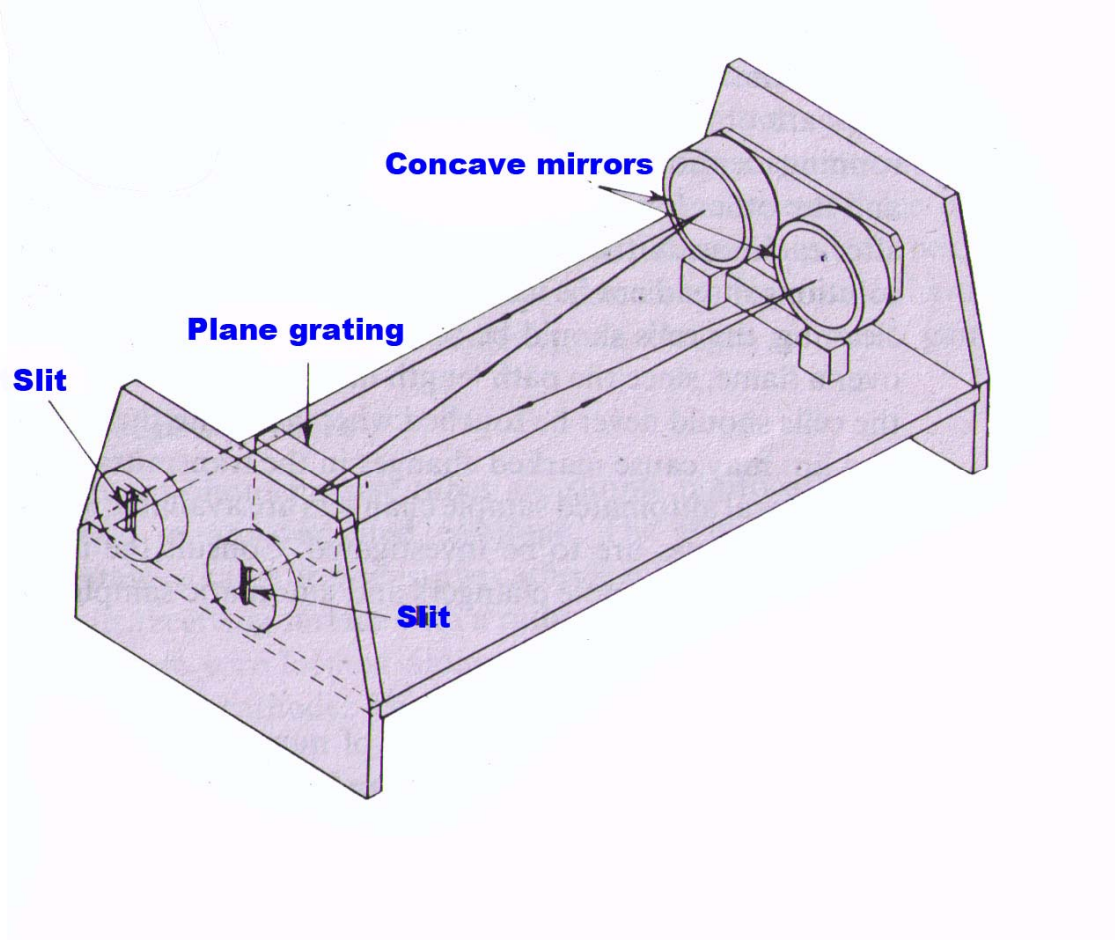
They serve to disperse the radiation into individual wavelengths. Prism based monochromators are wavelength dependent at a fixed geometric slit width. In gratings, monochromators are dependent on the grating constants and these improve as the number of lines passing increases.

The two most important mountings are the simple Littrow (A) monochromator and modified Czerny-Turner (B) form.

LITTROW MONOCHROMATOR



CZERNY- TURNER MONOCHROMATOR



In this connection, it should be mentioned that filter monochromators cannot be employed in atomic absorption spectrometry, since the required resolution cannot be obtained leading to the difficulties mentioned above.

The optical requirements for AAS are simple. From the flame, radiation is passed through mirrors/lens combination. Focusing the radiation from the flame to monochromator in AAS is also simple. From the materials standpoint, quartz or fused silica lenses are required because of the UV transmission characteristics.

SPECTRAL BAND SELECTION

The term monochromator is in reality, a misnomer. Monochromatic radiation is the radiation with only one wavelength. All spectral band selection devices pass a band of wavelengths that may be larger or smaller according to the quality of the device.

The basic requirement for a wavelength selector is the ability to separate the desired resonance line from other lines emitted by the sharp-line source. If any background radiation is emitted by the source, a curved calibration graph will be obtained, but curvature can be minimized by using a narrow-pass monochromator to reduce the propagation of unabsorbed light.

For alkali metals a simple glass or gelatin filter should be sufficient. For other metals interference filters are satisfactory. Sets of filters with selected cut-offs are commercially available.

The commonest and most versatile wavelength selector is a monochromator which can be set to pass any wavelength between 200-900 nm similar to an ordinary spectrophotometer.

DETECTION SYSTEM

A detection system includes the detector, associated power supplies, an amplifier and read out devices. The read out devices include analog meters, digital meters or strip chart-recorder. However , today computers are incorporated in all but the least expensive, bottom of the line instruments.

DETECTORS

The intensity of the resonance line emitted by the monochromator is measured with and without sample in the flame by photoelectric detector such as photomultiplier or photocell. A photomultiplier tube is essential if best results are to be achieved in the determination of metals. However, for general use it is desirable to modulate the output of the light source either with mechanical “chopper” or more conveniently by supplying the source with AC or modulated DC, and feeding the detector output to an AC amplifier which is rectified before being fed to a meter. In this way any signal caused by continuous emission from the flame is rejected.

However, any fluctuation in flame emission may give rise to an appreciable AC component and it is best to tune the amplifier fairly closely to the modulation frequency of the light source.

In single beam AAS instruments the accuracy of absorption in measurement is limited by the fluctuation and drift in the light source. Therefore a double beam technique is preferable. In such instruments the light from HCL is split into a sample beam modulated at a frequency 'f' which is passed through the flame and the reference beam is modulated at frequency '2f' which is passed through an equivalent air path. Subsequently the two beams are combined at the exit slit of the monochromator and the photomultiplier output is fed to an amplifier.

The amplifier signals from two beams are separated and their ratio is recorded on the pen recorder.

The demand for rapid routine analysis of large number of samples has led to the development of digital read-out and print outs whose output can be read directly in concentration units. These devices are used in conjunction with an automatic sampling device, so that the instrument can work unattended for considerable period of time.

The PMT (photomultiplier tube) has the ability to transduce radiation into an electrical signal with very high gain (of the order of 10^6). Fluctuations in the number of atoms in the flame dominate the noise in these systems. The shot noise associated with PMT's is an insignificant noise source for the system. Modern PMT's exhibit very good spectral response throughout the UV-visible range. Till date no other detectors have been used in commercial instruments.

READ OUT ELEMENTS

The most common type of amplifier electronics used in AAS is the lock-in amplifier. This type of device "locks in" on any signal of a specific modulation frequency, and therefore does not respond to signals at other frequencies. The radiation from the source (HCL or flame) is modulated at a fixed frequency that is synchronized with lock-in amplifier. This means that only signals of interest are amplified and the signal to noise ratio will be improved. The amplified signals can then be fed into a strip chart recorder or meter for evaluation. In more modern instruments it is converted into a digital signal and is fed to a computer for evaluation.

COMPUTERS

Most of the commercial instruments being marketed today have a dedicated computer. This provides maximum flexibility for data evaluation and signal processing. In addition, a computer gives the analyst many other desirable features. A computer can store information required for the instrument parameters for many elements. In recent advanced instruments, the computer provides control over the instrument variables and can set variables to optimum conditions for a particular determination. This also provides analytical calculation, curve fitting, concentration read out, standard addition etc. With computer optimization program even more sophisticated background correction and interference correction are also available.

AUTOMATION

The AAS is a very rapid analytical technique that has received greatest impetus and general recognition. The first automatic analyzer was introduced in 1996. Courner constructed an instrument for the analysis of trace elements consisting of a commercial atomic absorption spectrophotometer to which an automatic sample changer, a digital evaluator and printer were connected. This also consisted of an automatic dilutor, a sample changer, 200 sample vials, digital readout and a printer.

All stages of an AAS determination were carried out automatically and the results were printed out directly in concentration units. Modern AAS are provided with facilities for operation with auto samplers and often have the interface capabilities for direct on-line operation with an external computer. The spectrophotometer and all peripheral instruments are controlled by a central processor that also provides printout of a complete analytical report.

Automation in flame AAS does not bring any substantial savings of time. Savings of time can only be expected when several elements are to be determined in the same sample solution. Automation of sample introduction brings an improvement in the precision as well as facilitating operation. For AAS, automation is required to change from one element to the next. Multielement lamps offer certain advantages such as change of radiation source, setting other instrumental parameters such as wavelength slit, gain etc., and performing calibration etc., as these are the most time consuming procedures and also most difficult to mechanize and automate.

Nevertheless, modern microprocessor technology and stepper motors for wavelength drive etc., have made possible fully automatic element change.

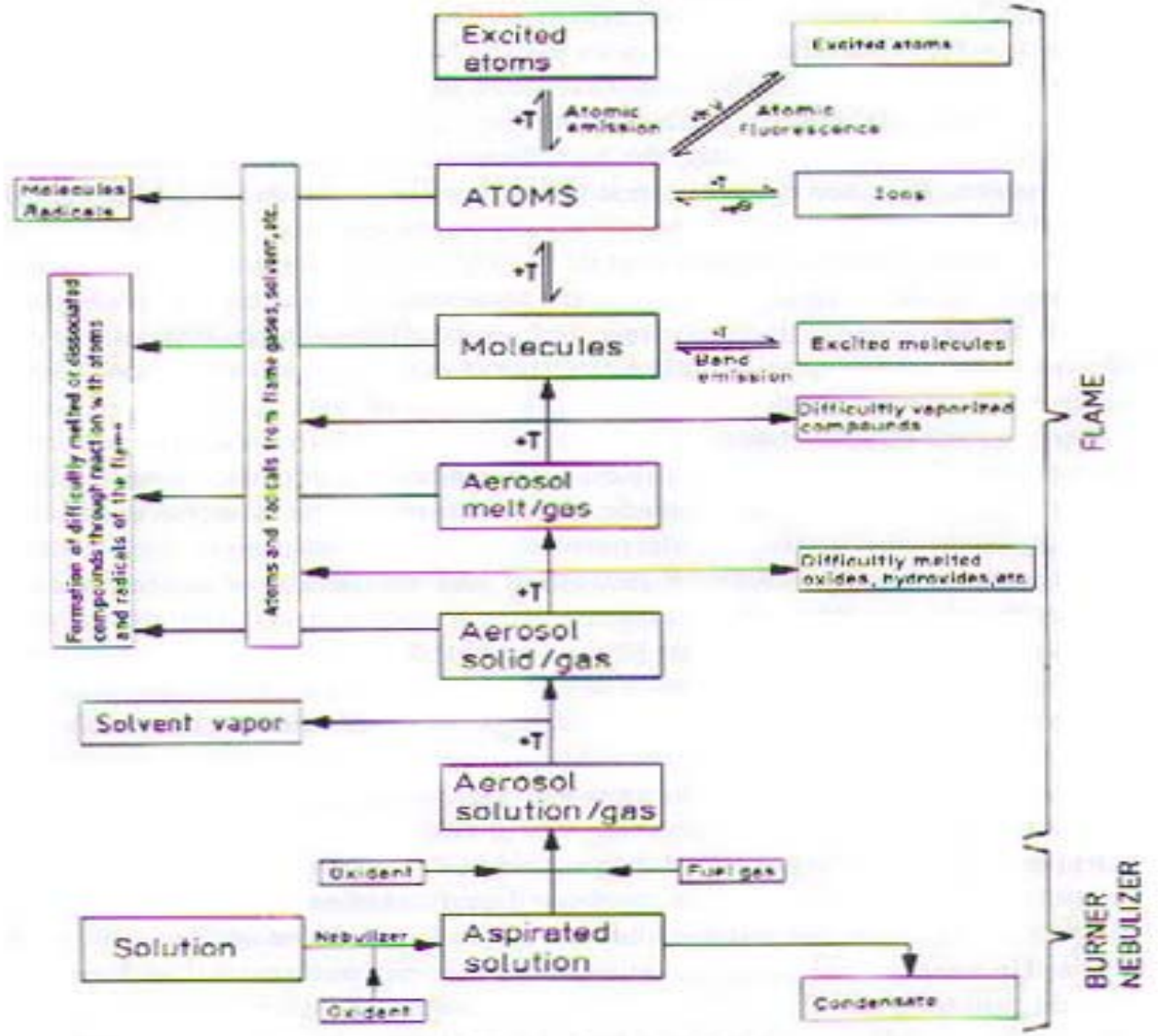
For simultaneous mutielement determination time dependent absorbance changes are required.

Increasing shortage of laboratory staff, centralization of laboratories in large agricultural, environmental, biological and clinical research institutes has led to an increasing need for semi-automatic or completely automatic analytical method. In order to meet this need, a number of automatic instruments have been developed which offer considerable advantages compared with manually operated instruments when large number of measurements have to be made.

THE TECHNIQUE OF FLAME AAS

Chemical analysis with flame AAS is performed by introducing standard solutions of the analyte into the flame through a pneumatic nebulizer into a spray chamber. The aerosol is carried into the flame where a number of processes take place culminating in the production of the ground state atomic cloud. The atoms absorb the radiation and the decrease in the intensity of the incident is recorded as the absorbance. Using the absorbance data a calibration curve is constructed and the sample concentration is determined by referring to the calibration curve.

ATOMIZATION PROCESSES



REACTIONS IN THE FLAME

$MeX \rightleftharpoons Me + X$ X = Cl, Br, I etc.

$Me \rightleftharpoons Me^{+} + e^{-}$

$Me + Y \rightleftharpoons MeY$

Hydrated chlorides, carbonates , sulphates can form oxides upon elimination of HCl.

Phosphates $\longrightarrow$ Pyrophosphates

Temperature of the flame plays an important role in the volatilization of salts after which the thermal dissociation process of molecules into atoms begins. This is a phase where non spectral interference occur.

In the flame, a variety of combustion products such as CO_2, CO, C, H_2O, O, H_2, H, OH, N_2, NO_X etc., are present. Solvent and other possible substances also evaporate. Atoms, radicals, ions etc., are formed by temperature dependent equilibrium reactions.

In principle, the flame can be considered as a solvent in which traces of metal atoms are found which leads to absorption.

Therefore chemical environment, the temperature and the residence time of the chemical species have greatest influence on the concentration of the atoms in the flame.

CO and hydrogen do not have sufficient free energy to reduce metal oxides but during the oxidation of C or H radicals enough free energy is available to reduce more stable oxides.

C_2 and CH radicals are found only in the lower zones of the flame. H radicals remain longer in the flame and hence they play an important part in the production of atoms via thermal dissociation.

INTERFERENCES IN ATOMIC ABSORPTION

- **Spectral interferences**
- **Transport interferences**
- **Solute – volatilization interferences**
- **Vapour – phase interferences**
- **Spatial distribution**

SPECTRAL INTERFERENCES

Spectral interferences occur in AAS when the emission wavelength from the primary radiation source or absorption of a concomitant element overlaps, with that of the analyte wavelength.

Sometimes in presence of higher concentrations of concomitants (in g/liter) substantial line broadening occurs. Radiation scattering of particles in the flame or molecular absorption by chemicals and radicals also introduces spectral interference when there is resonance line overlap.

For example CaOH band in air-acetylene flame in the determination of barium is a case in point.

Alkali halides cause spectral interferences below 300 nm. e.g NaCl in the determination of iron in serum.

When the spectral lines overlap or lie outside the resolving capacity of the monochromator, the interference is more serious. For example vanadium line 308.211 nm interfers with the aluminum line of 308.215 nm.

Similarly magnesium line of 285.200 nm and chromium line of 285.203 nm.

TRANSPORT INFLUENCES

Transport interferences are caused by alterations in the mass flow of the aerosol through the horizontal cross section of the flame at the observation height.

This depends on the rate of aspiration, physical characteristics such as viscosity, surface tension, vapour pressure and density of the solution. The causes include:

a) **Increase in the salt concentration above 1% (greater droplets)**
b) **Organic macromolecules such as proteins and sugars**
c) **Organic solvents – enhancements in the signal**

EFFECT OF ORGANIC SOLVENTS IN THE DETERMINATION OF COPPER

Solvent		Relative sensitivity*
0.1 M hydrochloric acid		1.0
Methanol	40%	1.7
Ethanol	40%	1.7
Acetone	40%	2.0
Acetone	80%	3.5
Acetone + Isobutanol	20% + 20%	2.35
Ethyl pentyl ketone		2.8
Methyl isobutyl ketone		3.9
Ethyl acetate		5.1

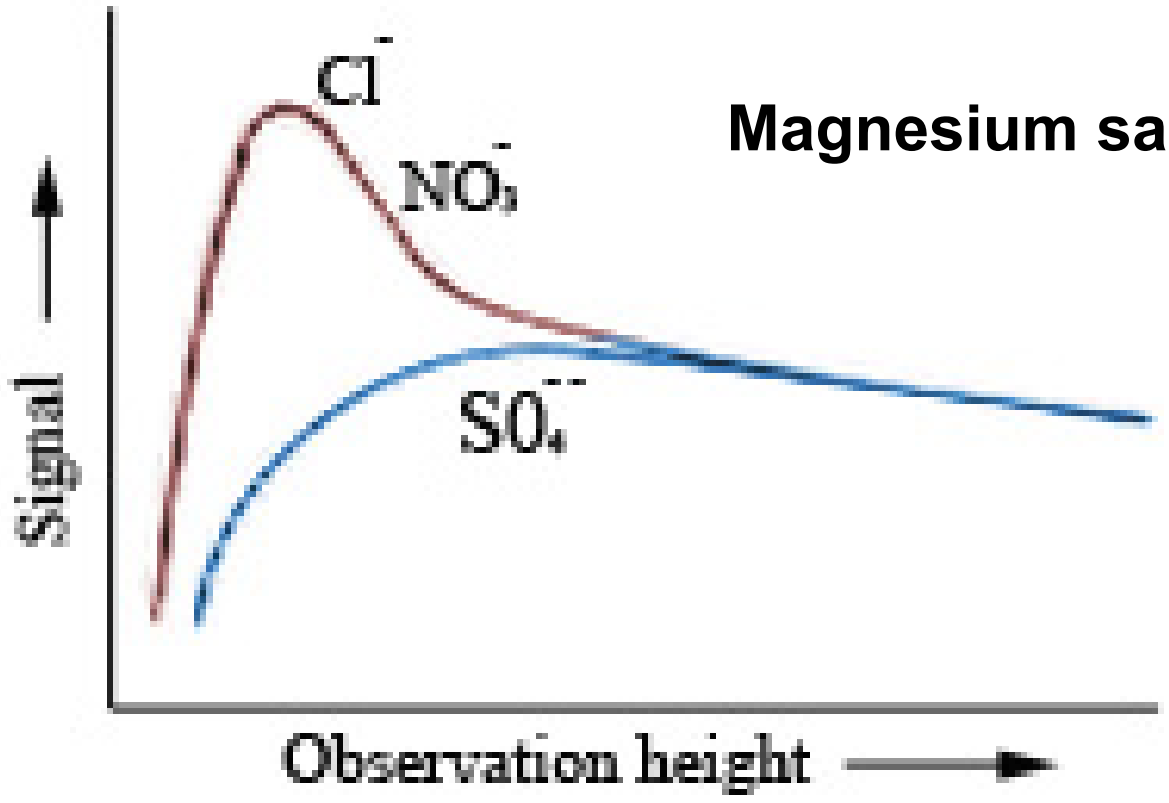
* Referred to water

SOLUTE VOLTILIZATION

Interaction of solute particles containing the analyte with concomitants can influence volatilization and cause enhancement or attenuation of the signal. They are generally specific and the signal depends on the properties of the compounds formed. Hence they may also be called chemical interferences.

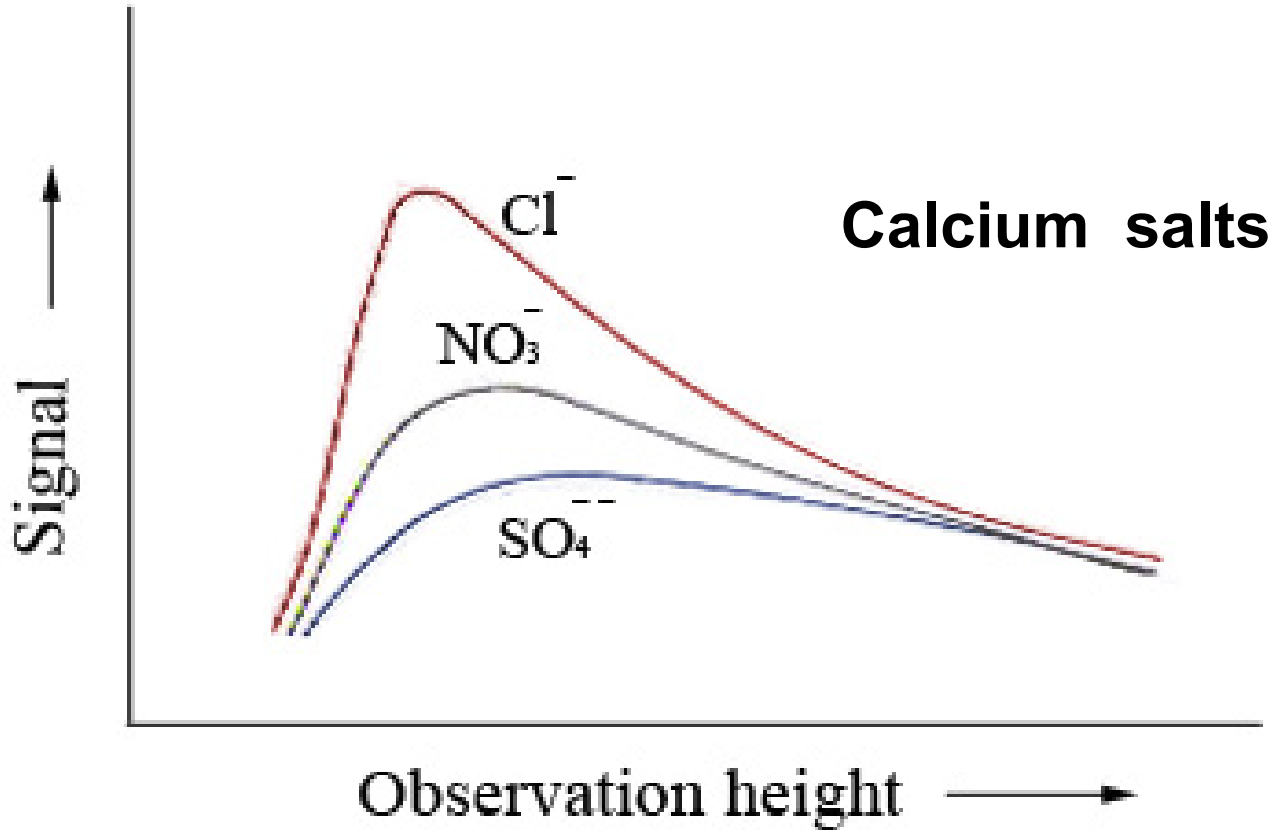
In premix burners, laminar flame volatilization begins as soon as they enter the primary reaction zone. Therefore the occurrence of interference depends on the observation height. The analyte can combine with anions or ligands or simply form refractory oxides.

EFFECT OF OBSERVATION HEIGHT



Magnesium salts

EFFECT OF OBSERVATION HEIGHT



Oxides of group III & IV of the periodic table form three dimensional polymer structures even in presence of hydrochloric acid. Spinel types ($MeO.Me_2O_3$) or ilmenite or pervoskites($MeOMeO_2$) form very stable lattices. Examples include titanium, zirconium, hafnium, molybdenum etc. the signal depression occurs for :

sulphates > chlorides > nitrates

Formation of carbides also follows the series:

M(VI) > Me(V) > Me(IV)

If the metal oxide is more volatile than the metal or the carbide, signal enhancement occurs.

VAPOUR-PHASE INTERFERENCES

The equilibrium and incomplete conversion of the analyte into spectroscopically active form (atoms) resulting in the attenuation of the signal may be considered as vapour phase interference. Such alterations occur in the primary reaction zone.

Diatomic and triatomic compounds (NaOH, BaOH, BeO etc), cyanides or oxides (Cu_2O) can alter the degree of ionization markedly.

Dissociation processes frequently take place between the chemical species and flame gases. Variation in the concentration of halides, free radicals, O, OH, CN, H in the flame gases can influence the dissociation equilibria.

$$MO + CO \rightarrow M + CO_2$$
$$MO + C_2 \rightarrow M + CO + C$$
$$2CO + O_2 \rightarrow 2CO_2$$
$$CN + e^- \rightarrow CN^-$$
$$CHO \rightarrow CH^+ + O^-$$

These ions suppress the ionization of the analyte.

SPATIAL DISTRIBUTION INTERFERENCES

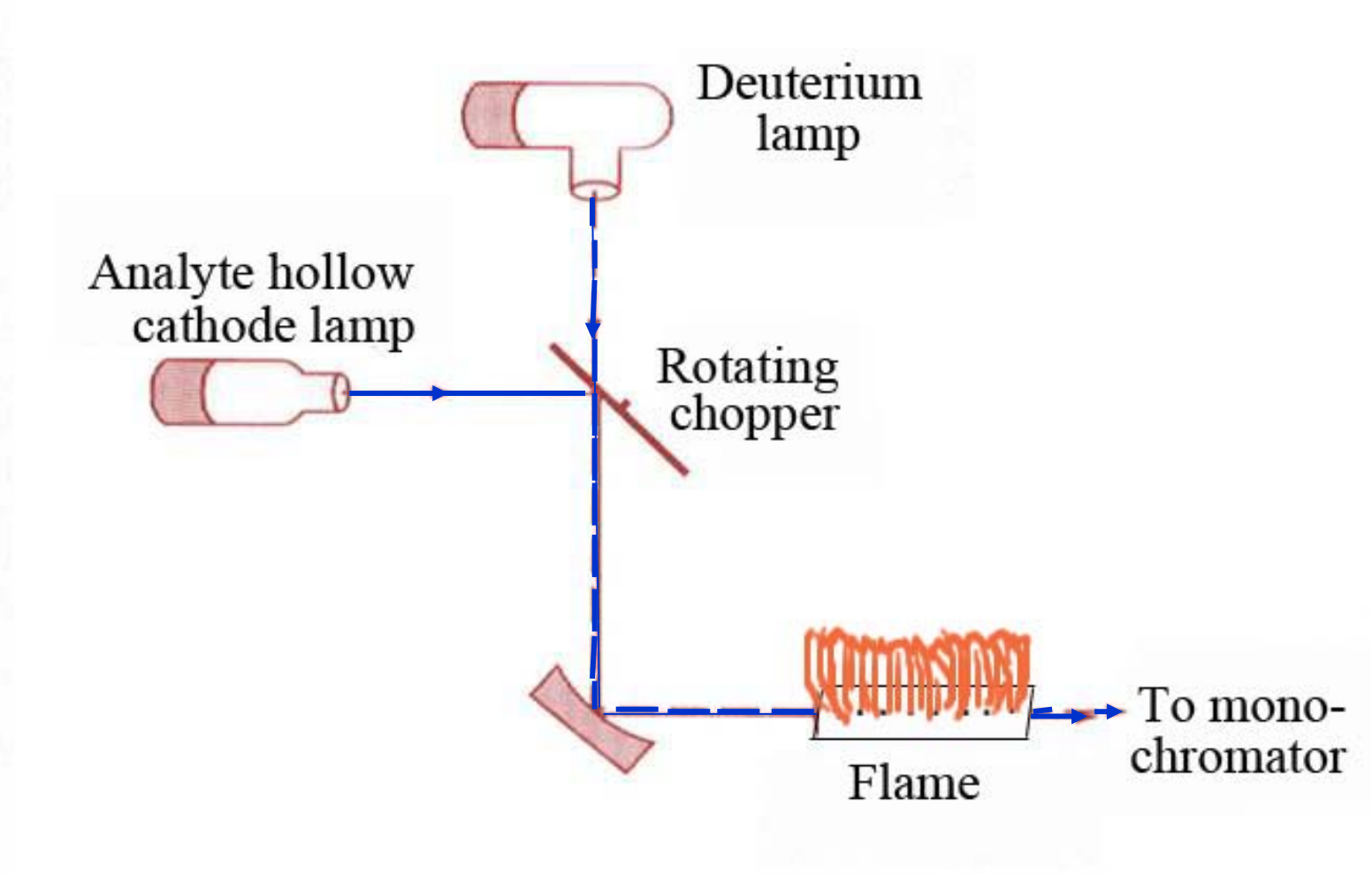
These interferences are caused by the changes in the flow rate or flow pattern of the sample in the flame. The quantities of combustion products can change the mass flow rate or flow pattern which in turn are influenced by the size and rate of volatilization of the particulates. Examples include signal enhancement of Al, Ba, Ca, Li, Sr etc.,

In general several types of interferences can occur in flame AAS due to several factors. Therefore even in the absence of specificity still signal enhancement or attenuation can occur.

BACKGROUND CORRECTION ON FLAME AAS

Most of the spectral interferences and all other types of interferences result in the attenuation of AAS signal to some extent. In general the attenuation varies from negligible to several percent depending upon the matrix. This signal is known more commonly as background absorption which can be easily estimated by aspiring a closely matching reference solution which does not contain the analyte. The absorbance of the reference (or blank as it is known) must be subtracted from that of the calibration standards as well as the samples. Alternately radiation from a deuterium lamp can be measured at the resonance wavelength to determine the background absorption.

A schematic configuration of a deuterium lamp background corrector can be measured at the resonance wavelength to determine the background absorption.

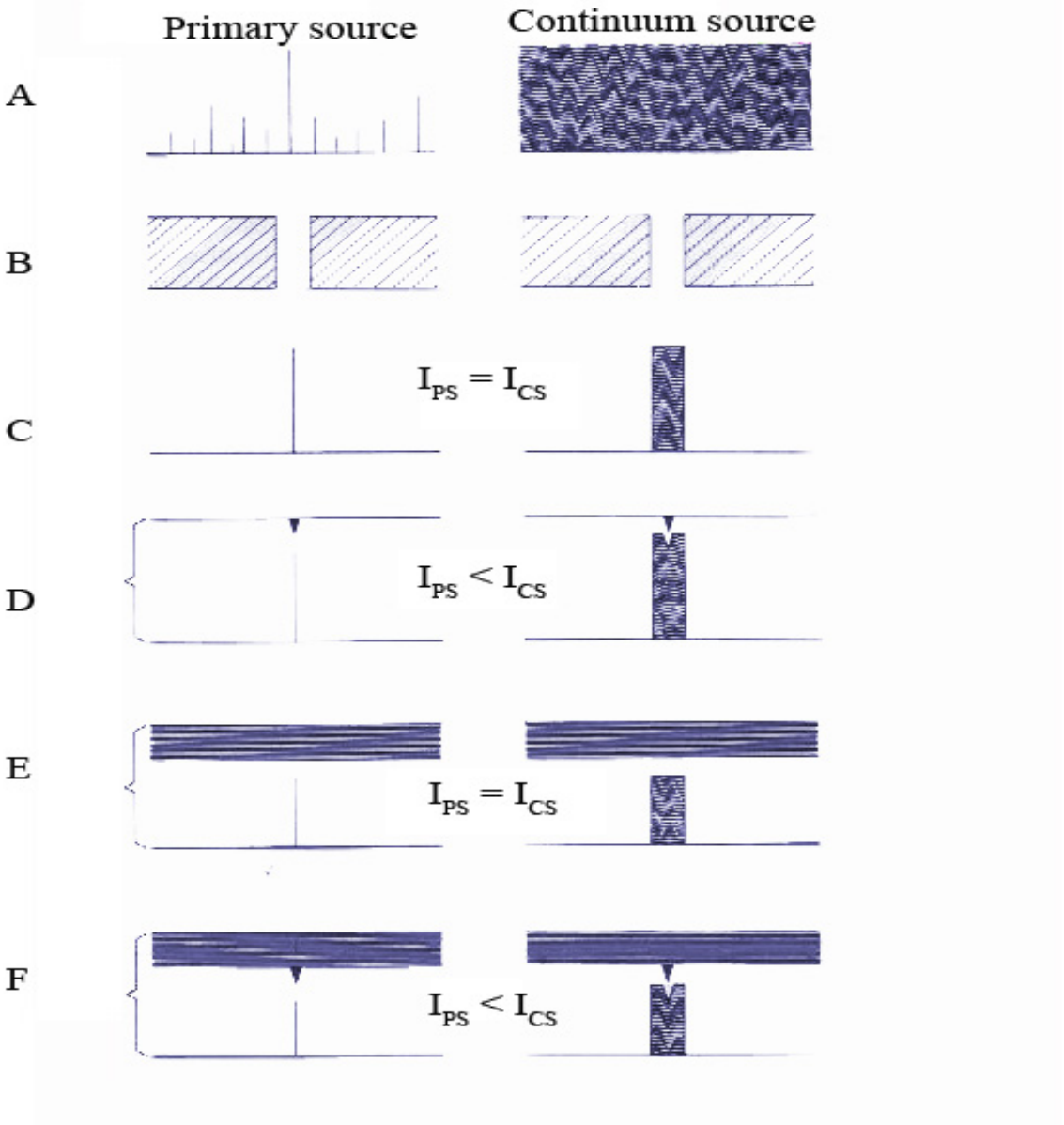


In this figure the exit slit of the monochromator separates the resonance line from the emission spectrum of the HCl equivalent to the bandpass width of 0.2 or 0.7 nm.

The intensity I_{PS} of the primary source is equalized to the intensity I_{CS} of the continuum source before the determination so that I_{PS}/I_{CS} ratio is unity.

For normal measurements less than 1% absorption from the continuum source is neglected (I_{CS}). At higher absorbance, I_{PS} is attenuated proportionally to the concentration of the analyte. In effect I_{CS} serves as a reference beam.

MECHANISM OF BACKGROUND CORRECTION



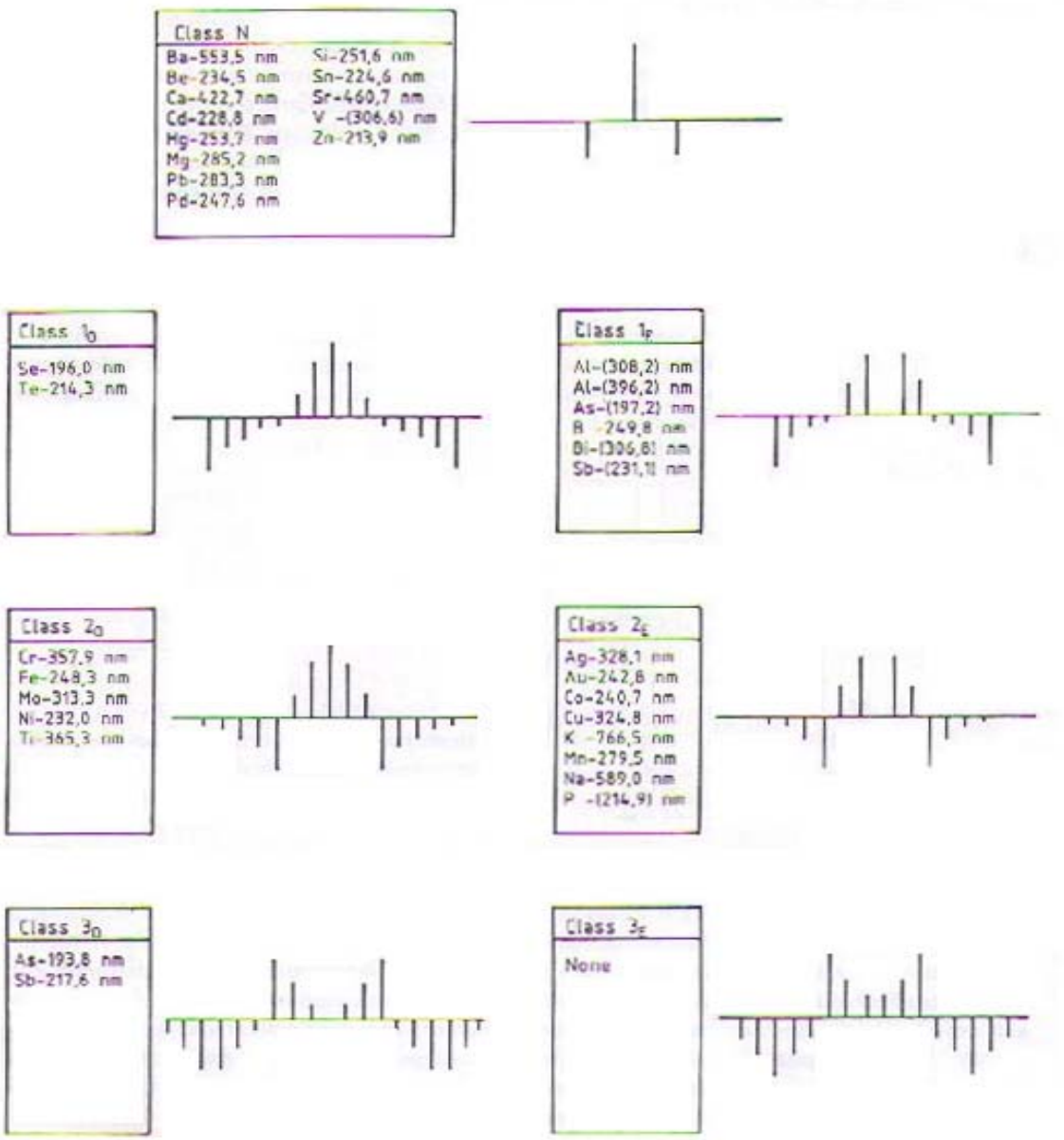
Background correction with continuum sources are incapable of correcting more than 0.5 absorbance. Further the noise increases by a factor of two or three.

ZEEMAN EFFECT BACKGROUND CORRECTION

When an atomic vapour is placed in a magnetic field (~ 10 kg) the energy levels (terms) split, which manifests as spectral line splitting. In the simplest case the spectral lines split into three components: the central π component whose energy and frequency is unchanged and two σ components are shifted to the right and left of the central π component. The separation of the σ components are of the order of 0.01 nm. The distribution of energy between σ and π components, $\sigma^+ : \pi : \sigma^-$ is 25:50:25, which is known as zeeman effect.

Simultaneously the radiation is also polarized. The extent of polarization depends upon the direction of the magnetic field. Some elements split into only 3 components. This is known as normal zeeman splitting (Ba, Be, Ca, Mg, Hg, Pb, Pd etc). Some elements split into more components but odd numbers. Some elements split into more even number of components. These are known as anomalous zeeman splitting. This effect can be used for background correction.

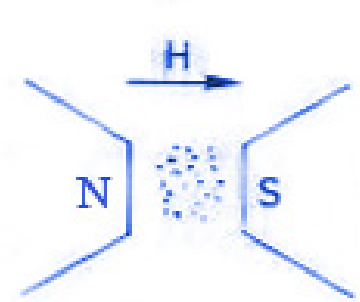
ZEEMAN SPLITTING OF COMMON ELEMENTS IN AAS



If the magnetic field is applied at right angles to the radiation beam, π component is polarized parallel to the applied field and σ components are polarized perpendicular to the applied field. This configuration is known as transverse zeeman effect.

When the magnetic field is parallel to the radiation beam, it is called longitudinal zeeman effect. In this configuration π component is missing and only two σ components are seen with fifty percent intensity.

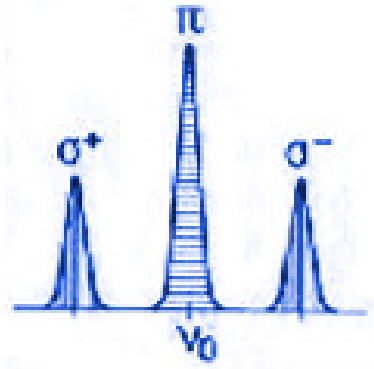
SCHEMATICS OF ZEEMAN EFFECT

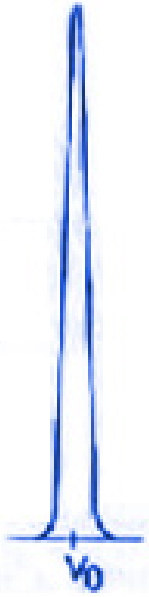


Atom cloud

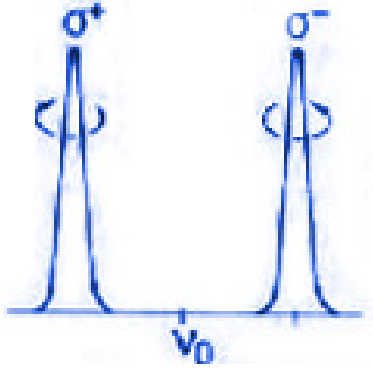
without
magnetic field

Transverse
ZEEMAN effect





Longitudinal
ZEEMAN effect



When the magnetic field is applied to the radiation source, it is known as direct zeeman effect. The magnetic field can also be applied to the atomic cloud. This is known as inverse zeeman effect.

In the inverse zeeman effect, the energy levels of the absorbing atoms are split and the absorbance values also change since the σ components are rotated out of the radiation line and only π component absorbs which can be measured.

For the direct zeeman effect absorption can be measured at both σ and π component wavelengths also.

If a magnetic field is applied by a permanent magnet or via a direct current, a rotating polarizer must be applied to measure the total absorbance.

By applying an alternating current, alternating magnetic field is generated which splits the energy levels only when the field is on. Thus eight possible configurations are possible.

VARIOUS CONFIGURATIONS OF ZEEMAN EFFECT IN AAS

Location of the magnet	Orientation of magnet to radiation beam	Type of magnetic field	Particularities
At the Radiation Source (direct)	Parallel (longitudinal)	Constant	Rotating polarizer
		Alternating	No polarizer required
	Perpendicular (transverse)	Constant	Rotating polarizer
		Alternating	Fixed polarizer
At the Atomizer (inverse)	Parallel (longitudinal)	Constant	Not applicable in AAS
		Alternating	No polarizer required
	Perpendicular (transverse)	Constant	Rotating polarizer
		Alternating	Fixed polarizer

AAS instruments with inverse zeeman effect (magnet at the atomizer) are preferable but a rotating polarizer is required if a constant magnet is used. Therefore alternating magnetic field is used.

In this configuration absorbance is measured with field off (normal AAS) and with field on (background). This is a true double beam technique since both beams originate from the same source, measurements are made at the same frequency, follow the same optical path and fall on the same detector. The sensitivity remains unaltered.

SMITH HIEFTJE BACKGROUND CORRECTION METHOD

This method is based on the self absorption behaviour of radiation emitted from hollow cathode lamps when they are operated at high currents. Application of high currents produces large concentrations of unexcited atoms in the hollow cathode lamps. These atoms are capable of absorbing the radiation produced from the excited atomic species. High currents also broaden the emission lines of the excited species. Net effect is to produce a line that has a minimum at its centre (resonance line).

To obtain corrected absorbances, the lamp is programmed to run alternately at normal and high currents in quick succession at the rate of every 5 milli seconds.

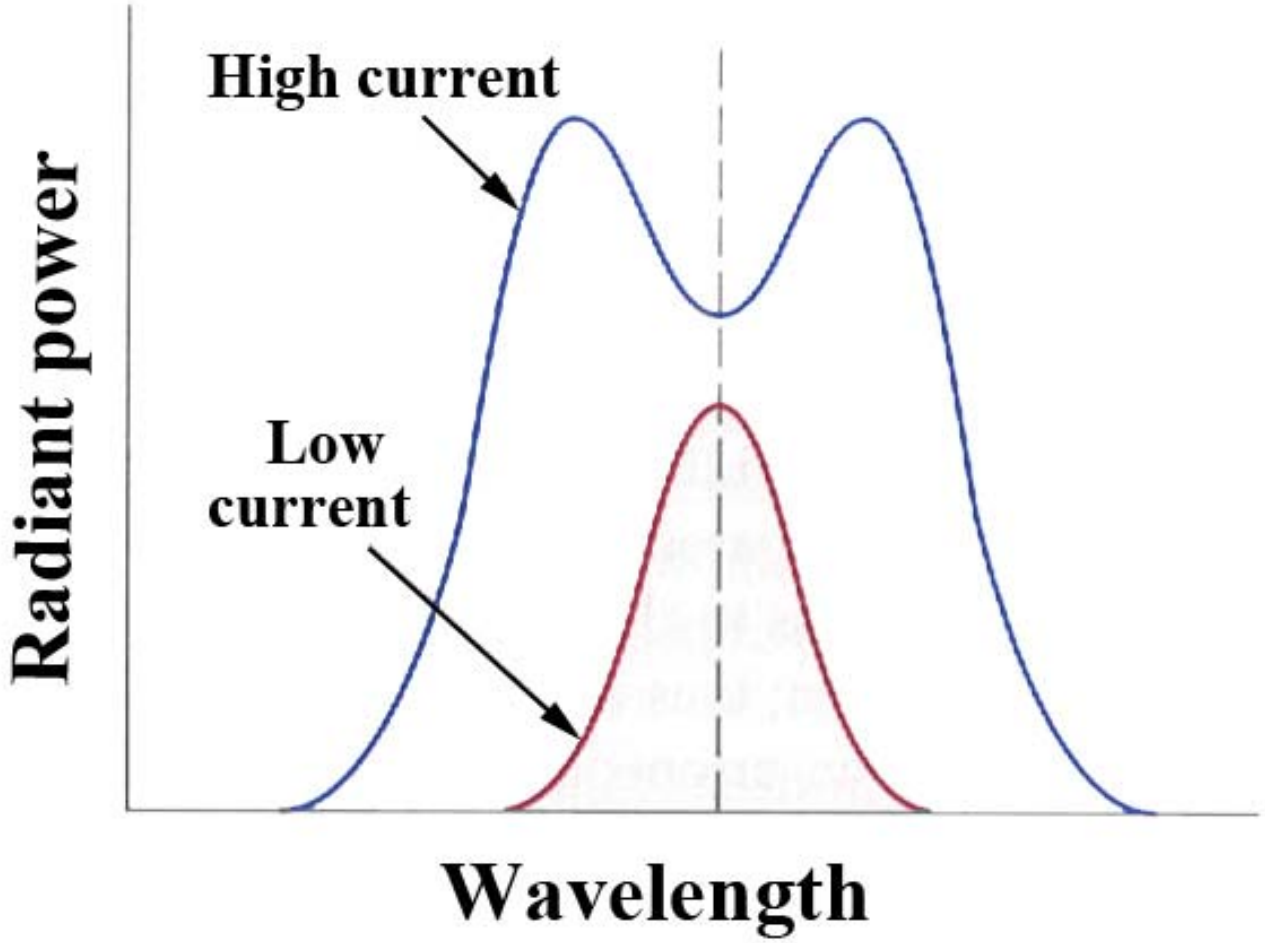
During normal operations background and the atomic absorption data is provided.

During the second part, when the absorption peak is at a minimum, only the background is measured and absorbance of the analyte is minimum.

The data acquisition system then subtracts the two signals to give a corrected value.

This is a remarkably simple means of background correction which compares very well with zeeman effect method. Several instrument manufacturers offer Smith-Hieftje technique for background correction.

EMISSION LINE PROFILES IN S-H METHOD



CHEMICAL REACTIONS IN AAS - INTERFERENCES

Any analytical instrumental technique, however sensitive, simple or rapid, is not free from all interferences. Hence as analytical chemists we must be aware of the origin or the source of the interferences, so as to provide analytical data very accurately and precisely. AAS is one such analytical instrumental method and it has got much inherent interference from the sample introduction stage to the detector. Originally it was thought that AAS is free from interferences as we measure very narrow resonance line from the hollow cathode lamp passing through the atomizer either in the flame or non-flame.

The interferences may be classified as follows:

- **Physical Interferences**
- **Chemical Interferences**
- **Ionization Interferences**
- **Spectral Interferences**
- **Non-specific Interferences**

The physical interference occurs at the sample introduction stage and the remaining chemical, ionization, spectral and non specific interferences occur in the flame.

PHYSICAL INTERFERENCES

The Physical Interferences are dominant at the sample introduction stage in the transport of sample solution to the nebuliser and from the nebuliser to the spray chamber and burner. The most important factors are viscosity (influencing the sample aspiration rate), surface tension (influencing the size of the aerosol droplets), and the vapour pressure of the solvent (influencing solvent evaporation rate). Because transport, affects all the elements equally, they constitute interferences not specific to particular elements.

The physical processes that occur during nebulisation have a large influence on the sensitivity and selectivity of flame methods of analysis. The nebulisation efficiency depends on the nature of the nebulising gas and the sample solvent. The variation in the viscosity, surface tension, density and temperature of the sample solution interfere in the nebulisation process and hence on the sensitivity.

This interference can be controlled by preparation of the standard solutions used to construct the calibration curve at similar physical conditions of the solvent of the sample. These interferences can also be eliminated by diluting the sample solutions or by the method of standard addition.

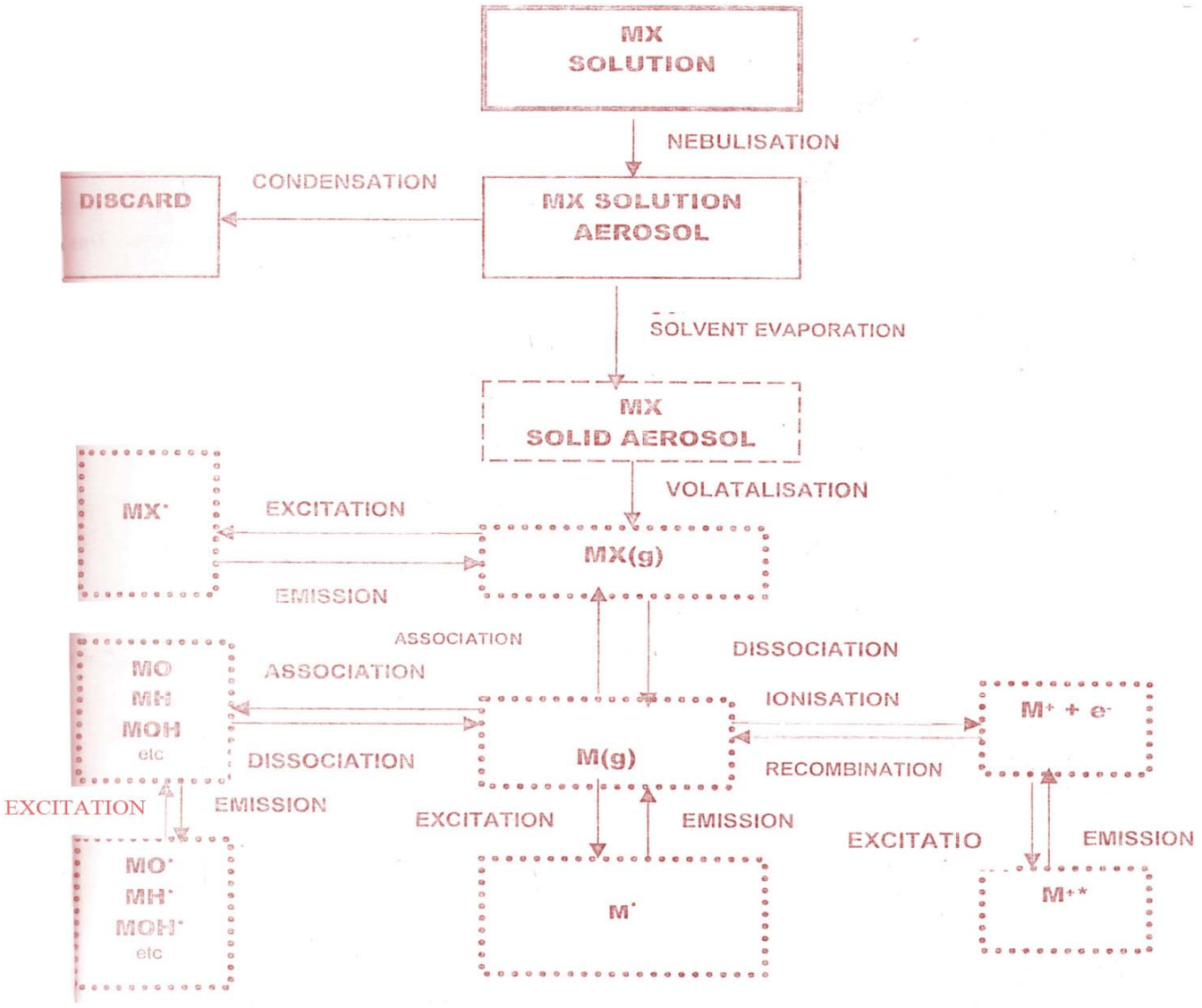
The presence of high concentrations of dissolved salts in a sample can reduce the analytical signal. It also leads to the formation of incrustation of the nebulizer and the burner head and may lead to high signal noise levels. In general it can be said that the physical interferences can result if the sample and the standard solution vary greatly in bulk composition. The normal sample solution uptake rate is about 6-7 ml/min and the nebulisation efficiency in a pneumatic nebulizer in AAS is only 10%. So any change in these normal values cause physical interferences and lead to spurious signals.

CHEMICAL INTERFERENCES

As it is already explained that the physical interferences occur from sample introduction stage before nebulisation till it reaches the burner, whereas the chemical interferences dominate at the atomization place, i.e., either in the flame or in the electro thermal atomization. So to understand the chemical interferences, we should know first of all the various stages that the sample solution undergoes in the flame.

The Schematic Diagram as shown below represents the various processes which must occur in producing the atoms of some metallic element M from a solution of the salt MX in the sample solution.

FLAME ATOMIZATION PROCESS



The sample solution first enters the nebulisation where it gets fragmented into fine droplets of about 10 micron size in the aerosol. The bigger size droplets go to the drain thus giving nebulisaiton efficiency of only 10%. The aerosol then enters into the flame from the spray chamber. Here it undergoes many changes before the production of the atoms. First the solvent molecules get evaporated leaving solid particles of the metal salts. These molecules then change into vapour stage and then dissociate into the metal atoms in the vapour phase.

These free metal atoms can undergo a variety of reactions.

(i) It again associates with the O or H or C and forms the respective oxides, hydrides or carbides

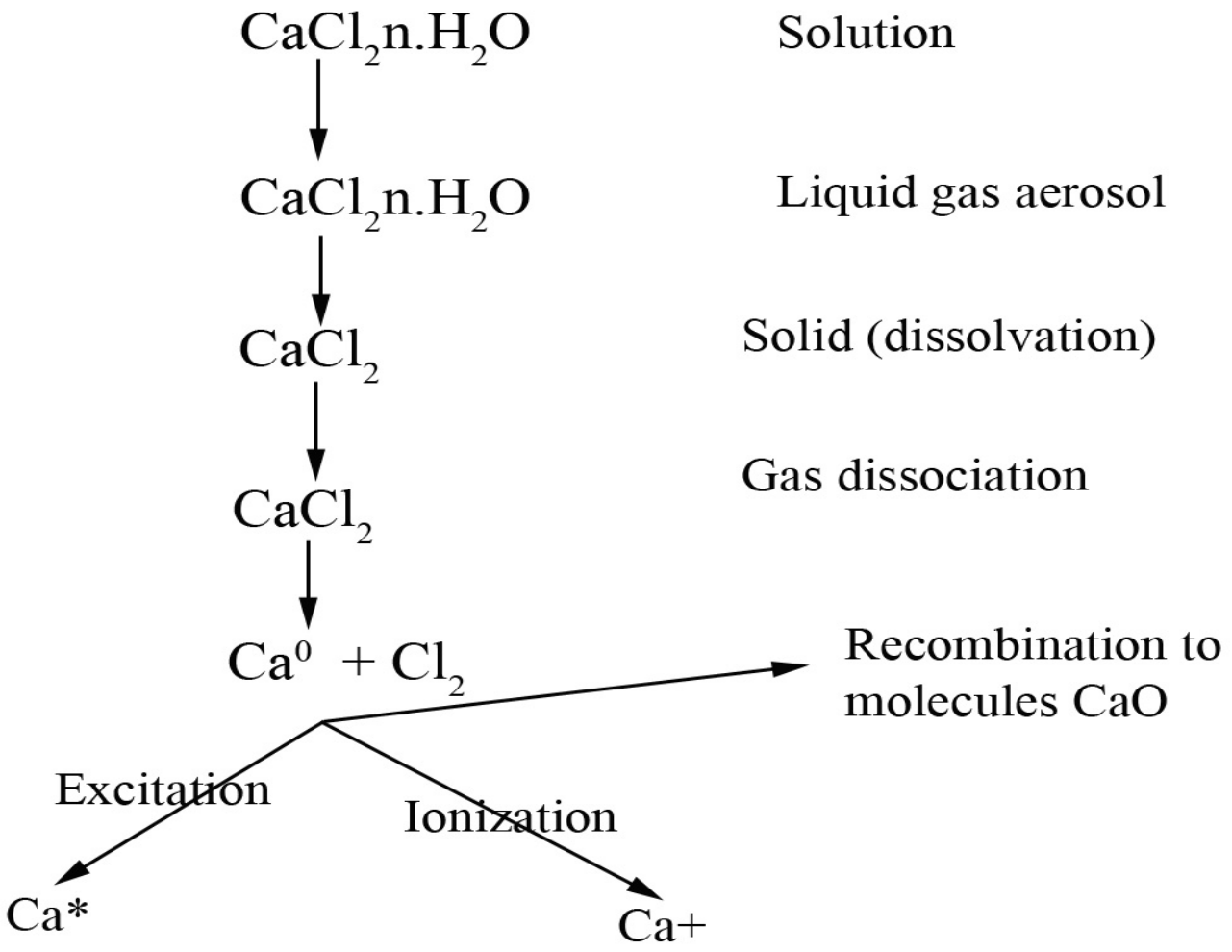
(ii) The metal atom gets excited by the flame temperature

(iii) The metal atoms become cations due to ionization.

For the atomic absorption to give maximum sensitivity the metal atoms should remain in the free atom stage without undergoing the compound formation or excitation or ionization.

Chemical interferences are the most common interferences encountered in atomic absorption spectroscopy. If the sample being analysed contains a thermally stable compound with the analyte that does not dissociate at the operating flame temperature, a chemical flame temperature, a chemical interference exists. A chemical interference can prevent, enhance or suppress the formation of ground state atoms in the flame.

As an example let us consider the mechanism of atomization of Ca atoms in the flame. This is shown in the figure.



Calcium when present as $CaCl_2$

$$CaCl_2.H_2O \rightleftharpoons Ca^0 + Cl_2$$

$$CaCl_2.H_2O \rightleftharpoons Ca^0 + 2HCl$$

$$CaO \rightleftharpoons Ca^0 + O$$

Calcium when present as $Ca(NO_3)_2$

$$Ca(NO_3)_2.3H_2O \rightleftharpoons CaO + NO_2 + 3H_2O$$

$$CaO \rightleftharpoons Ca^0 + O$$

In chloride medium $CaCl_2$ dissociates into Ca atoms and chlorine atoms. The formation of CaO from $CaCl_2$ in the flame is very less. However, in the case of $Ca(NO_3)_2$ it dissociates first into CaO and from this calcium atoms will come. So comparatively there is less number of Ca atoms from nitrate medium than from chloride medium.

As explained earlier the most common chemical interference is the compound formation. Most of the elements in particular the alkaline earth elements Be, Ca, Sr, Ba etc., form highly refractory metal oxides in the flame resulting in the loss of these atoms available for atomic absorption.

The dissociation of these metal oxides back into free metal atoms depends upon the temperature of the flame. The higher the temperature of the flame the more the dissociation and hence the better sensitivity. The air-acetylene flame gives a temperature of around 2600^0 C. At this temperature most of the metal oxides dissociates except the refractory ones like alkali earth element oxides, Nb, Ta, Al, Zr etc. So a flame which gives a temperature higher than air-acetylene is required. This is obtained by the nitrous oxide-acetylene, whose temperature is around 2900^0 C. Normally the elements whose dissociation energy is more than 5.0 ev cannot be determined by air-acetylene and Nitrous oxide-acetylene provides the necessary sensitivity. It is not always the temperature of the flame that is important.

Many a times the C/O ratio in the flame determines the sensitivity. Hence a reducing flame providing more fuel than the stoichiometric requirement is desirable for many of these refractory metal oxides. So one should always optimize the flame conditions in the fuel to oxidant ration, height etc., to get maximum sensitivity. In our laboratory we have carried out some investigations using sugar to alter the C/O ratio in the flame favourable for atomization.

It has been observed that for elements like Mo, V, Ti, Al, Ba, Y, Dy, Ho, there is enhancement in the absorbance values while there is no enhancement in the case of less refractory elements like Cu, Cd, Co, Mi. The other type of compound formation is the alkaline earths forming refractory phosphates and double oxides in the flame with Al, Si, etc., Strontium reacts with Al or Si and forms refractory $SrOAl_2O_3$ and $SrOSiO_2$. Similarly with phosphate it forms $Ca_2(PO_4)_2$ during evaporation of liquid droplets in the flame, this compound is converted to calcium pyrophosphate with heat and is very stable in the air – acetylene flame.

This reaction reduces the free Ca atom population in the flame as compared to that obtained from solutions in the absence of phosphate. This type of interference can be eliminated by the addition of a releasing agent. The releasing agent such as lanthanum preferentially combines with the interfering ion, thus releasing the analyte atom. In other cases the releasing agents such as EDTA combines preferentially with the analyte atoms and then dissociate in the flame releasing the analyte atoms.

The addition of lanthanum or strontium releases the calcium atoms from the calcium phosphate preferentially forming La/Sr phosphates. The addition of EDTA preferentially forms the calcium EDTA complex, an easily volatile compound which can dissociate relatively easily than the calcium phosphate. We have published a research paper on the determination of indium in geological samples by adding a mixture of tripotassium citrate and ascorbic acid in place of lanthanum to eliminate the interferences. This type of interference can also be eliminated by the method of standard addition. In this method the multiplicative interferences can be taken care of and not the additive interferences. This type of chemical interferences always takes place in condensed phase.

IONISATION INTERFERENCES

This is also a type of chemical interference. While the chemical interferences take place in the condensed phase, the ionization interferences take place in the vapour phase. When the analyte atoms get dissociated and vapourised, these interferences are observed. The atoms of the elements possessing very low ionization potentials can become ionized at the flame temperature. Thus instead of having more number of ground state atoms for atomic absorption, the ions of the analyte atoms will be more. This again depresses the sensitivity and causes a lot of interferences in the final analytical measurements. Alkali metals are more prone for this type of interferences (Li, Na, K, Rb, Cs).

The analyte undergoes the following reactions in the flame.

$$M \longrightarrow M^{+} + e^{-}$$

This interference can be controlled by the addition of excess of an element whose ionization potential is very low to both the samples and standards. Potassium chloride is preferably chosen due to its high purity and lack of visible emission in the flame.

The ionization potential of lanthanum is very close to lithium and therefore lanthanum in addition to being a releasing agent also acts as an ionization buffer for metals such as Ca, Mg, Si, Al etc., The addition of La or K as ionization buffer provides more number of electrons in the flame and shifts the ionization equilibria to the left. In other words, by providing more number of electrons, the ionization is suppressed and free ground state metal atoms are restored.

ANALYTE OCCLUSION

There are other types of chemical interferences not related to the stable compound formation or ionization. Though there is no chemical reaction involved between the analyte and the interferent, the occlusion phenomena may be considered as chemical interference. When the solid particles remaining after evaporation of the solvent consists of analyte atoms dispersed in the matrix of the interferent, the volatility of the matrix has an important bearing on the yield of free analyte atoms. Depression or enhancement may be obtained, depending on whether the matrix is less or more volatile than that resulting from dissolvation of the reference solution.

An example is the depression of chromium and molybdenum absorption in the presence of high iron concentration in the air-acetylene flame. Several observations indicate that there is no specific compound formation between chromium or molybdenum and iron. The decrease in the analyte signals levels off only at high iron concentrations and the iron analytical signals are not affected much by high chromium concentration.

Hence it is thought that at high Fe/Cr ratios, the chromium atoms are occluded in an iron matrix (b.p. 3000^0 C) which is incompletely volatilized. In the reverse situation when iron is determined in the presence of an excess of Cr, the formation of the more volatile Cr matrix (b.p. 2400^0 C) does not alter the number of free iron atoms available for atomic absorption. This type of interference effect can be overcome by the use of nitrous oxide-acetylene flame or by the addition of ammonium chloride, sodium sulphate or boric acid and sulphosalicylic acid.

BIBLIOGRAPHY OF INTERFERENCE STUDIES

ANALYTE ELEMENT	FLAME	INTERFERING CHEMICAL SPECIES	ACTION
Al	Air-Acetylene	Ca, Cu, Mg, Na, Pb, PO_4, SO_4, Zn, Cl, Fe	0
	N_2O-C_2H_2	SiO_3	--
Ca	Air-Acetylene	Al, NO_3, PO_4, SiO_3, SO_4, K, La, Li, Na, Mg, Sr	--
	N_2O-C_2H_2	PO_4, K	--
Mg	Air-Acetylene	Al	+
	N_2O-C_2H_2	Al, Ti	0
Mn	Air-Acetylene	SiO_3	+
K	Air-Acetylene	Rb, Cs, Na	+
Si	N_2O-C_2H_2	Al, Ca, Fe	+
Na	Air-Acetylene	Rb, Cs, K	+
Sr	Air-Acetylene	Al, PO_4, SiO_3, SO_4	+
	N_2O-C_2H_2	K	0
Zn	Air-Acetylene	NO_3, Ca, Cl, Mg, SO_4	+

0 = No Interference ; + = Positive Interference; -- = Negative Interference

SPECTRAL INTERFERENCES

Atomic absorption spectrometry is remarkably free from spectral overlap interferences. As you all know that the atomic absorption phenomena is based on the very narrow resonance line absorption. The hollow cathode lamp emits atomic emission radiation of a specific element which is able to induce absorption by atoms of that element only in the sample. This arrangement has been called lock and key effect. Hence, unlike emission technique the spectral interferences are very less in atomic absorption spectrometry.

A spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the bandwidth of the absorption line of the element of interest. Results will be very high due to the contribution of the interfering element to the analyte signal. In AAS the spectral interferences may be classified into three groups:

(1) More than one absorption line in the spectral band pass

(2) Non absorbed line emitted by excitation source

(3) Spectral overlap in atom source. Atomic spectral interferences observed in flame AAS and reported literature are shown in following table.

NON SPECIFIC ABSORPTION

The non-specific interferences enhance the actual readings obtained, but the sensitivity is not improved. In this case a spurious absorbance is added to the true value. The non-specific absorbance is seen either by scattering the absorption line by the solid particles or the absorption of the resonance line by undissociated molecules i.e. molecular absorption. The scattering phenomena is analogous to the turbidity in molecular spectrophotometry. The solid particles are formed by the inability of the flame to vaporize all the dissolved solids of the sample solution or may be due to the formations of carbon particles in the flames. The magnitude of this effect varies considerably with the wave length at which measurements are being taken. Normally light scattering effects particularly those elements that absorb at lower wave lengths.

The molecular absorption occurs when a molecular species in the atomizer has an absorption profile that overlaps that of the element of interest. This problem is most serious in the wave length region below 300 nm. Molecular absorption bands are relatively broad compared to atomic absorption profiles. The molecular absorption and light scattering are also known as non specific or back ground absorption. This background interference can be detected if the Beer's law graph does not pass through the origin.

The non-specific absorption was initially attributed to light scattering by salt particles, but strong evidence has been produced to indicate that scattering is often insignificant by comparison with molecular absorption both in flame and non flame situation. Thus background absorption plays a vital role in the determination of trace elements in varied complex matrices. Hence different methods have been worked out by the manufacturers to control the background absorption.

Methods for background absorption correction:

- **High temperature flame**
- **Selection of a non-absorbing line.**
- **Deuterium lamp**
- **Zeeman effect**
- **Smith Hieftje**

I Background absorption can be controlled to some extent but not fully by using a higher temperature flame, which brakes down the absorbing molecular species.

II It can also be controlled by selecting a non-absorbing line about 10 nm away the resonance line. The signal from the non-absorbing line should be deducted from the signal obtained from the absorbing line. The selection of the non-absorbing line. The selection of the non-absorbing line is such that it should not be absorbed by the sample matrix.

III The most widely used method for background correction is by deuterium lamp. As it is already pointed out that the atomic absorption lines are very narrow of the order of 10-50 nm. When an atomic line from a hollow cathode lamp passes through an atomizer it will be absorbed by both the atoms and molecular absorption remains the same, however, the atomic absorption contribution is almost nil (SBW=0.2-0.5). So by subtracting the background value from the total absorption, the true absorption by the free atoms is obtained.

The deuterium lamp which is used for this purpose gives a broad continuum up to about 300nm.

The method of back ground correction works as follows:

The absorbance of the sample occurring with the hollow cathode lamp is A_c i.e., sum of atomic absorption (A) and background absorption (A_b).

$$A_c = A + A_b.$$

The absorbance with the deuterium lamp is only background absorption (A_d).

$$A_d = A_b.$$

Initially both the signals from hollow cathode lamp and deuterium lamp are made equal.

Hence True absorbance $= A_c - A_d$ (since $A = \log I_o / I_t$)

$= \log I_{co} / I_{ct} - \log I_{do} / I_{dt}$

$= \log I_{co} \cdot L_{dt} / I_{ct} \cdot I_{do}$

Initially $I_{co} = I_{do}$ (original signals made equal)

Therefore true absorbance $= \log I_{dt} / I_{ct}$

$$= \frac{\text{Intensity of transmitted light from deuterium lamp}}{\text{Intensity of transmitted light from hollow cathode lamp}}$$

In this method the speed of background correction is critical. There must be minimum delay time between the total absorbance and the background absorbance. The magnitude of the back ground signal can change rapidly with time. For example within 20 milli seconds the background value can change up to 0.2 absorbance. So, if the difference between the measurements is about 10 milli seconds it leads to an error of 0.1 absorbance. In ultra pulse system the time gap is only 1 mill seconds and hence the error is only 0.01 units.

ADVANTAGES OF ULTRA PULSE BACKGROUND CORRECTION

Description	Ultra Pulse	Smith Hieftje	Zeeman
Sensitivity loss	None	Upto 6	Upto 3
Flame Furnace & vapour generation	Yes	Yes	No
Calibration Linearity	Normal	Reduced	Normal
Dynamic Range	Normal	Curved	Curved
No of sample readings per sec	200	10	50
Background measurement delay	1ms	4.5 ms	10ms

SOME OF THE DRAWBACKS OF THE DEUTERIUM CORRECTION ARE:

- Incorrect results in the presence of structured background
- No correction for spectral interference
- Different geometrical and optical paths
- Loss of light

SMITH HIEFTJE EFFECT

It has been known that when an excess current is passed through a hollow cathode lamp, its emission line is broadened and self reversal takes place. Hence in this method the lamp is first run at low current and its light is absorbed by the analyte as well as by the background. Then a brief pulse of much higher current is passed through the lamp causing self reversal which is absorbed by the background only. By subtracting one from the other the true absorbance is obtained.

Advantages of the method are:

(a) Background correction can be applied in the UV and visible range.

(b) Accurate correction for structured background.

(c) A single light source is used.

(d) Correction of spectral interference is possible.

(e) No bending of calibration curve.

MODULATION

The signal received by the detector consists of the resonance radiation from the hollow cathode lamp and the resonance emission line at the wave length of absorption from the atom source. For atomic absorption measurements only the resonance radiation originating from the source lamp is to be measured. To achieve this selectivity the lamp output is therefore coded by modulation and the post detector amplifier is tuned to the same modulation frequency. This prevents the DC emission signal form the flame being measured. The modulation can be done either by a square wave AC supply current or by interposing a synchronous chopper in the light beam before flame.

THE HYDRIDE GENERATION AAS TECHNIQUE

Arsenic, antimony, bismuth, selenium, tellurium, lead, mercury and a number of other elements of the periodic table belonging to group IV, V and VI are known to form volatile covalent hydrides with nascent hydrogen. Marsh's test and Gutzeit's test have been employed for the detection of arsnic since more than 100 years.

The property of volatilization as a gaseous hydride can be utilized to advantage for the separation and enrichment of the analyte element which also accomplishes the reduction and even complete elimination of interferences.

In the early 1950s a number of analytical methods based on colorimetry were introduced for the determination of arsenic and other hydride forming elements.

The hydride was formed in acid solution using zinc powder and the gaseous reaction products were conducted into solutions containing ammonium molybdate or hydrazine sulphate which formed characteristic colored complexes with the hydride. Some of these techniques are still in use even today.

Holak in 1969 was the first to apply hydride generation technique to AAS. He generated arsenic hydride and collected it in liquid hydrogen. Subsequently he warmed the trap and conducted the arsine with a stream of nitrogen into an argon-hydrogen flame to measure atomic absorption. Several papers were published in the following years describing modifications and optimization of the technique. However the technique found wide acceptance only after the reliable accessories were introduced in the market.

HYDRIDE GENERATION TECHNIQUE

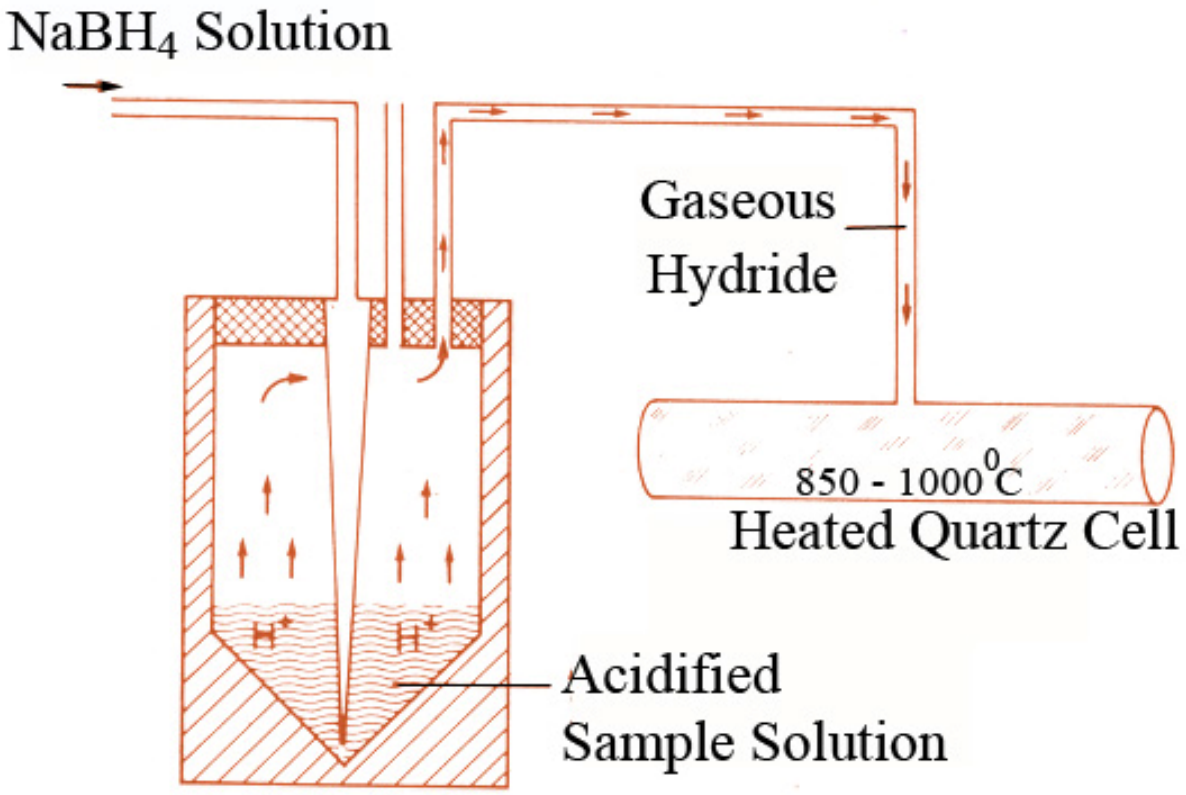
The most commonly used method to generate nascent hydrogen is addition of zinc or aluminum to hydrochloric acid. Mixtures of titanium trichloride and magnesium have also been used for the generation of nascent hydrogen.

Metal acid reactions have a number of disadvantages such as:

1) **Requirement of high purity metals**
2) **High values of blanks**
3) **Low release of hydrogen (only 8%)**

Most of these disadvantages have been overcome by the introduction of sodium borohydride as a reductant. Reproducibility and control over the reaction can be easily achieved with the addition of sodium borohydride solution stabilized in sodium hydroxide solution. In 6M HCl solution and using nitrogen stream to release hydrogen, yield can be increased to 40 – 60%.

APPARATUS FOR HYDRIDE GENERATION



The released hydrogen is collected in a trap cooled with nitrogen which is warmed to vapourize it. Before freezing the hydride must be dried properly using calcium chloride. The latter develops a high heat of hydration that prevents hydride from being dissolved or absorbed.

For routine determination direct 'online' introduction into the flame through a quartz tube is quite satisfactory.

Peak area integration frees the method from kinetic interferences.

ATOMIZATION OF THE HYDRIDE

Soon after the development of the hydride technique, the use of electrically heated quartz tube or heated in a flame for atomization of the hydrate were proposed. Some workers used a quartz tube with sealed quartz windows. The tubes were heated to 1100^0 C. With this procedure a very high degree of atomization (~ 100%) can be obtained.

The reactions can be summarized as follows:

$$Zn + HCl \longrightarrow ZnCl_2 + H_2\uparrow$$

$$NaBH_4 + HCl \longrightarrow NaCl + BH_3 + H_2\uparrow$$

$$Se + H_2 \longrightarrow SeH_2$$

$$SeH_2 \xrightarrow{1100^0\ C} Se + H_2\uparrow$$

As of now the procedure can be easily automated to obtain a high throughput of 30 samples per hour! The hydride technique has a decisive advantage over other systems because only the analyte can be separated as a volatile hydride from the sample matrix. The relatively small number of other components reaching the atomizer make their interference rather unlikely.

The greatest advantage of hydride technique is that it is an absolute technique and not concentration dependent. The sample volumes required for analysis are very low. Only 10 ml of the reagent and 0.5 ml of the sample are sufficient.

Most reaction vessels for hydride technique are designed to accept 50 – 100 ml but also require a minimum volume of 5 – 10 ml. In practice 10 ml of the reactant volume and 0.5 ml of the sample are satisfactory.

ATOMIZATION MECHANISMS

Atomization is brought about by free radicals produced in the primary reaction zone of the diffusion flame.

$$\dot{H} + O_2 \rightleftharpoons \dot{O}H + \dot{O}$$

$$\dot{O} + H_2 \rightleftharpoons \dot{O}H + \dot{H}$$

$$\dot{O}H + H_2 \rightleftharpoons H_2O + \dot{H}$$

In presence of excess hydrogen only OH and H radicals are formed . The last reaction is very rapid and the concentration of H radicals is several orders of magnitude higher than that of OH radicals.

$SeH_2 + \dot{H} \rightarrow SeH + H_2$ $\Delta H = -189$ KJ/ mol

$SeH + \dot{H} \rightarrow Se + H_2$ $\Delta H = -131$ KJ/ mol

A corresponding reaction

$Se + \dot{H} \rightarrow SeH$ $\Delta H = -305$ Kcal

is also possible. But this reaction is strongly exothermic and needs a third partner to take up the energy. It can be reasonably assumed that this reaction is very much slower than the formation of Se atoms.

Similar mechanisms can be prevailing for other hydride forming elements.

INTERFERNCES

For absorption in flames, variations in the transparency occasionally occur when the hydride along with hydrogen enters the flame. But this signal is very small and constant and caused by HCl, it can be subtracted like a blank value.

Kinetic interferences occur in direct on-line systems and caused by varying rates of formation or liberation of the hydride from solution. For example very dense foam produced by the addition of the alkaline sodium borohydride retains a portion of the hydride.

For elements of VA group, the sensitivity difference in peak heights between +3 and +5 oxidation is less than a factor of 2. This difference can be partly eliminated by peak area integration.

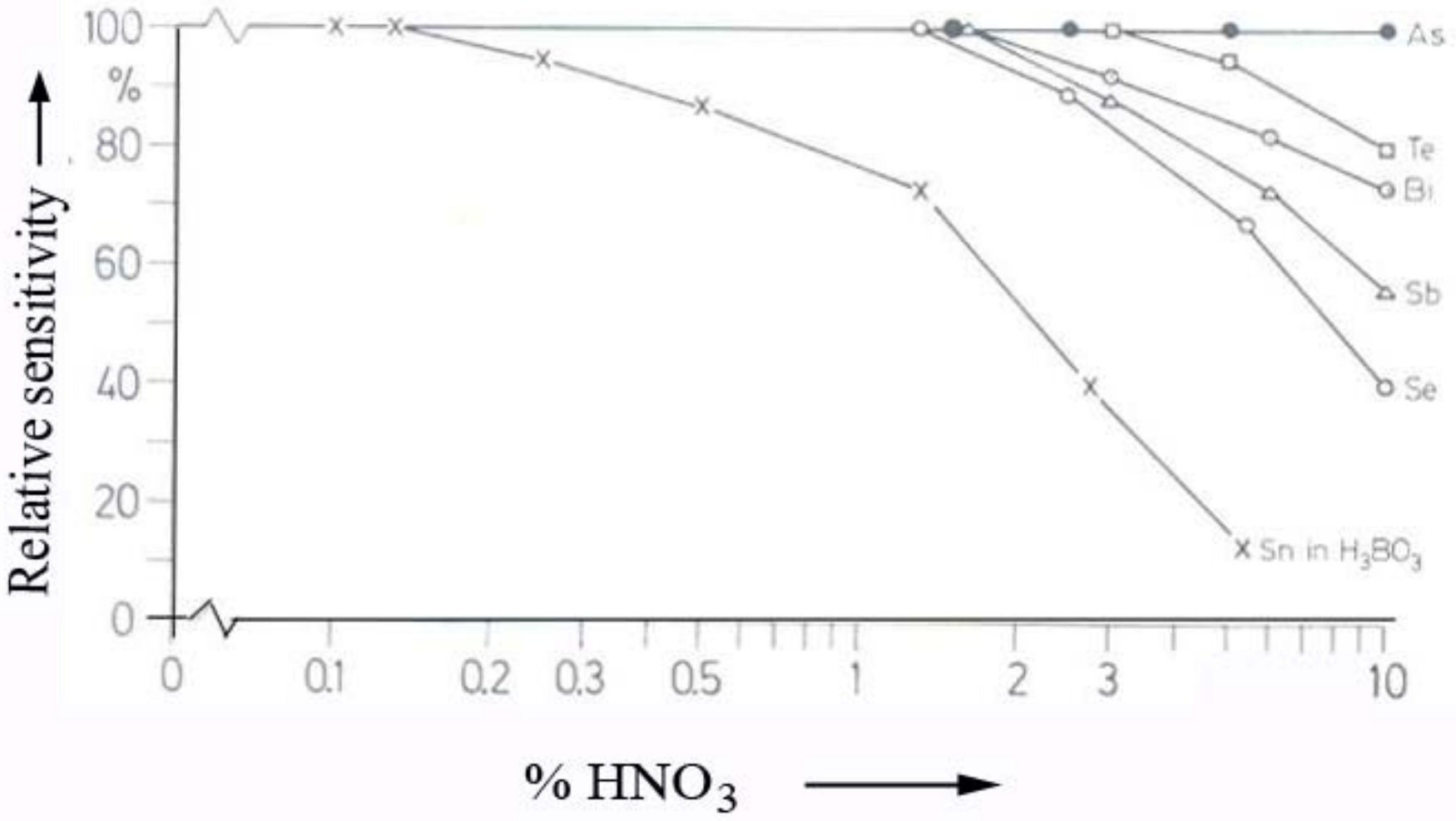
For arsenic, +5 state gives an 80% signal as compared to arsenic (III). Similarly for antimony (V) there is 50% reduction in the signal as compared to antimony (III).

For group (VI) elements, +4 and +6 oxidation states exist and +4 gives a measurable signal.

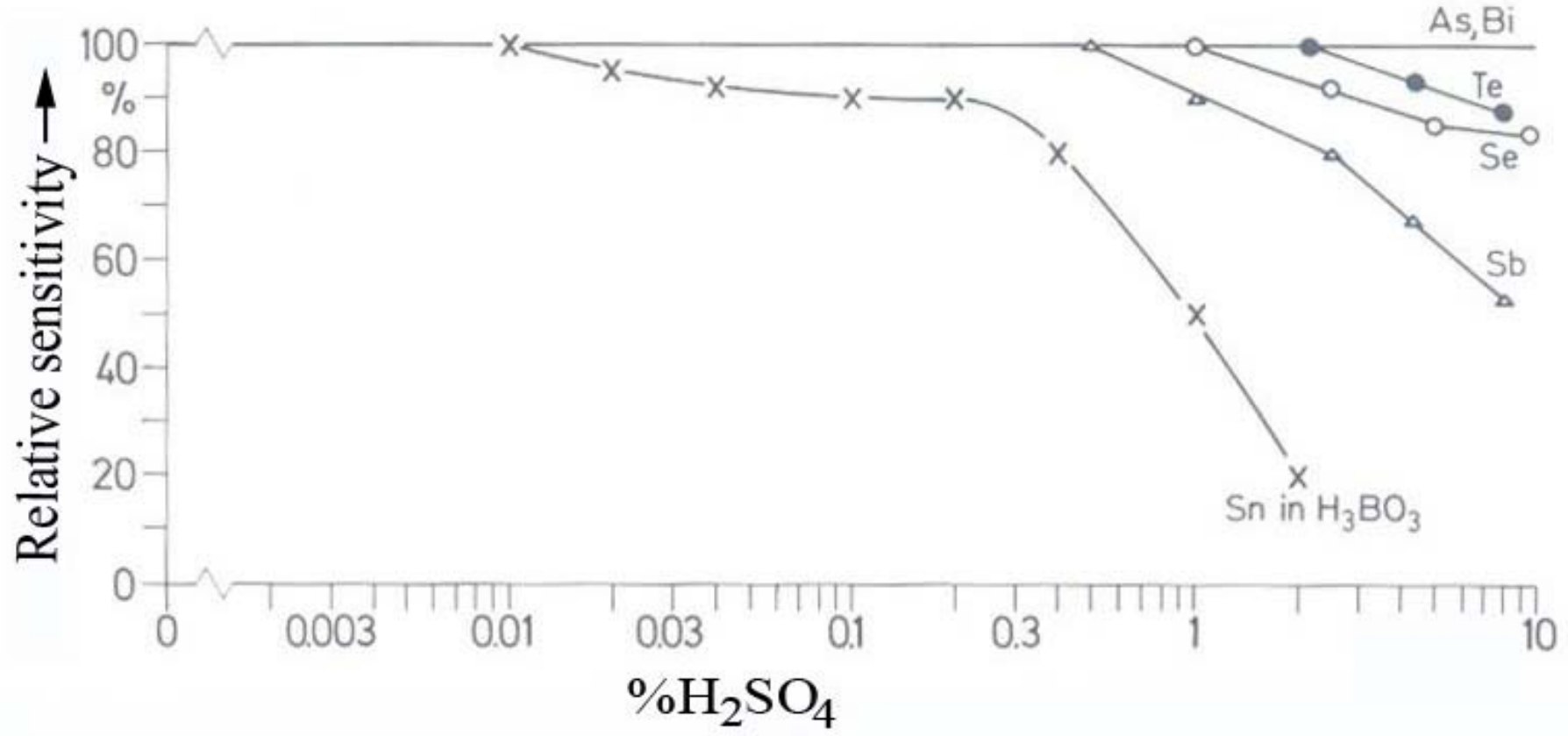
In practice a pre-reduction of selenium and tellurium is always required in hot 4 M or 6 M HCl medium.

HCl, H_2SO_4 and HNO_3 depress the signal if present in high concentrations.

EFFECT OF NITRIC ACID



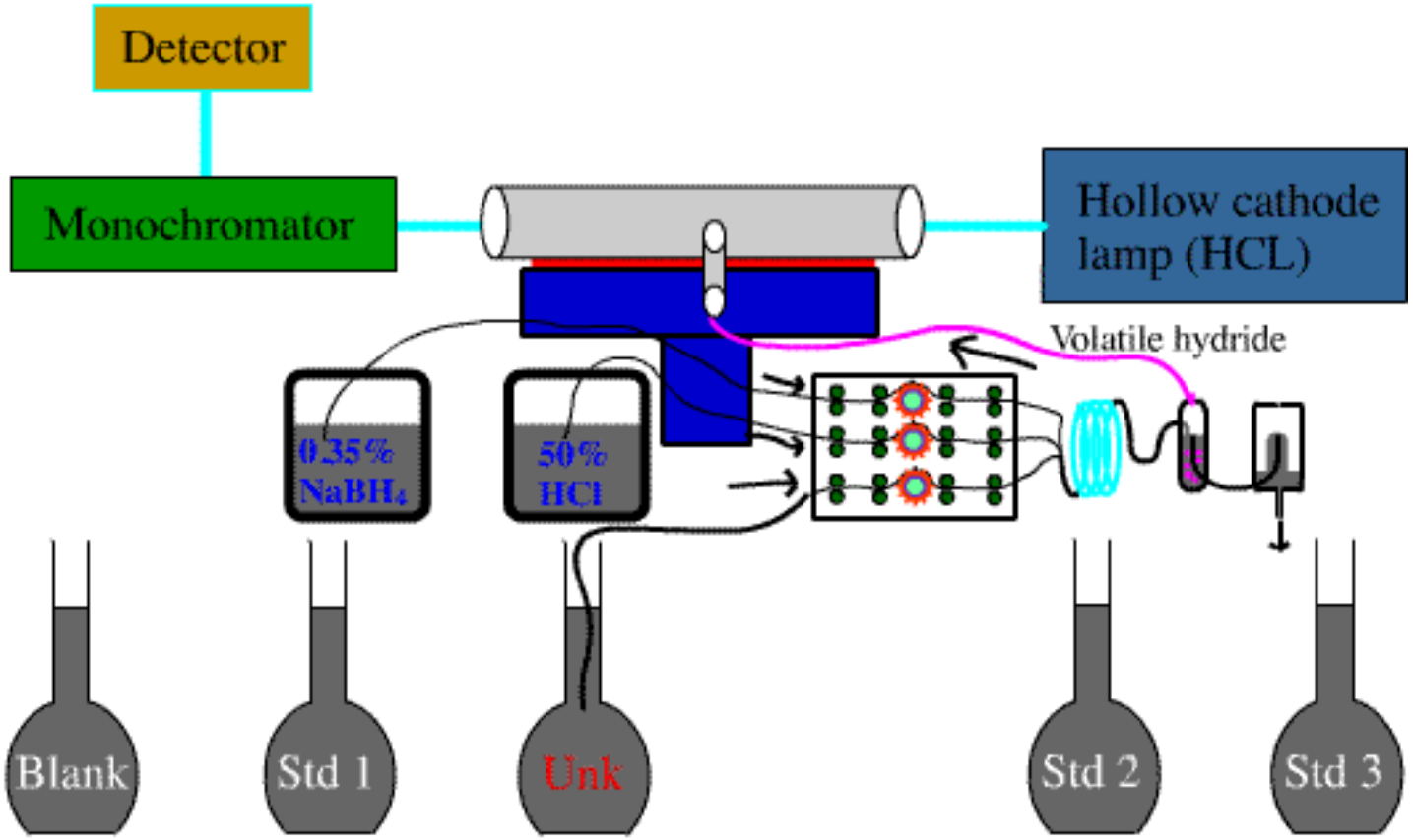
EFFECT OF SULPHURIC ACID



INTERFERENCES

Elements from group VIII and IB of the periodic table owing to the formation of precipitates, and some elements like nickel, platinum etc., absorb the hydrogen. Transition elements interfere in ionic forms at high concentrations. EDTA, cyanides and thiocyanates mask the interference. All hydride forming elements interfere mutually. Thus interference is dependent upon the absolute concentration but not on the analyte/ interferent ratio. As-Se interference is gas phase type which can be eliminated by using a buffer to delay the transfer of arsenic.

INSTRUMENTATION



DETERMINATION LIMITS OF METAL HYDRIDES

Element	Hydride Technique
As	0.02
Bi	0.02
Sb	0.1
Se	0.02
Sn	0.5
Te	0.02

AUTOMATION

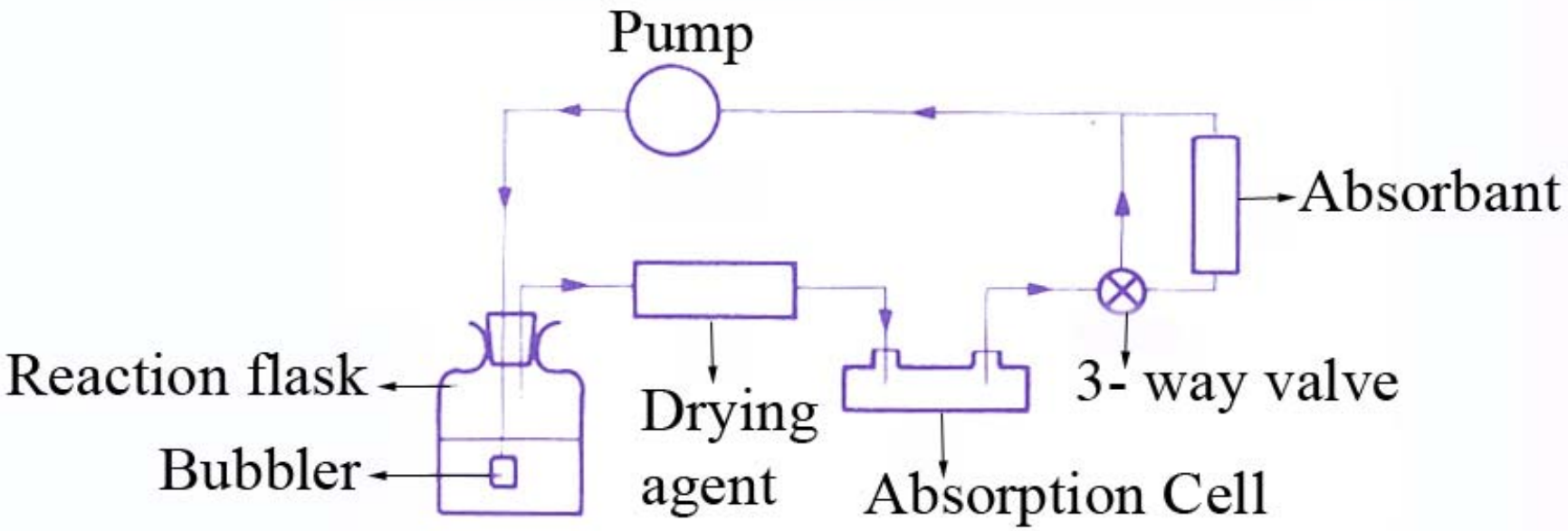
High sensitivity of the hydride technique and the environmental pollution potential of arsenic, selenium, lead etc., have prompted researchers to automate the hydride technique. Nowadays the automated hydride accessories are available which employ peristaltic pumps for mixing the reagents and use nitrogen for hydride transport. These operations can also be integrated into the software of AAS and throughputs of 30 samples per hour is possible.

MERCURY COLD VAPOUR TECHNIQUE

Mercury is the only metallic element that exists in the atomic state at ambient temperature. It has a vapour pressure of 0.0016 m bar at 20^0C which corresponds to about 14 mg per cubic meter. Given the environmental pollution potential of mercury, attempts have been made since 1939 well before the development of AAS, for the determination of mercury in air. The most successful among these was the electrolytic deposition of mercury using a mercury vapourization cell.

Polluktov and Vitkun were the first to use the stannous chloride to reduce mercury in sample solutions which resulted in an usually large absorbance signal for mercury in AAS. Subsequently they eliminated the flame and nebulizer and passed only air to conduct the vapour through a 30 cm quartz cell mounted in the optical path of the radiation beam in AAS. With this technique they obtained detection limit of 0.5 ng mercury.

A general scheme of generation of mercury vapour is shown here.

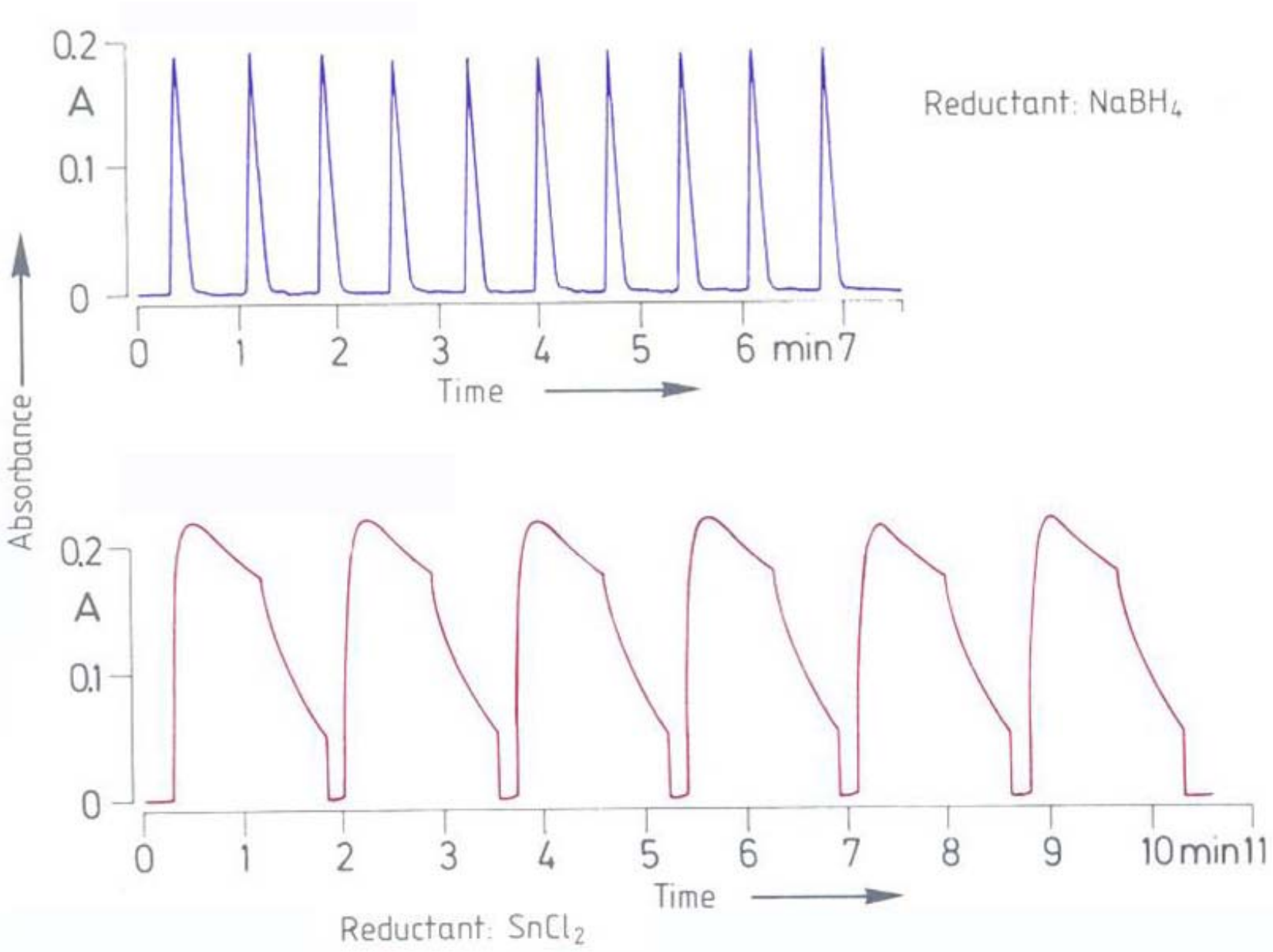


Nowadays the determination of mercury is carried out by an apparatus similar to that of hydride generator but provided with some modifications.

When stannous chloride is used as a reductant, air must be pumped through the solution to agitate as well as transport the mercury to the absorption cell. The dynamic signal generated in this way shows a slightly lower absorbance compared to sodium borohydride – acid solution.

With sodium borohydride a great quantity of hydrogen is liberated when acid is added. This hydrogen in fact, transports the majority of the metallic mercury to the absorption cell. Further, the reaction with sodium borohydride is much faster so that peak height measured with the open system is almost equal to that of stannous chloride ($SnCl_2$) in a closed system.

MERCURY COLD VAPOUR SIGNAL



By using a well designed reaction vessel with a conical bottom and by introducing the reductant near the bottom of the vessel thorough and turbulent mixing of the reductant ensures complete displacement and carry over of the mercury. The time required for the reaction is only one to two minutes.

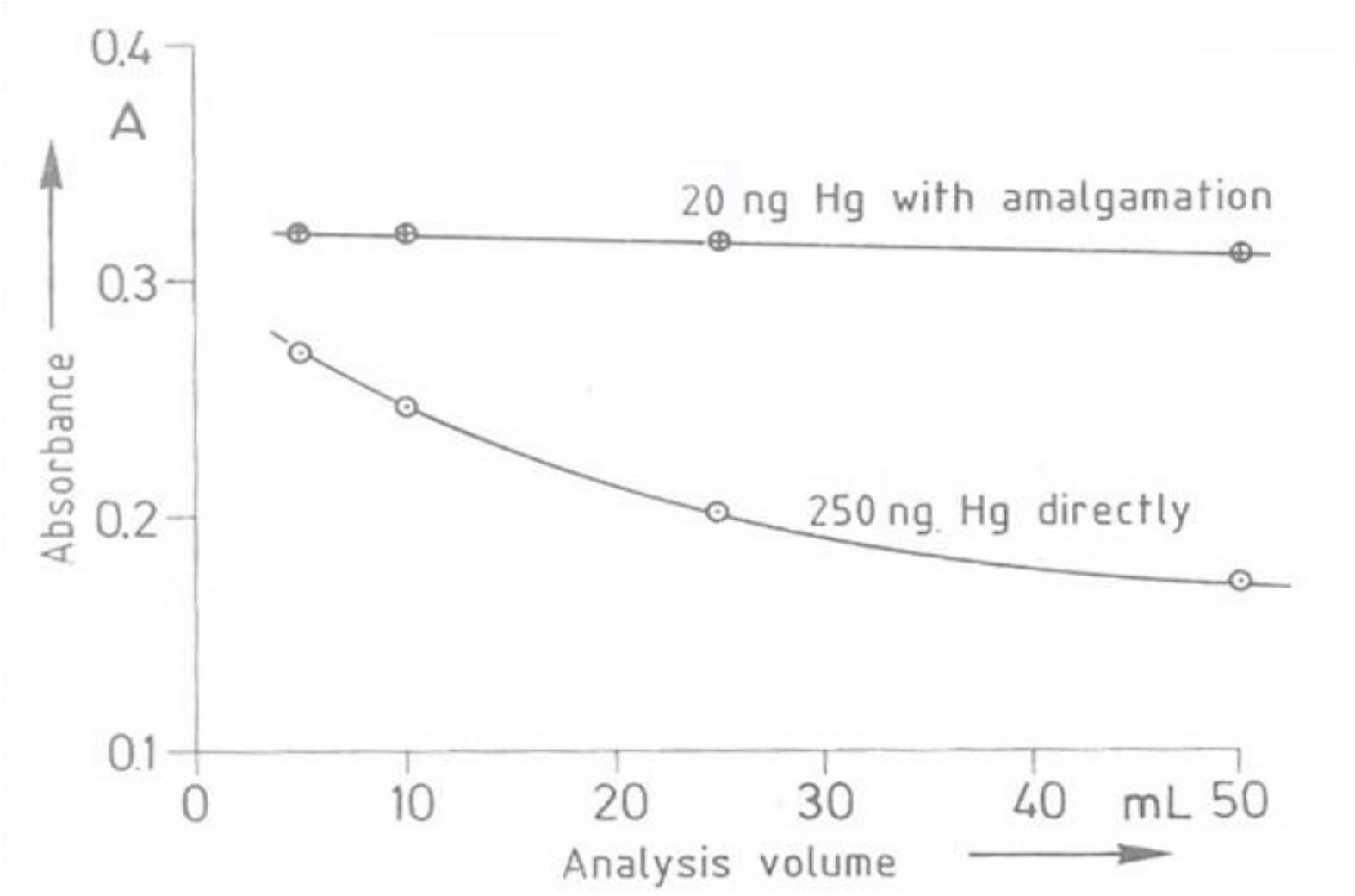
Since mercury vapour is in contact only with tubes and other components of the apparatus only for a relatively short time exchange reactions play only a minor role.

In contrast, on a closed system losses occur through adsorption and carry over problems from one sample to the next are more.

The necessity of determining mercury in ultra trace quantities has led to the development of enrichment and separation techniques. The fact that mercury forms stable amalgams with noble metals such as copper, silver or gold can be used to advantage for enrichment.

The mercury vapour is merely collected by amalgamation on a gold gauze for a sufficiently long time to concentrate it . Subsequently the gauze is heated up to 500 – 700^0 C and the vapour is carried over to the absorption cell for measurement. Thus an enhanced signal is obtained as compared to direct analysis.

ENHANCEMENT OF SENSITIVITY



Since the amalgam technique preconcentrates the mercury, the method becomes independent of the volume of the sample and absolute determination is possible. In this way the detection limit of the cold vapour technique is also improved.

INTERFERENCES

Virtually there are no spectral interferences in the determination of mercury .

Systematic errors occur to a large extent owing to the blank values, contamination due to the reagents, laboratory glass ware, losses due to volatilization, adsorption or chemical reaction. In the extreme cases these phenomena can lead to substantial errors. In non-contaminated regions in the atmosphere, the concentration of mercury rarely exceeds a few nanograms per cubic meter.

However in the laboratory atmosphere, values of 100 ng/ m^3 are not uncommon.

Typical sources of errors are listed below:

- ✓ During the storage of sample (e.g soils, glass ware etc).
- ✓ Diffusion of mercury through plastic foils.
- ✓ Adsorption of mercury on to the glass walls of the containers.
- ✓ Contamination of the reagents and acids.
- ✓ During sampling, digestion, storage or actual measurement.
- ✓ Precipitation of mercury on noble metal surfaces.
- ✓ Chemical exchange reactions with rubber tubing, PVC etc.
- ✓ $CaCl_2$ is an unsuitable drying agent . Magnesium perchlorate is better.

CHEMICAL INTERFERENCES

Element	Limiting concentration (weight%) of mercury	
	$SnCl_2$ reduction	$NaBH_4$ reduction
Ag	0.005	0.005
As	10	0.25
Bi	10	0.25
Cu	10	0.25
I	0.003	1
Sb	1	2.5
Se	0.005	0.5

PROCESS INTERFERENCES

- Gold, platinum, rhodium and ruthenium interfere in the determination of mercury when present at 1g/L concentrations in the analyte solutions. This is due to the reduction of these metals and subsequent amalgamation with mercury. Similarly copper and silver interfere. Silver interference can be eliminated by adding bromide to form silver bromide(AgBr) while mercury remains in solution as tetra bromo mercurate ion $(HgBr_4)^{2-}$.

- Iodide interference is noticeable when the sample is treated with nitric acid (as in sea weeds).

- Hydroxylamine hydrochloride which is added to reduce permanganate can have a substantial influence on mercury at higher concentrations. In this case mercury is not liberated at all!

- **Sulfhydryl groups (e.g cestine etc.) interfere when the sample is not completely ashed.**

- **Organomercury compounds are volatilized and only partially reduced by sodium borohydride but the sensitivity of determination decreases in the order:**

  Inorganic mercury (Hg^{2+}) > CH_3Hg^+ > $C_6H_5Hg^+$

  However above 700^0 C the sensitivities are identical.

- **Poisoning of the gold gauze by other gases causes incomplete amalgamation. Therefore frequent reconditioning of the gold gauze is necessary.**

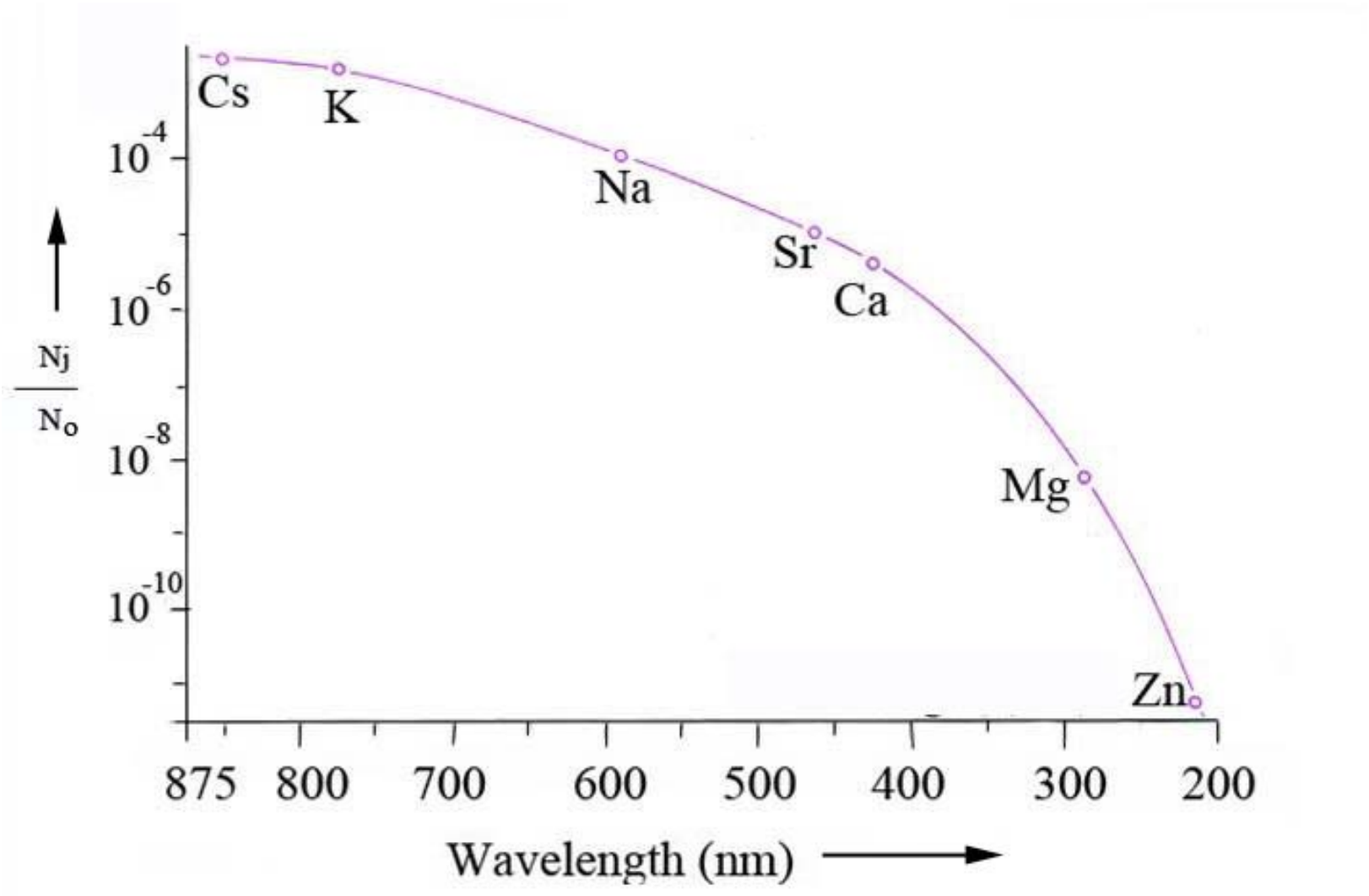
FLAME ATOMIC EMISSION SPECTROMETRY

Thermal excitation of atoms as dipicted by the equation,

$$\frac{N_i}{N_o} = \frac{P_j}{P_o} e^{-Ej/KT}$$

has been used to demonstrate the lower sensitivity of flame AES. The ratio of the non-excited atoms is more unfavourable in the short wavelength range of the spectrum than in the long wavelength range.

ATOMIC CONCENTRATION AT 2500 K



However it is not correct to state that AAS is always more sensitive than AES because the number of the excited atoms is always smaller than the number of atoms in the ground state. In flame AES, apart from N_j, the lifetime of the excited atoms is also more important. Experience has shown that AAS is more sensitive than AES only when the excitation potential is greater than 3.5 ev. With lower potentials flame AES is usually more sensitive.

Flame AES and AAS are more complementary to each other than competitive. Majority of commercial atomic absorption spectrometers nowadays permit flame emission measurements also.

Flame emission spectrometry has been in use since 1900s. Combustion flames provide a means of converting analytes into vapour forms by supplying the energy necessary to promote the electrons from the ground state to the excited state. The intensity of the radiation emitted by these excited states while returning to the ground states provides the basis for analytical method.

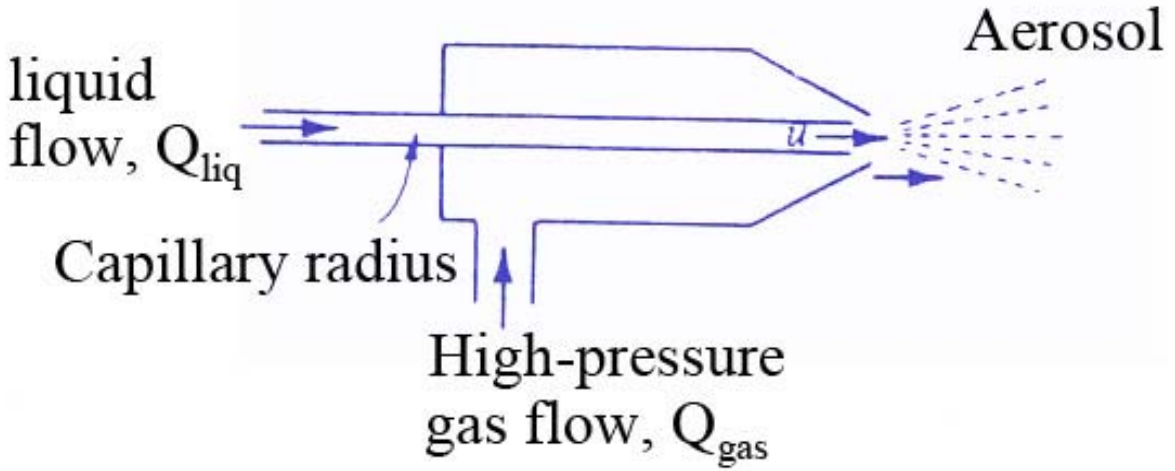
The basic components of the flame spectrophotometers include:

1. **Sample delivery system**
2. **Flame as excitation and emission media**
3. **Optics to isolate the desired spectral lines**
4. **Detectors and**
5. **Recorders**

THE SAMPLE DELIVERY SYSTEM

Essentially similar considerations as we had discussed for flame AAS prevail in the flame emission systems also. The most popular sample delivery system is the numatic nebulization. The sample is introduced through a capillary of 0.5 mm diameter tube into a high velocity gas jet of the oxidant (usually butane in FAES or acetylene in the case of AAS). In the spray chamber the larger droplets are broken into an aerosol of liquid and gas carried into the burner.

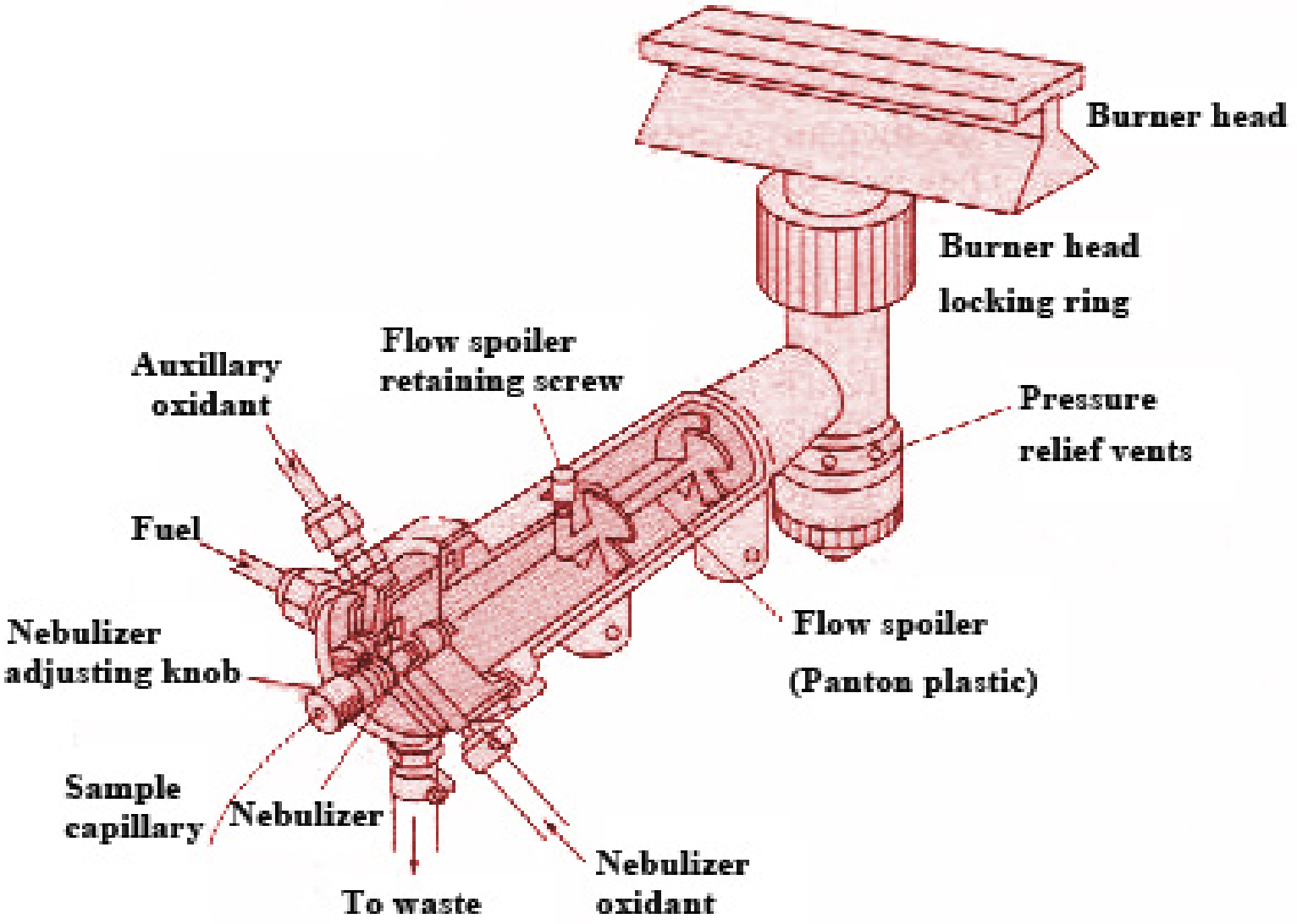
Typically droplets bigger than 20 μm diameter are collected and discarded. The distribution of the drop size is a function of the solvent as well as the concentration of the components.



(A) CONSTRUCTION OF PNEUMATIC NEBULIZER

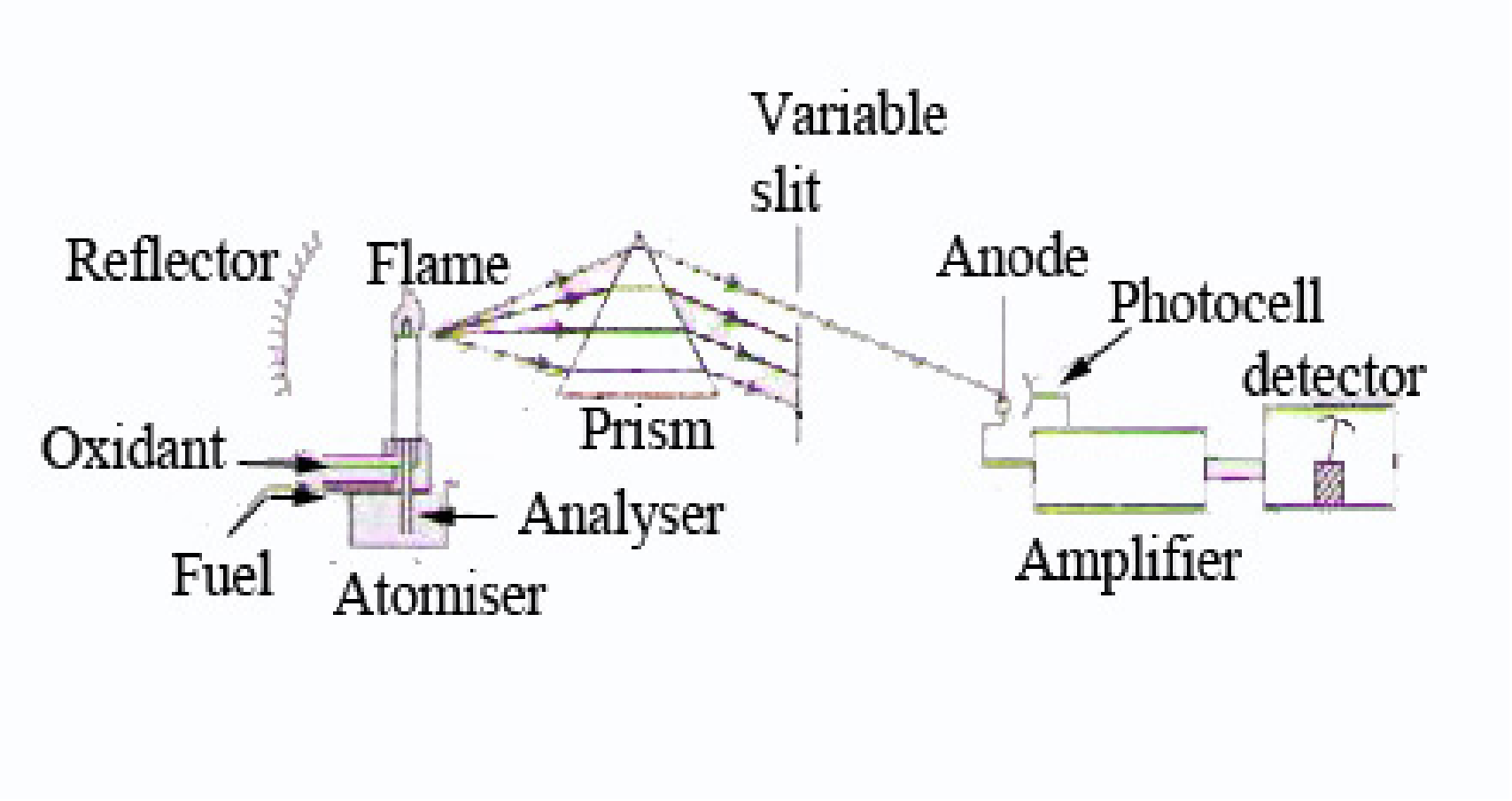
(B) BREAKDOWN OF LIQUID FILAMENT INTO DROPLETS

AAS NEBULIZER



A typical flame photometer is composed of a pressure regulator and flow meter for fuel gases, an atomizer, a burner, mirror, slit, optical system, photosensitive detector and recording output for the detector. Nowadays microprocessor controlled flame photometers are the norm.

OPTICAL DIAGRAM OF THE FLAME PHOTOMETER



Pressure regulator and flow meter are used for proper adjustment of the pressure and flow of gases. A 10 lb gauge for fuel and 25 lb gauge for oxygen are needed. Double diaphragm and needle valves are used to control the pressure. A rotameter is inserted in the gas line to obtain 2 - 10 ft/ hour of gas flow.

FLAME REQUIREMENTS

i. The flame should possess the ability to evaporate the liquid droplets from the sample solution resulting in the formation of solid residue.

ii. It must be capable of decomposing the solid into atoms.

iii. It must be capable of exciting the atoms to higher energy state.

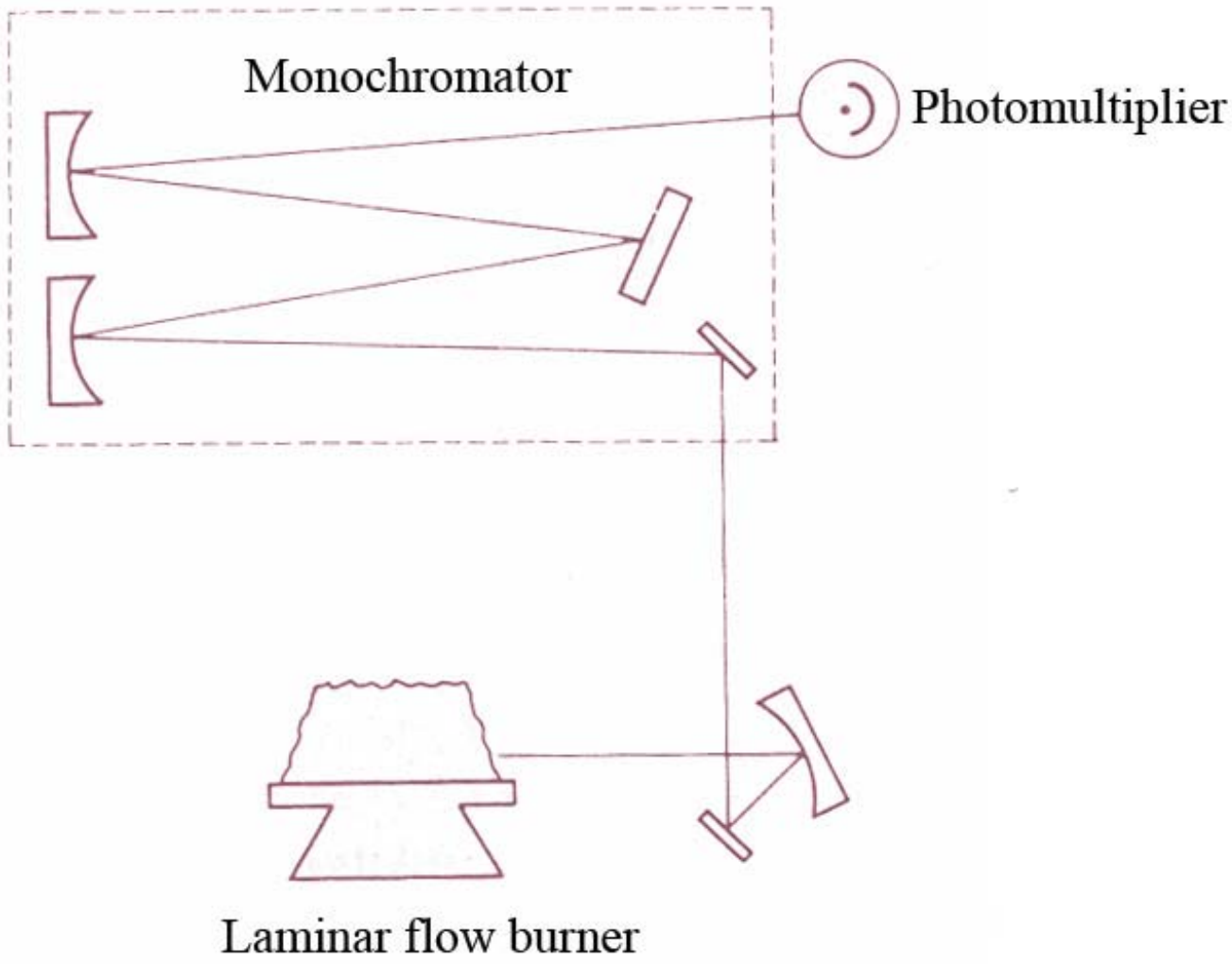
Mecker burner, total combustion burner, premix or laminar flow burner are employed.

The radiation from the flame is collected from a concave mirror placed behind the burner. The focal point of the mirror lies at the entrance of the monochromator slit. The exit slit is kept between the monochromator and the detector.

The optical system functions as a collector and the monochromator focuses it on the detector. Use of absorption filters or interference filters is more common in dedicated flame photometers. However better isolation of the emitted radiation line is achieved using a monochromator.

Most of the dedicated flame photometers use photocells with amplifier units to boost the output. However photomultipliers offer best sensitivity.

SCHEMATIC ARRANGEMENT OF A FLAME EMISSION IN AAS



A grating spectrometer equipped with a laminar flow burner and good detection read out system as in AAS serves equally well for flame AES. For this reason flame emission is routinely offered as an alternative operation mode in most of the AAS instruments. Since most of wavelengths usually fall into the visible or ultraviolet region photomultiplier tubes offer best detection limits for alkali and alkaline earth metals.

Both single beam and double beam flame emission spectrophotometers are available in the market.

Single beam flame spectrometers contain only one set of optics. In double beam spectrometers a second light path for the light emitted by the internal standard element which is added to each test solution and calibration.

The signal from one detector opposes that of the other through a suitable indicating device to produce a ratio method of comparing the light intensities between the analyte and the internal standard.

OPERATION OF FLAME AAS

Just like AAS, AES is also a relative technique. Therefore a series of standard solutions need to be prepared. The standards and the analyte are fed into the flame sequentially and the response is fitted into a linear or a polynomial curve. The concentration of the analyte is read off from the calibration curve.

INTERFERENCES IN FLAME PHOTOMETRY

Not many spectral interferences are known to occur in the determination of alkali and alkaline earth metals.

Interference may also arise from the background emission due to hydroxyl and cyanogen radicles. This is usually in the form of a scatter which can be controlled by measuring against a matrix matching solution.

Self absorption can be significant at low concentrations. This effect is more pronounced for lowest resonance line.

CHEMICAL INTERFERENCES

1. Stable compound formation or refractory oxide formation. This leads to incomplete dissociation.

2. By increasing the flame temperature this interference can be reduced. Another method of reducing the interference is by adding releasing agents.

$$M - X + R \rightleftharpoons R - X + M$$

Addition of excess of R will shift the reaction to the right. Hence if R-X is a stable product, this will result in the enhanced concentration of gaseous metal atoms M.

3. Ionization causes serious interference. Thus determination of calcium, strontium and barium in acetylene- air flame reduces the sensitivity.

This can be reduced by adding ionization suppressants. For example addition of potassium salts releases a large number of electrons there by increasing the sensitivity of calcium, strontium and barium.

4. Anion interference.

5. Cation interference sodium intensity doubles in presence of potassium . Addition of radiation buffer reduces this effect to a considerable extent.

6. Interference due to other element emission lines. A good quality monochromator reduces this type of interference.

7. Interference due to salts and acids. This effect can be reduced to a large extent by matrix matching.

   e.g Sodium chloride interferes (21.3.9 nm) in the determination of zinc.

8. Instrumental errors.

INSTRUMENTAL ERRORS

Most of the instrumental errors in flame photometry arise from the instability of the flame. To obtain stable flame the flow rate of the fuel and the oxidant must be controlled within 1%. The fluctuations of the detector and the amplifier also leads to instrumental errors. Another source of the analytical error is the atomizer function . Quite often the capillary gets clogged due to the deposition of salts. Therefore regular maintenance of the instrument is very essential.

APPLICATIONS OF FLAME PHOTOMETRY

1. Qualitative analysis for alkali and alkaline earth metals.

2. Quantitative analysis

Extensively applied for the determination of sodium, potassium, lithium, calcium, magnesium, strontium in the analysis of water, glass, biological fluids, petroleum products, cement, metallurgical samples, agrochemicals etc. Typical analysis range varies from 1-50 ppm of the metal ions.

ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

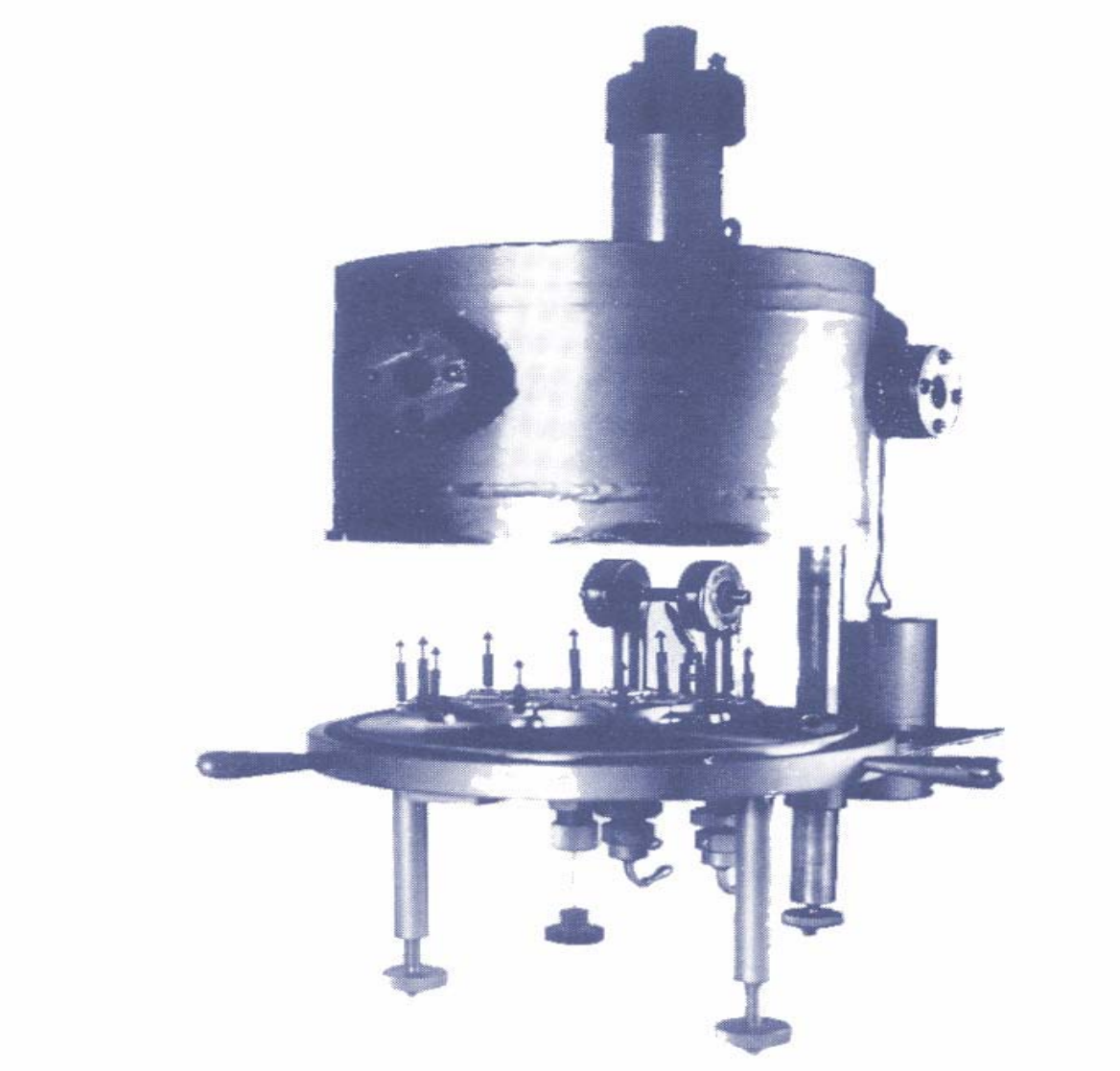
Atomic absorption analysis using flame atomization pre-supposes that the sample is in solution. For the analysis of solids in ppm level, bringing the sample in solution itself involves a dilution so that the concentration of the analyte in ppm will become a small fraction of the original content. Thus the limit of detection for a particular element is directly proportional to the concentration of the atoms in the flame, which is further dependent upon the flow rate of solution, efficiency of nebulization and atomization efficiency. Since the flow rate of the gases is always high, the time spent by the free atoms in the flame is very short, of the order of 10^{-4} sec. Increase of free atoms by higher intake of the sample is restricted by the burner design and moreover causes a deterioration of flame stability.

All these factors tend to limit the atomic concentration in the flame leading to a significant reduction of sensitivity and limit of detection. Further when the sample size is very small (5-10 µl) it is necessary to work at absolute detection limits. (expressed as µg). Therefore non-flame atomization methods were investigated to overcome these problems. The main focus in this development is the direct volatilization of the sample by direct heat. Several techniques based on application of electron bombardment, flash method, laser and plasma have been tried but they have not gained popularity.

Among these, L'vov and later Massmann's design of an electrically heated graphite tube based on the volatilization of the sample by direct heating of graphite cuvettes with low voltage, high current in argon atmosphere have evolved into a powerful AAS technique popularly known as electrothermal atomic absorption spectrometry which can give detection limits of the order 10^{-12} - 10^{-14} g/ lit.

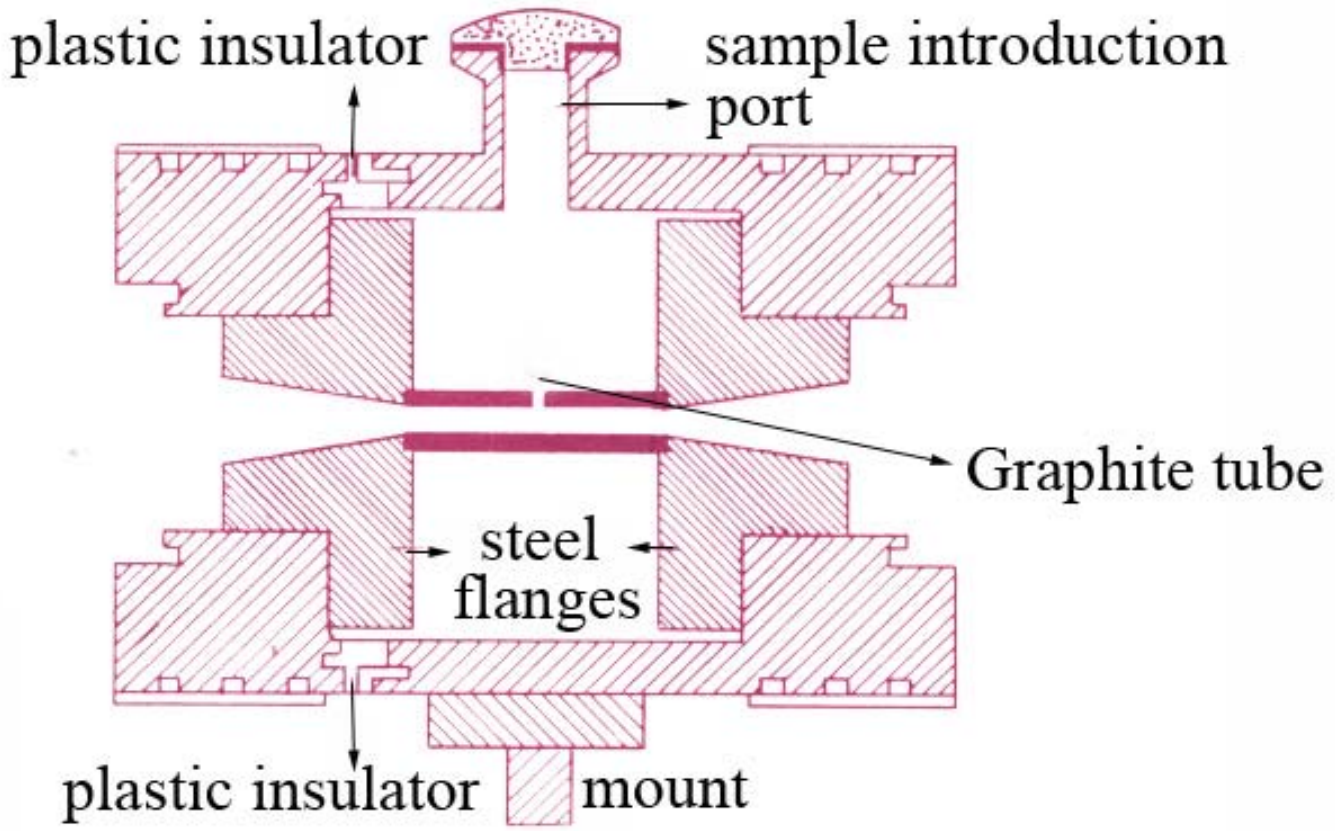
In the L'vov design the graphite tube is mounted in a chamber filled with argon at reduced pressure. The sample is deposited in the graphite cuvette, volatilized and atomized by Joule heating (resistance heating) at 3000^0 C. L'vov obtained typical detection of 10^{-12} -10^{-14} g with this design. But this apparatus is very complex and cumbersome in operation.

L'VOV'S ARGON CHAMBER



Massmann constructed a simplified graphite furnace in which the tube was continuously flushed with argon to prevent oxygen interaction with graphite. But because of continuous flushing and slower rate of heating the detection limits were one or two orders of magnitudes lower than L'vov. Nevertheless because of its simplicity and ease of operation, most of the graphite furnaces in use today are based on the Massmann design i.e they are tube furnaces with resistance heating which offer flexibility in programmability and operating convenience. Massmann design is shown here.

MASSMANN GRAPHITE FURNACE



The tube is mounted in the optical path of the resonance line in such a way that beam encounters only the atomic cloud unhindered by the tube geometry. The rest of the instrumentation is same as that of flame atomic absorption except, the software which has to handle several other tasks that are typical of a dynamic signal.

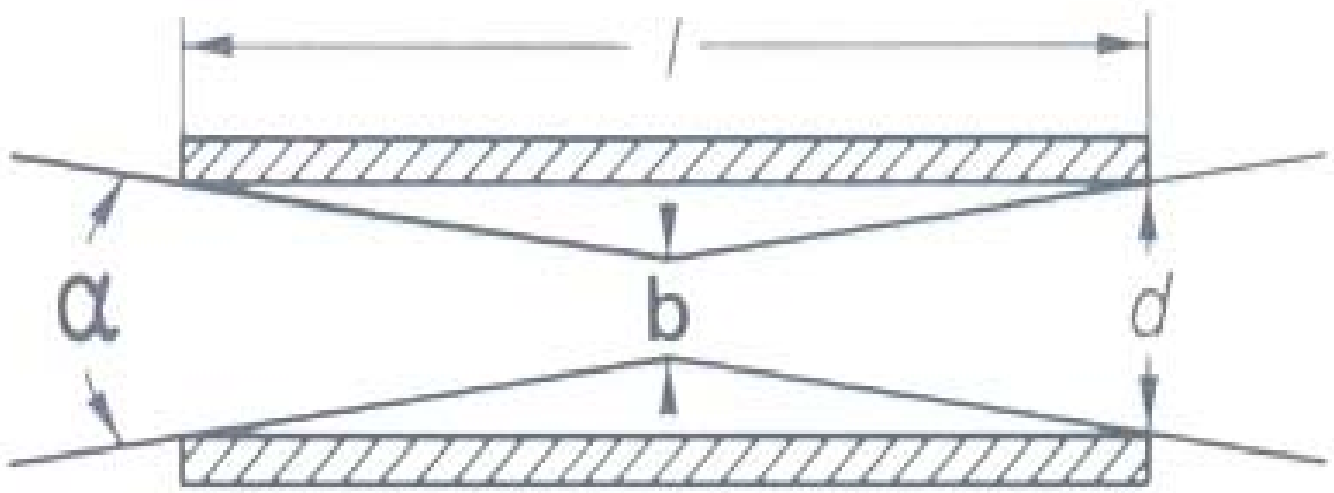
Introduction of the sample in to a graphite furnace (5-100 µl) followed by volatilization and atomization leads to an absorption versus time signal which resembles a gas chromatography peak lasting a few seconds. The shape of the curve is dependant upon the total number of atoms injected, residence time of the atoms in the optical path and the response time of the detector. Either the peak height or peak area (abs.sec) can be measured as a function of concentration, the latter being more suitable for routine applications.

GRAPHITE TUBE CHARACTERISTICS

For a good signal the graphite tube should be as long as possible and as narrow as possible. This facilitates longer residence time and hence good absolute sensitivity. The dimensions of the tube must be such that the whole tube should have uniform temperature, though this is seldom the case.

Apart from good geometry, the tube material and surface characteristics are very crucial in ETAAS. It is well known that at high temperatures graphite surface is highly permeable to metal atoms.

OPTIMUM DIMENSIONS OF GRAPHITE TUBE

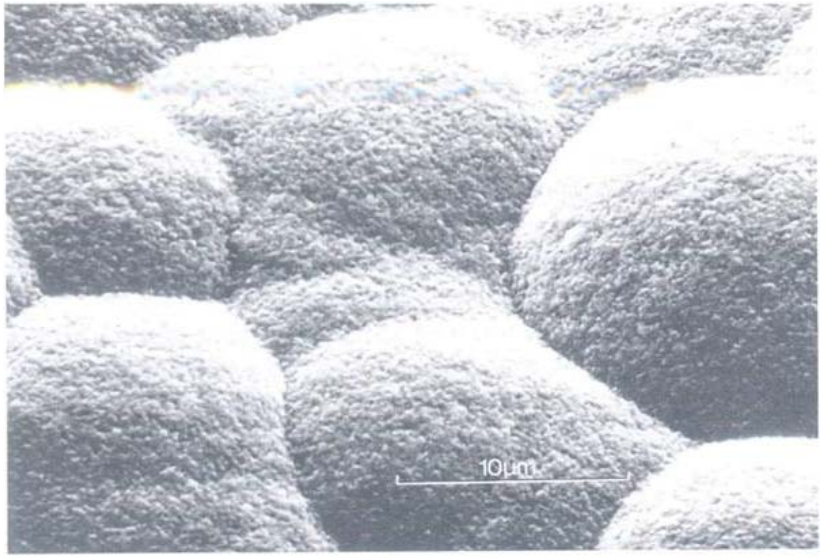


$$d = b + l \tan\alpha$$

Attempts to prevent the permeability were directed towards treatment of tubes with tantalum, molybdenum and tungsten salts which resulted in better sensitivity and reproducibility. This was attributed to the sealing of cracks and defects in the graphite surface. L'vov found that tubes made of pyrolytic graphite had the same properties. A dense, hard, impermeable and oxidation resistant pyrolytic layer of about 30-50 mm is highly resistant to oxidation thus permitting the determination of refractory elements with highest sensitivity.

GRAPHITE SURFACE CHARACTERISTICS

(A) Normal graphite tube



(B) Pyrolytic graphite tube

(C) Cross section of pyrolytic graphite tube

I SYSTEM CONSIDERATIONS

It is important to use argon in ETAAS. The purge gas performs the following functions.

i) Being inert, it prevents the ingression of atmospheric oxygen into the graphite furnace thus prolonging the life of the tube.

ii) It prevents metal atoms reacting with atmospheric oxygen to form refractory oxides which reduce sensitivity.

iii) It physically transports the matrix components out of the radiation beam before atomization, thus eliminating much of the background radiation.

iv) It is possible to precisely control the flow of purge gas or even reduce it to zero during measurement to obtain better sensitivity.

II TEMPERATURE CONTROL

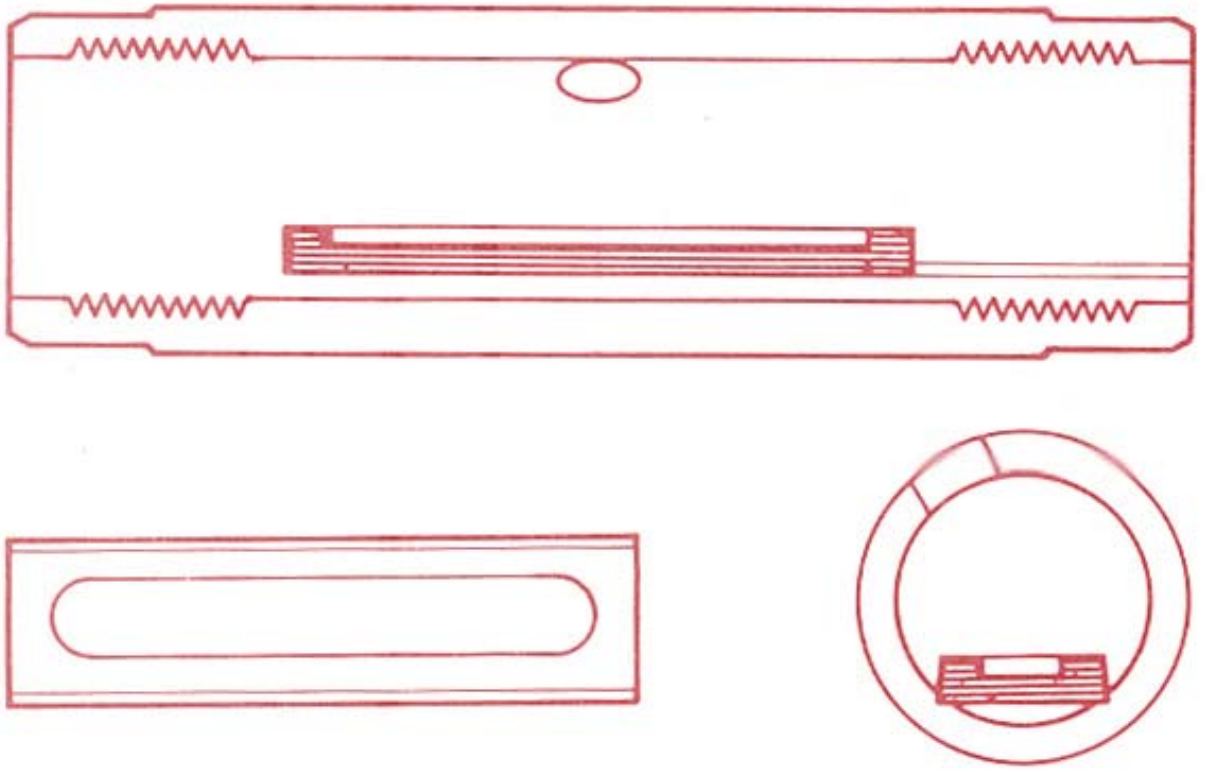
In electrothermal AAS it is possible to heat the tube and hence the sample at a controlled rate in a series of stepwise increments. This permits the removal of unnecessary matrix components in a predetermined manner. Thus it is possible to raise the temperature of the tube to 90^0 C within 1 second, ramp it to 120^0 C at 2^0 C per second, hold it for 10 seconds to remove water etc.

Similarly other temperature programmes may be incorporated to remove organic matter, inorganic salts etc, until all the concomitants are removed and only metallic elements are left. For the atomization, a maximum heating rate is selected to obtain best sensitivity. All such pretreatments may be standardized in the preliminary experiments before optimizing the temperature programme.

III THE STABILIZED TEMPERATURE PLATFORM CONCEPT

It has already been mentioned that the detection limits in L'vov furnace are 2-3 orders of magnitude higher than the Massmann design. This is because the sample after vaporization is not in equilibrium with volume or time and temperature. Sturgeon and Chakrabarty found that 60% of the atoms formed diffused to the cooler ends of the graphite tube which was 1500^0 C compared to the middle temperature of 2500^0 C . Equilibrium with time is even more difficult to achieve.

GRAPHITE TUBE AND PLATFORM ARRANGEMENT

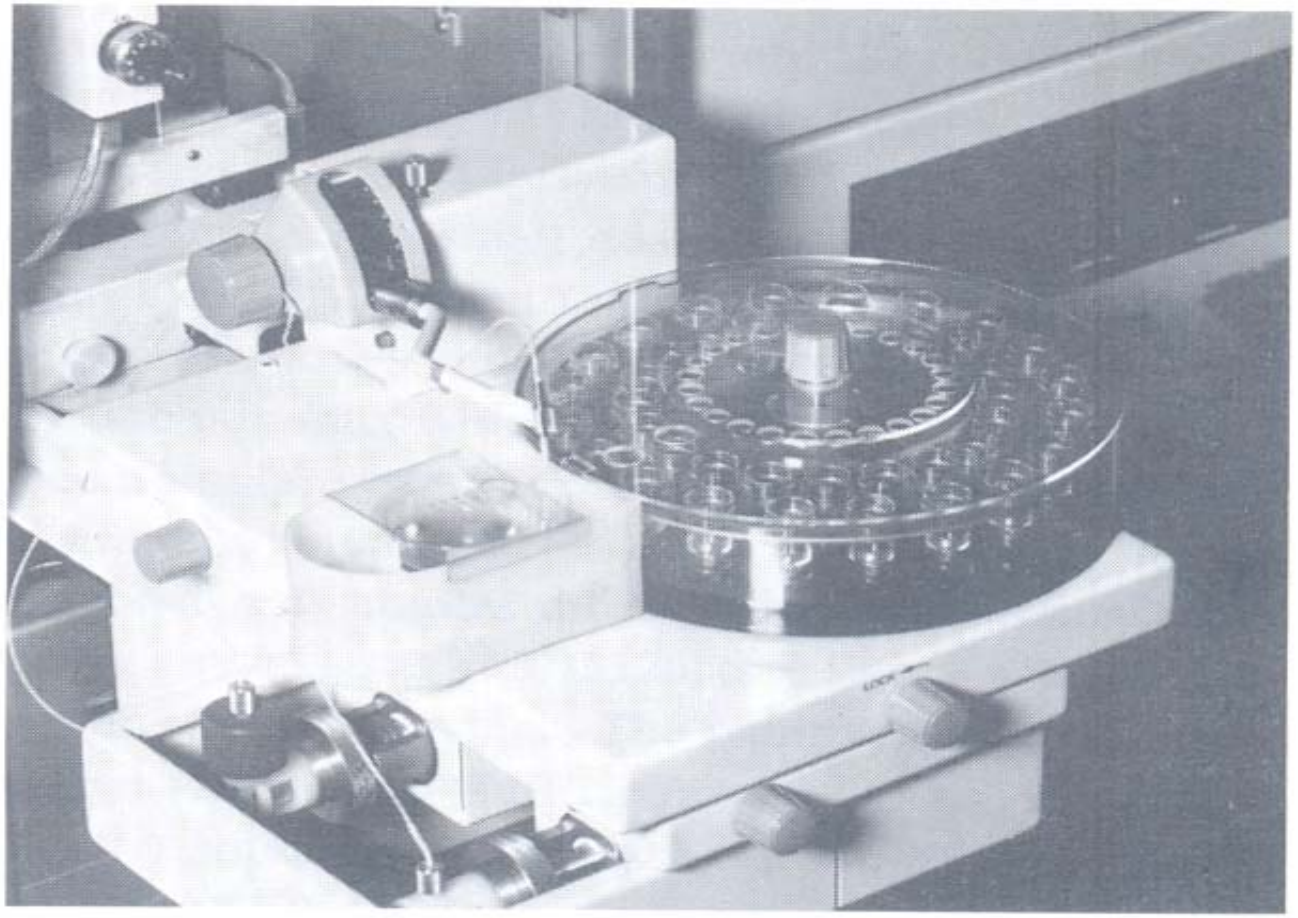


Hence L'vov et al. proposed that the sample be dispensed on a loosely fitted pyrolytic platform in the graphite furnace which will be heated only by radiation but not by direct contact. Such an arrangement does not permit heat conduction at right angles to the plane of graphitization. In such an arrangement platform temperature follows the tube temperature rather sluggishly which permits better equilibrium conditions. In such a system it has been proved that interferences are very few.

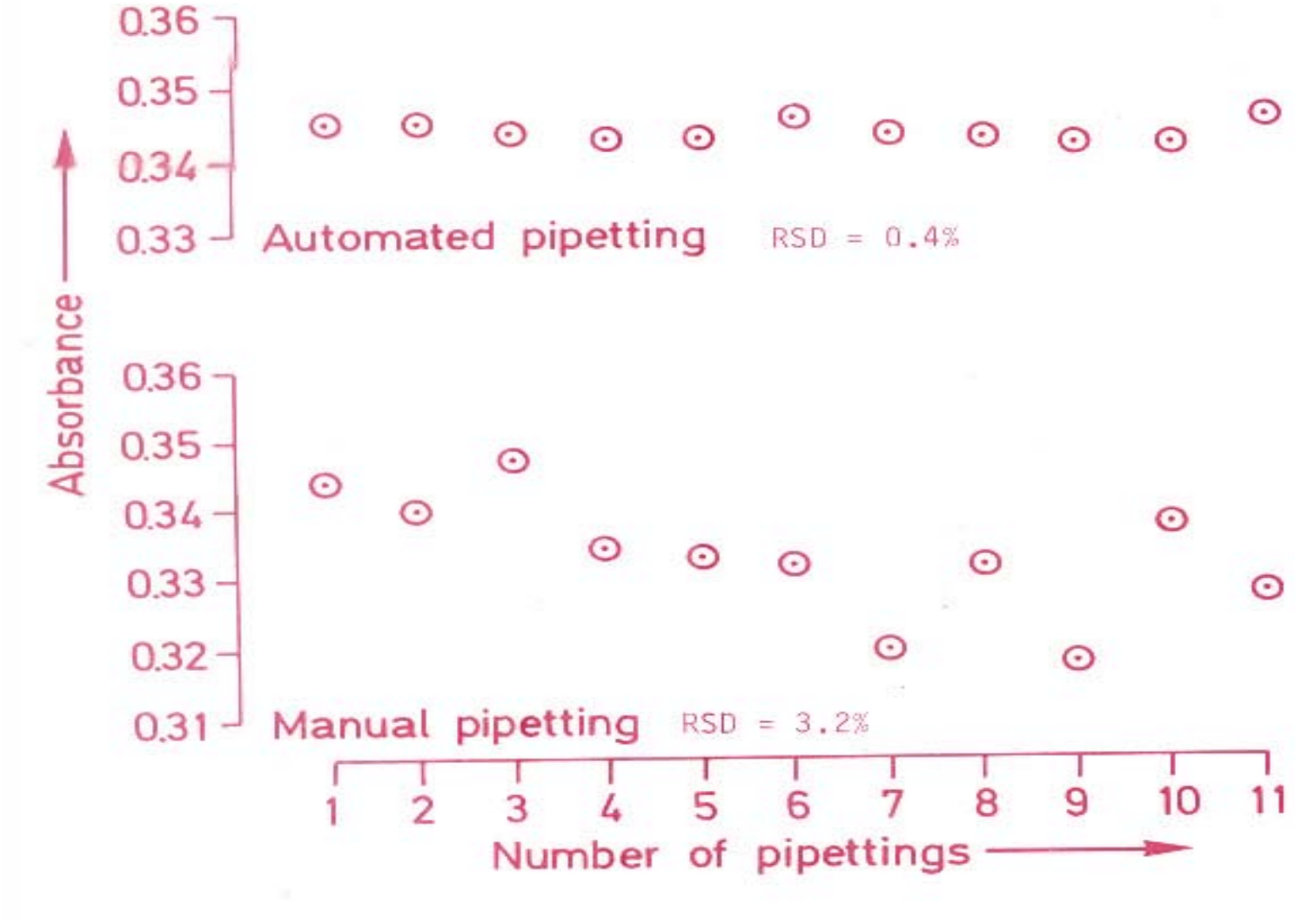
AUTOMATION

In graphite furnace the sample to be handled is rather small (5-100ml) but the sensitivity is rather high. The sample has to be introduced exactly in the same place every time through a small hole (about 1 mm dia) in to the graphite tube or on to the platform. There is also the risk of sample contamination with the graphite hole edges and pipette tips. All these factors lead to poor precision with manual pipetting. It is also cumbersome. Therefore automatic pipetting is preferred. Several programmable automatic dispensing units with teflon capillary are available in the market and also offered as a standard accessory with graphite furnaces. The reproducibility with automatic dispensers is about 1% with an RSD of 0.4% compared with 5% for manual pipetting with an RSD of 3.2%.

SAMPLE CARUSEL



MANUAL VERSUS AUTOMATED PIPETTING



METHODOLOGY OF GRAPHITE FURNACE TECHNIQUE

The ETAAS permits the analysis of liquid and solid samples. A known volume or weighed quantity of the sample is deposited on to the platform or directly in the tube where it is subjected to a series of stepwise temperature programmes culminating in final rapid increase in temperature for atomization. Usually pretreatment steps are aimed at separating the concomitants or the matrix components as much as possible. The inert atmosphere enhances the reducing properties of carbon leading to better atomization.

A majority of the elements may be atomized around 2500-3000^0 K. Both pretreatment and atomization curves may be optimized as a function of the absorbance signal. Since atomization emanates from the metal, it is important to reduce the sample to metal early in the thermal pretreatment stage. However the pretreatment temperature must stop below the decomposition temperature of the metal which is also the appearance temperature of the metal as evidenced by the absorption signal.

Campbell and Ottaway have postulated a reduction mechanism for many metals in ETAAS.

$$MeO + C \longrightarrow Me + CO$$

They calculated the free energy for the corresponding reaction and compared the values thermodynamically with the appearance temperatures and found good agreement.

Sturgeon and chakrabarty investigated atomization mechanisms on the basis of a thermodynamic/kinetic approach and proposed four mechanisms.

1) $MO_{(s)} \xrightarrow{C} M_{(l)} \rightleftharpoons 1/2\ M_2(g) \rightleftharpoons Mg$

where M = Co, Cr, Cu, Fe, Mo, Ni, Pb, Sn, V

2) $MO_{x(s)} \xrightarrow{T} M_{(g)} + x/2\ O_2\ (g)$

where M = Al, Cd, Zn, Si

3) $MO_{(s)} \rightleftharpoons MO_{(g)} \longrightarrow M_{(g)} + 1/2\ O_2$

where M = Cd, Mg, Mn, Zn

4) $MX_{2\,(s)} \longrightarrow MX_{2\,(l)} \longrightarrow MX_{(g)} + g \longrightarrow M_{(g)} + X_2$

where M = Cd, Fe, Zn

Mechanisms 1 & 2 require intimate contact with graphite surface but decomposition of oxides and halides occur in the vapour stage and hence are largely temperature dependent.

Frech and Pearson have investigated the determination of phosphorous in a graphite furnace. It has been proved that PO (g) , PO 2(g) are present at 1800 K , so that substantial losses must be expected at lower pretreatment temperature. Non-coated graphite tubes are sufficiently reactive to reduce partial pressure of oxygen which will also reduce phosphorous losses. It has also been shown that from the retained water methinophosphide (HCP (g)) is formed. To prevent this, atomization from pyrolytic graphite is carried out.

SPECTRAL INTERFERENCES IN ETAAS

Genuine spectral interferences are as rare in graphite furnace as in the flame technique. However background attenuation due to absorption of molecular bands of volatilized concomitants and radiation scattering of sample particles are quite frequent. Interferences also occur by the interaction of the analyte element and the condensed and vapour phases. Thus molecular absorption by alkali halides and radiation scattering are two important interferences because the concentration of the concomitants is more than 4-5 orders magnitude than the analyte element is most cases. While medium absorption is reproducible, radiation scattering can vary from sample to sample but it follows molecular absorption. This they attributed to molecules migrating to cooler ends.

Molecular spectra may be classified into dissociation continuum and broad band electronic spectra. Long wavelength maxima correspond to the dissociation of molecules into neutral atoms while the short wavelength maxima are attributed to the dissociation into the excited atoms. While the broad band spectra may be due to CN, OH, NH_2 bands, the dissociation spectra always exhibits sharp maxima as in the case of sulphite ions.

$SO_3 + h\nu \rightarrow SO_2 + O \quad (\lambda_{max}\ 330\ nm)$

$SO_2 + h\nu \rightarrow SO + O \quad (\lambda_{max}\ 190\ nm)$

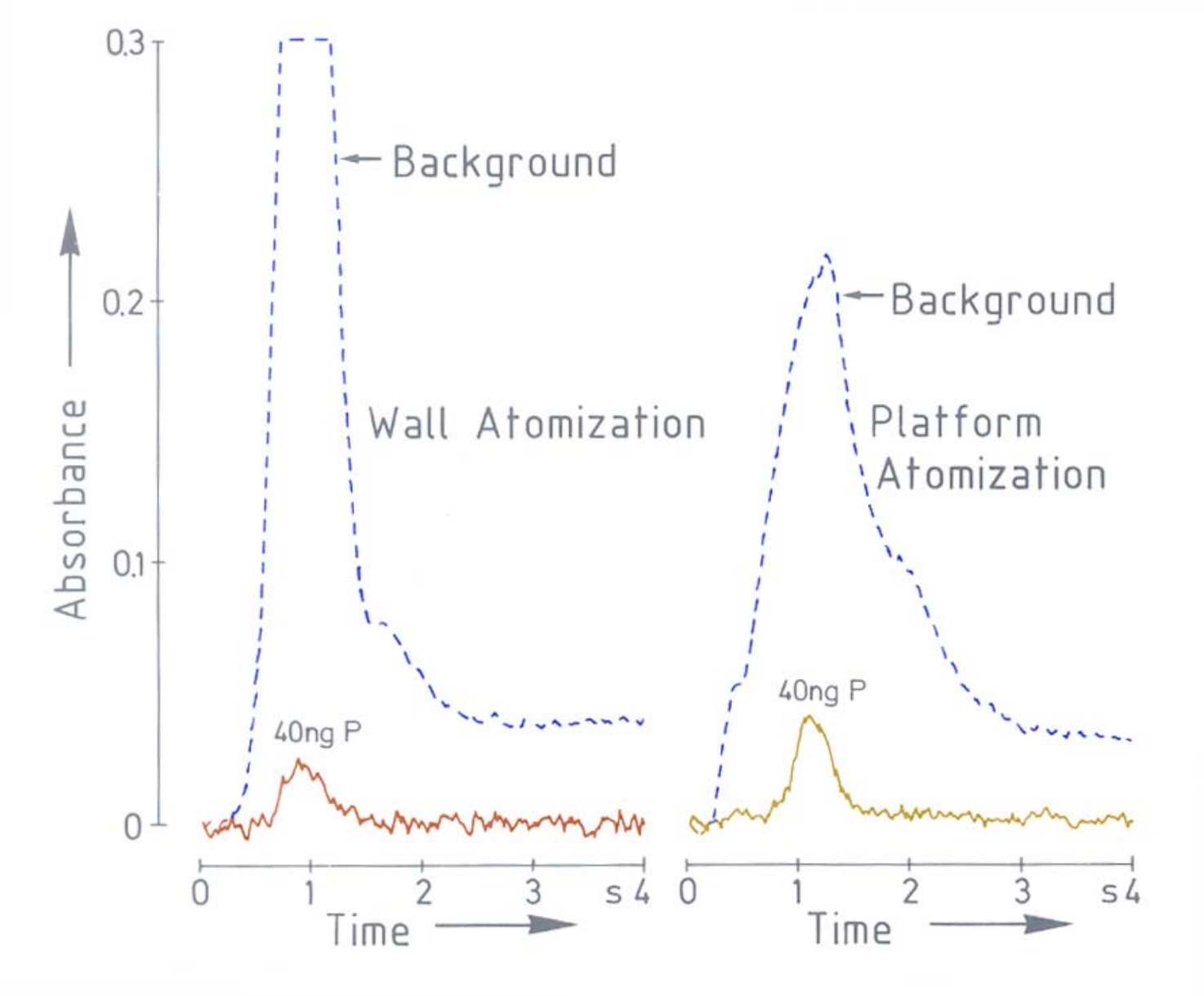
$SO + h\nu \rightarrow S + O \quad (\lambda_{max}\ 245\ nm)$

Similarly nitrogen containing molecular bands exhibit λ_{max} at 430 and 470 nm which also contribute to the background absorbance.

Radiation scattering also can arise due to the formation of smoke or soot during thermal treatment of biological and organic samples or form the sublimed graphite at high temperature. Most of these as well as other molecular bands will not have much impact if the temperature is carefully controlled at the atomization stage by the use of a platform.

By selecting suitable pretreatment temperature programme, numerous matrix components can be effectively reduced or eliminated. Then the analyte element can be analysed without interferences.

BACKGROUND REDUCTION IN PLATFORM TECHNIQUE



If the analyte element is also volatile, a low temperature atomization must be considered even though it leads to lower sensitivity, but the matrix components would not volatilize. Thus cadmium can be determined in presence of 2% sodium chloride at 750^0 C where NaCl does not volatilize.

When the volatilities of the matrix and analyte are similar thermal pretreatment alone can not guarantee satisfactory separation of the element. In such cases, phosphoric acid and nitric acid may be employed as 'ashing additive' for biological and organic samples.

Ammonium nitrate has also been routinely used to increase the volatility of the matrix and simultaneously reduce that of the element.

The most probable reaction is:

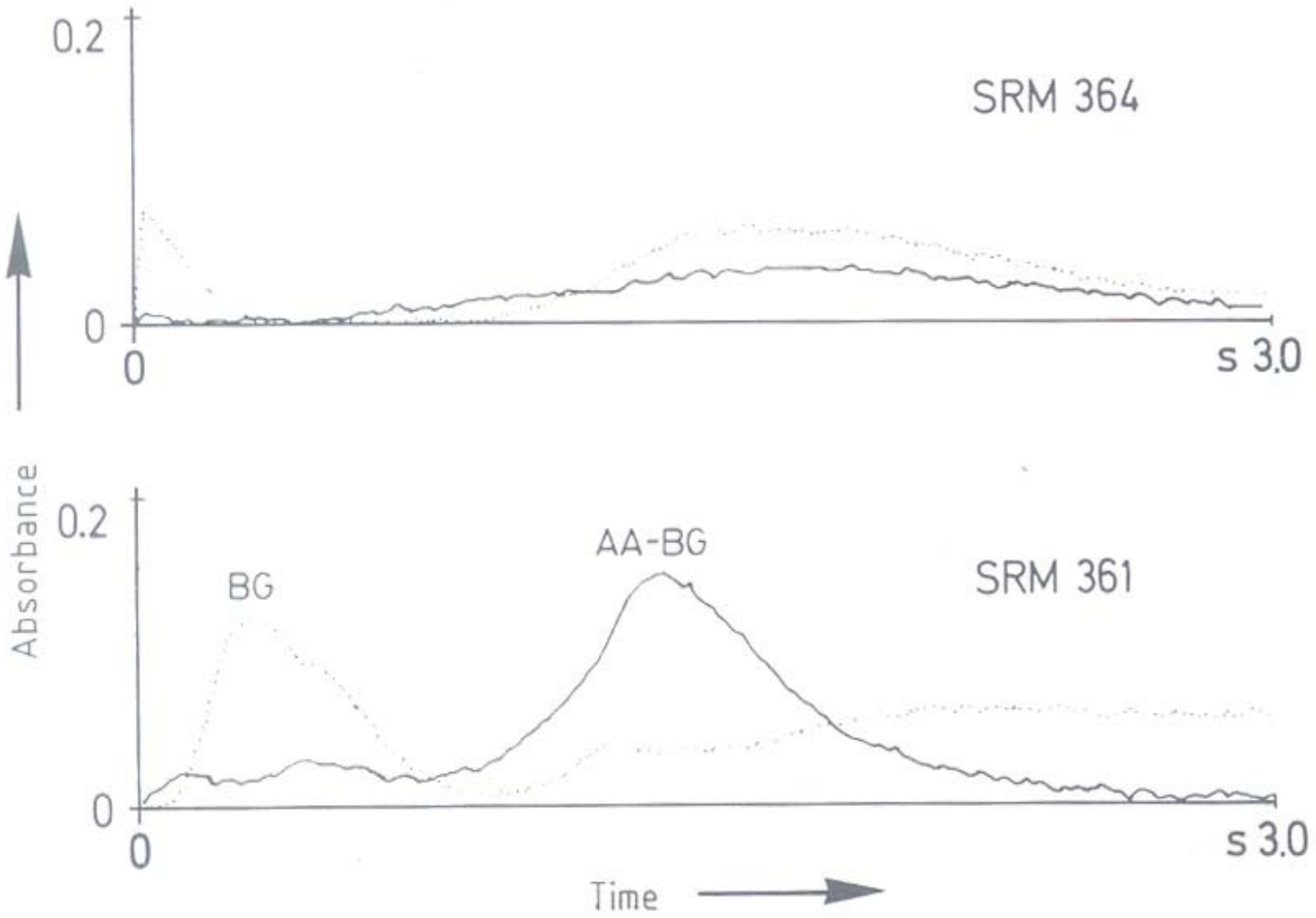
$$NaCl + NH_4NO_3 \rightleftharpoons NaNO_3 + NH_4Cl$$

Both reaction products can be easily decomposed or sublimed around 400^0 C. Thus background attenuation may be considerably reduced if not eliminated by the use of matrix modification.

The use of other gases such as hydrogen as the purge gas reduces the spectral interferences in the determination of chromium in urine. Similarly background signals for NaCl and CaO could be substantially reduced if the graphite tube was flushed with hydrogen for 10 seconds before atomization.

Solvent extraction and electrolytic deposition techniques may also be used to remove matrix components, but such steps need extreme precaution to prevent contamination by external sources.

DETERMINATION OF LEAD IN STEEL



Despite the fact that continuum source background correction are not ideal to handle spectral interferences quite a few investigators achieve success for majority of cases. Some of these are tabulated below.

Element	Interferent	Matrix	Cause	Remedy
Se	Iron(196nm)	-	rotational lines	BG CORR Zeeman
As, Sb, Se, Te	Calcium phosphate	-	P_2 rotational bands	BG CORR Zeeman
Cd	Aluminum	Aluminum	P signals	Zeeman BG CORR

VOLATILIZATION INTERFERENCES

Volatilization interference are quite complex and have not been understood completely. All the processes involving thermal pretreatment, formation of carbides, intercalation compounds, sublimations, other analyte–matrix interactions and kinetic effects play a role in such interferences.

A simple carrier effect was observed with the volatilization of NaCl in the determination of lead. But when iron is determined in presence of halogenated organic solvents, volatile iron chloride was found to be the cause of depressed signal.

Even perchloric acid decreases the signal for aluminum, gallium and thallium by more than 95% when present in 0.5 M concentration. It forms a thermally stable product with graphite which decomposes only around 1700^0 C. Thus a pretreatment at 1700^0 C is a must if the sample is decomposed with perchloric acid.

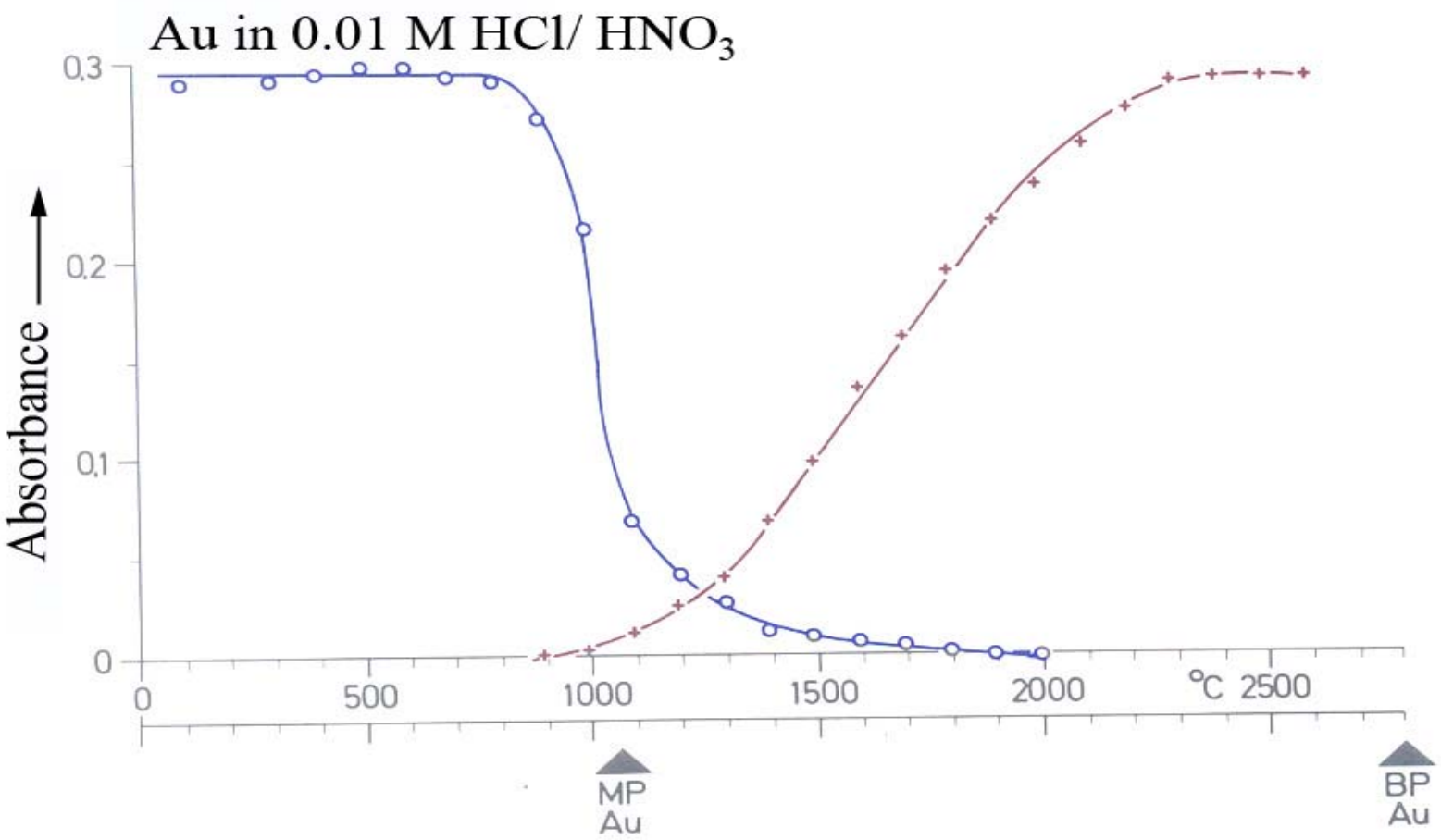
The interference of magnetism chloride on the determination of lead could be easily eliminated by the addition of oxalic acid. Both oxalic acid and finely dispersed carbon reduce lead oxide to metallic lead. The interference can be termed as a vapour phase effect.

The matrix modification technique proposed by Edliger is a major advance in handling complex systems which causes the concomitants to be more volatile and converts the analyte into a less volatile form. Use of ammonium nitrate as a matrix modifier along with nickel salts has been widely prevalent for arsenic, selenium and bismuth. It has been proposed that nickel forms arsenide, selenide and bismuthate which are stable up to 1400^0 C , 1200^0 C and 1200^0 C respectively. Therefore pretreatment temperature may be raised to this level, thus ensuring the removal of all other matrix components. Copper, silver and molybdenum salts have also been tested as matrix modifiers for arsenic and selenium.

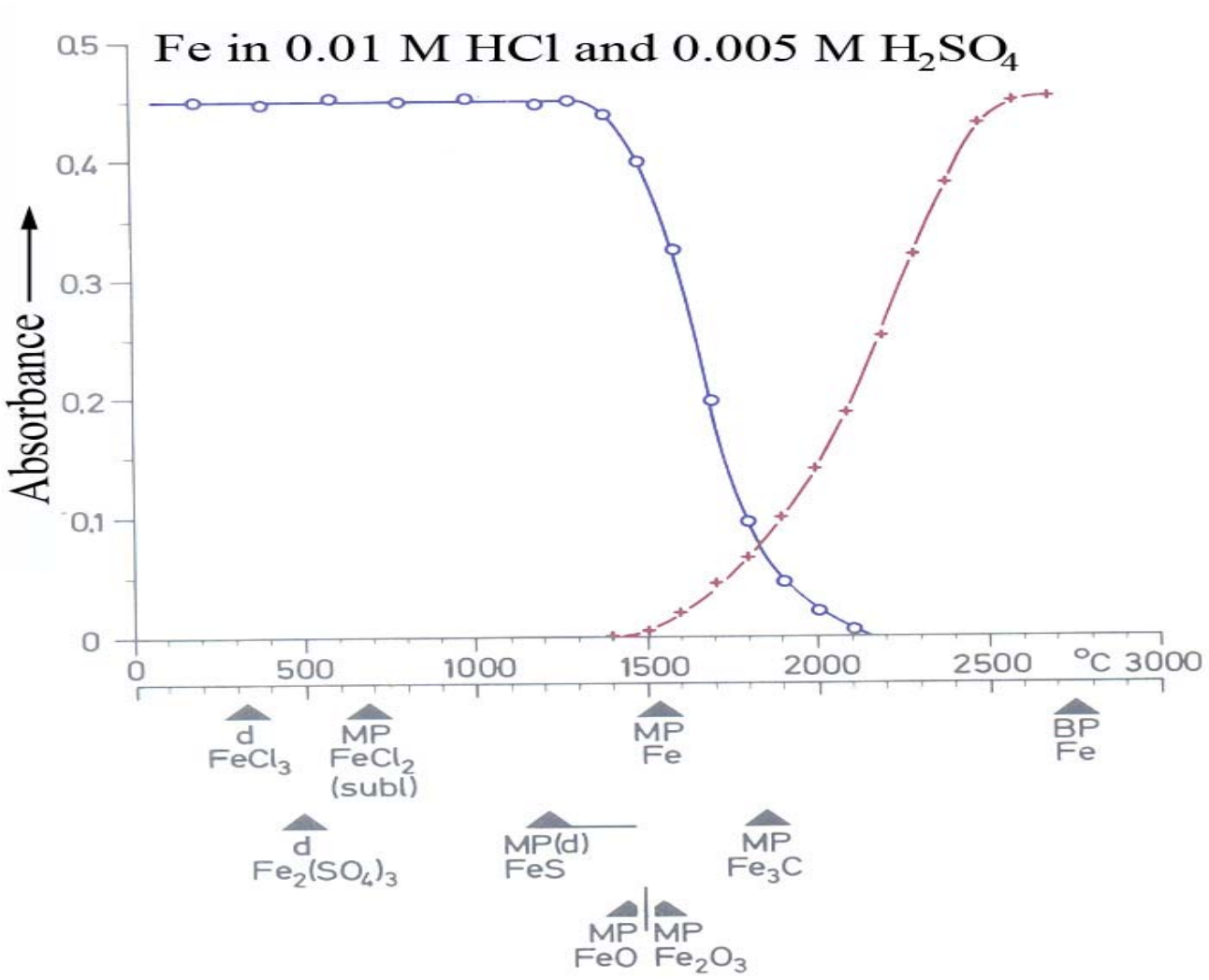
Several other matrix modifiers have been investigated over the years. These include lanthanum (for Pb), phosphoric acid (Cd), calcium nitrate (Mg), potassium dichromate (Hg), magnesium nitrate (Mn, Al , Cr, Co, Ni). Apart from increasing the stabilization temperatures up to 1200-1400^0 C numerous interferences are also eliminated when these modifiers are used.

Welz and Mudakavi showed that a mixture of magnesium nitrate and palladium nitrate could act as a universal matrix modifier. They showed that Pd-Mg matrix modifier could be applied to 21 elements including thallium and mercury with stabilization ranging from 1000-1900^0 C while decreasing the atomization temperatures by 200-300^0 C.

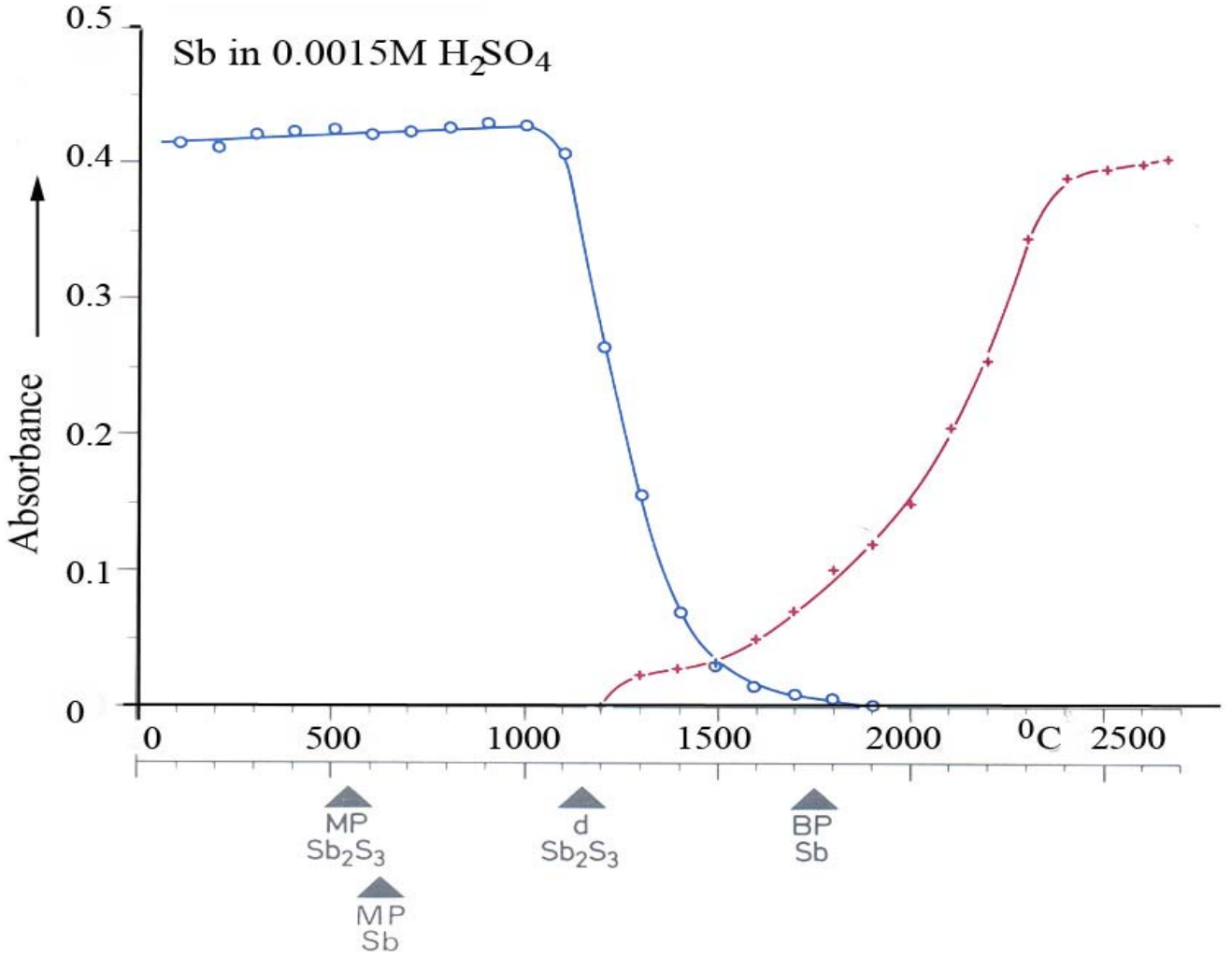
PRETREATMENT AND ATOMIZATION CURVES



PRETREATMENT AND ATOMIZATION CURVES



PRETREATMENT AND ATOMIZATION CURVES



It has been widely accepted that in any aqueous system, water is retained even after 15 minutes at 1200^0 C in vacuum. At higher temperatures the watergas equilibrium is prevalent.

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

Thus in an uncoated tube there is always a relatively high partial pressure of hydrogen. If chloride salts are present (as in the case of lead) then it is most likely that hydrochloric acid is formed and expelled around 600^0 C. But if the sample is present in nitric acid solution, the partial pressure of oxygen could be quite large leading to the formation of lead oxides and hence loss in sensitivity.

Similarly if phosphoric acid and / or phosphates are used as matrix modifiers PO, PO_2 and P_2 will be present at lower temperatures. Only at higher temperatures phosphorous atoms will be present. Thus while calcium phosphate could be detected, phosphoric acid gave no signal! Frech et.al, explained this by the formation of stable calcium oxide formation according to :

$$Ca_3PO_4 \xrightarrow{C_{(s)}} CaO_{(s)} + P_{(g)} + (PO, PO_2, P_2)_g$$

When pyrolytic graphite platform was used phosphorous could be detected easily because water can hardly penetrate the platform.

A number of authors have pointed that oxygen is chemisorbed on graphite to form carbon-oxygen complexes with active sites where arsenic is attached. These intercalation compounds undergo loss of water and oxygen thus reducing the stability of interlamellar arsenic compounds. But such compounds are formed at the defects sites in the crystal lattice which are very difficult to atomize and even if possible the absorbance-atomization curves show a long tailing. Such tailing are actually seen in practice.

Since nitric acid also increases the distance between the graphite layers thereby increasing the active sites the signal should be enhanced which has already been proven. Other oxidants also behave in a similar way.

L‘vov developed a microkinetic theory of sample volatilization for the graphite furnace. According to this theory the sample is distributed in the form of microcrystals, droplets, particles etc., well separated from each other. The sample penetrates into the graphite tube by capillary action which is uniformly distributed in the width of the tube after drying. Upon atomization the sample is physically removed from the tube surface. In contrast with pyrocoated graphite the sample is only distributed in space since it is inactive and possesses a hard inert surface.

This theory gains credence when used graphite tubes are examined by electron microscope after treatment with lead samples which showed the presence of oxide or metal embedded in a film of carbon. A similar treatment off the pyrolytic platform shows only a heap of atoms of the matrix. Slovak and Docekal reported an interesting observation that such a heap can also act as "miniplatform" delaying the atomization and increasing the sensitivity. L'vov and Slavin have repeatedly emphasized that for quantitative volatilization of the sample under isothermal conditions using a platform with zeeman effect background correction, peak area integration with maximum power and zero gas flow condition during atomization provides optimum conditions for minimum interference.

SIGNIFICANCE OF DOUBLE PEAKS

It has been observed that double peaks appear for a number of volatile elements such as zinc and lead. When ascorbic acid or hydrofluoric acid or hydrogen peroxide is added to a lead sample double peaks appear with a shift in time delay. This has been attributed to condensation in cooler parts followed by delayed revolatilization atomization . While this theory does explain peak broadening, it is still not satisfactory for double peaks.

Another plausible theory is that, oxygen chemisorbed onto the active sites of graphite tubes is responsible for double peaks and a shift in the appearance temperature. Metals with volatilization temperatures around 500^0 C and desorption around 950^0 C exhibit this phenomenon. Atomization is preceded by reduction on graphite surface. On the other hand when stable surface oxides are formed. A different atomization mechanism with higher activation energy is prevalent.

Double peaks cause errors in the peak height as well as peak area calculation. Such double peaks can be avoided by matrix modifiers.

VAPOUR PHASE INTERFERENCES

In graphite furnace, just like flame, dissociation and ionization take place according to the law of mass action. However owing to high concentrations of free electrons, ionization is quite slow. Moreover the atmosphere in electrothermal atomization is reducing in contrast to the oxidizing atmosphere in the flame. Thus cyanides and dicarbides are the predominant species for most of the elements.

The presence of sodium sulphate hinders the quantitative atomization of a number of elements. This is also due to the presence of oxygen. Further proof is obtained when oxygen is mixed with the purge gas which also produce smaller number of atoms (hence a smaller signal) and delayed appearance.

Similarly excess nitrate in a sample also leads to the errors when compared with nitrate free reference solutions. Salts easiest to decompose decrease the signal where as others enhance the signal. This is quite important, because even the simplest samples contain nitrates.

Some other significant vapour phase interferences have been tabulated in Table 2. In conclusion it is clear that vapour phase interferences can be reduced or eliminated by the same means used for the elimination of many spectral or volatilization interferences.

These measures include careful pretreatment programming , matrix modification and highest possible pretreatment temperature , followed by peak area integration.

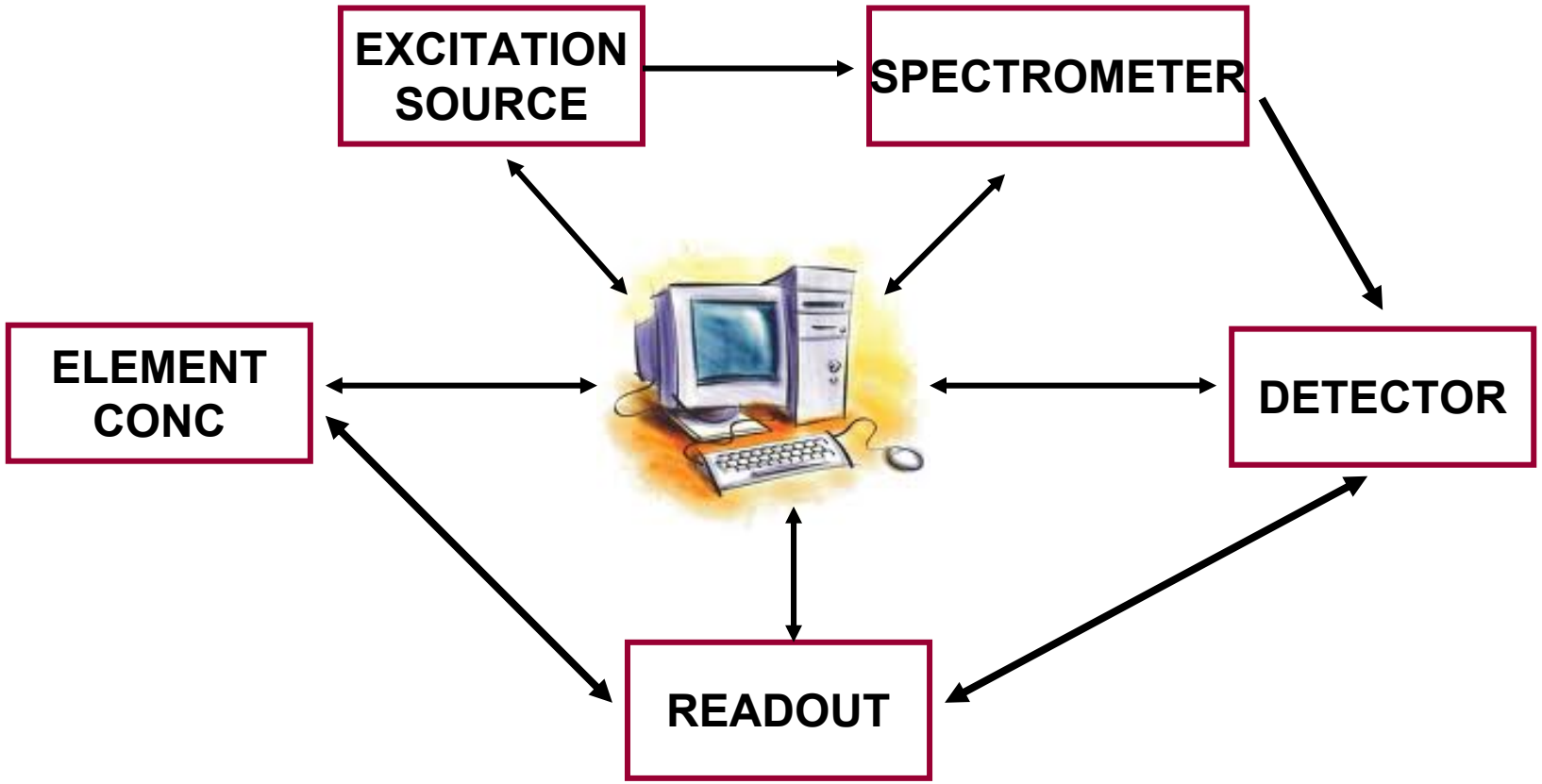
ANALYSIS OF SOLID SAMPLES

According to L'vov's calculations to obtain a relative detection limit of 10^{-6} % it is necessary to introduce solids at the rate of 1g/sec which is almost impossible in the flame.

INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

When an atom is exposed to high temperature source energy is transferred to the atom by collisions with energetic particles and also by the interaction with the electromagnetic radiation. The excited atom decays to a lower energy level with emission of its own characteristic electromagnetic radiation. The measurement of the electromagnetic radiation emitted by the atoms, ions and isotopes can be accomplished by employing suitable optics which also permits concentration determination.

SCHEMATIC DIAGRAM OF ATOMIC EMISSION

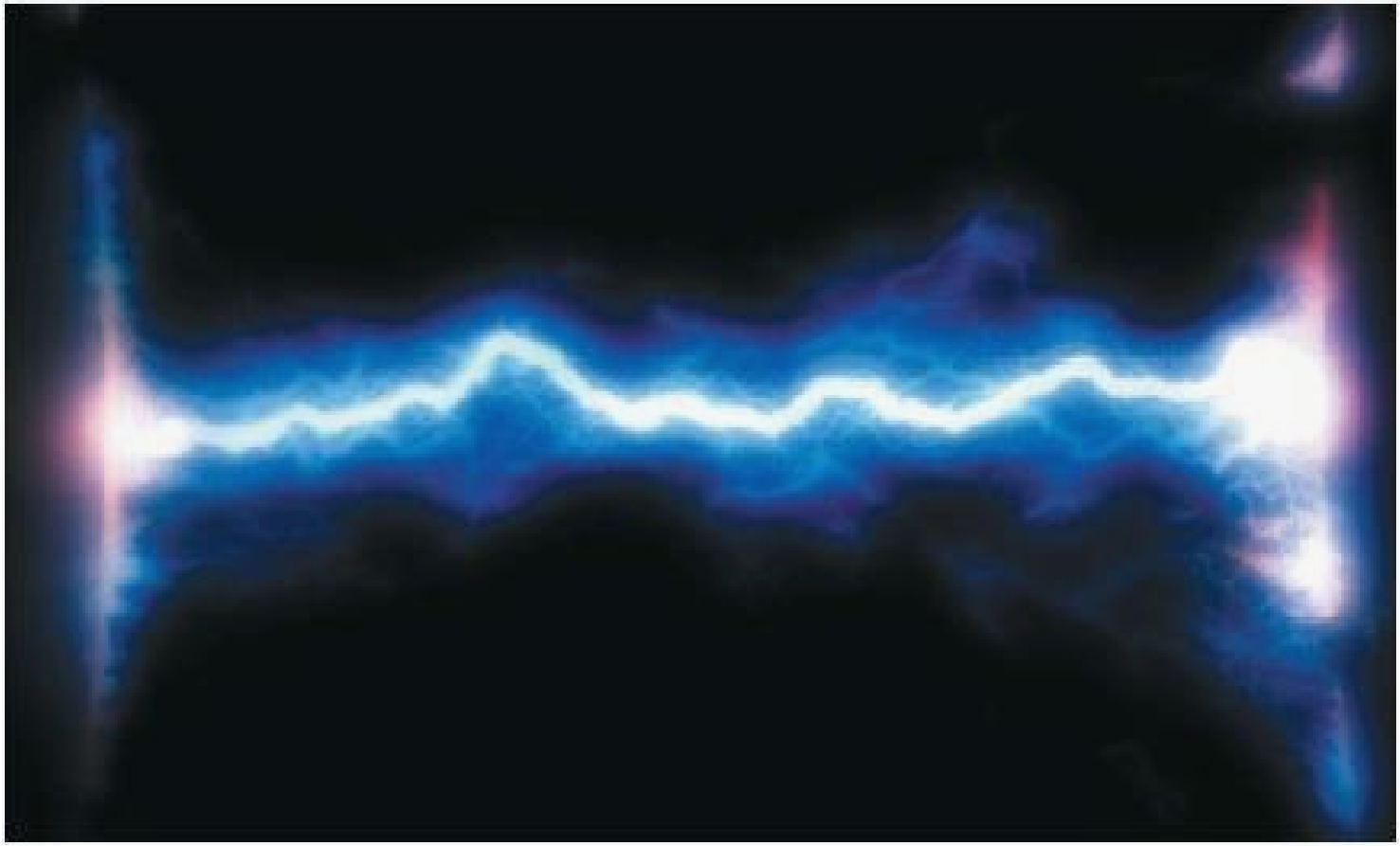


A. GENERATION OF EM RADIATION

ARC Discharge

Sample is mixed with a conducting material such as graphite and packed into the crator of a carbon electrode. A DC arc discharge between the sample electrode and the counter electrode vapourizes the sample, decomposes molecular species produced in the plasma and atomizes the analyte. The atoms are excited to higher energy by the energetic particles in the plasma.

ARC DISCHARGE



The DC arc is generated from a rectified power supply which provides 5-30 A^0 and 10-25 V, generating temperatures from 4000 – 6000^0 k. However the arc tends to wander resulting in poor analytical precision. As the arc temperature is determined by the species in the arc plasma, the composition and temperature changes with time and space. Molecular species such as cynogen etc., exist in the plasma.

Many of these limitations can be minimized or eliminated. The DC arc is more suited for qualitative analysis which finds extensive applications in foundries, steel & metallurgical industries.

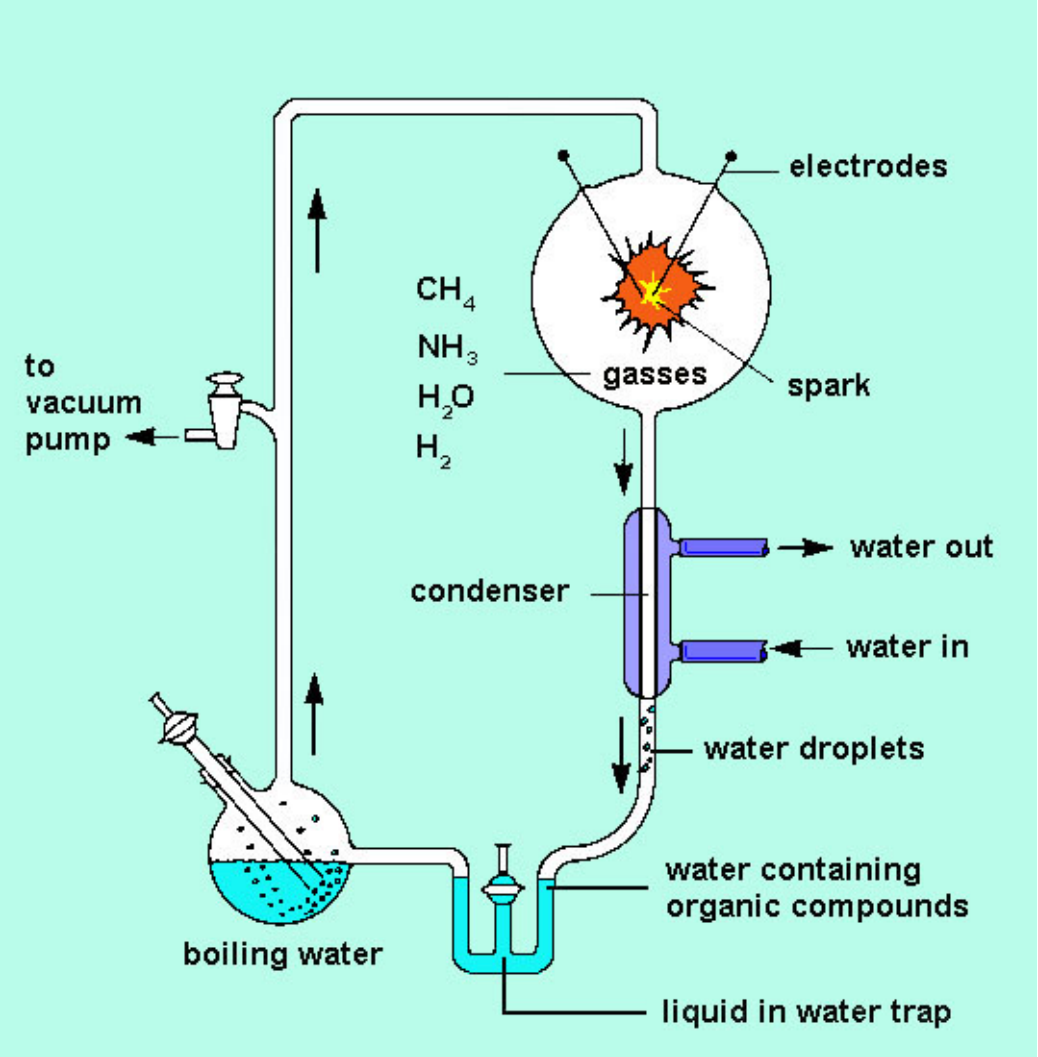
An AC arc provides more uniform sampling of the electrode compared to DC arc. It operates at voltages ranging from 1100 – 4400 V .The polarity of the discharge is reversed at each halfcycle and the discharge is extinguished when the voltage drops to zero. The sampling is random, resulting in improved precision compared to the DC arc. The sensitivity is less that of the corresponding DC arc.

HV SPARK

The circuit consists of HV transformer used to charge an oil filled capacitor and an auxiliary control gap to initiate and control the discharge. A potential of 15000 - 45000 V develops across the analytical gap. An HV spark discharge between the metal sample and counter electrode generates sufficient energy to vapourise the sample and generate atoms and excite them. The emitted radiation is monitored through a quartz window mounted on the excitation stand. A thoriated tungsten electrode is used as a counter electrode and argon is used to purge the gas chamber.

The spark technique is useful for major, minor and trace elements in metals and alloys for analysis and production control. The intensity of the emission is measured relative to iron and plotted against the concentration ratio to eliminate errors resulting from the fluctuations. Typical detection limits are of the order of 0.001 to 0.1% by weight.

SPARK DISCHARGE



GLOW DISCHARGE

It consists of a flat sample cathode and cylindrical anode mounted in a sealed chamber filled with argon.
At 600 – 1800 V , the gas is ionized and accelerated to the cathode. Collisions with the cathode surface causes vapourization of the sample material and excitation. The emitted radiation is viewed from a quartz window.

The cathode block which is in direct contact with the sample is water cooled to remove excess heat. The sample is pressed against the open end of the cathode body and held in vacuum. After evacuation the chamber is filled with argon to 5-15 torr pressure. Standard calibration curves for the determination of trace elements in pure materials are linear over three orders of magnitude in concentration.

LASER INDUCED PLASMA

Pulsed laser beams have been used in AES of extremely small samples and occlusions on surfaces of metal alloys laser beam is focused on sample surface and the material is vapourized. The plasma plume formed above the target passed through an auxiliary electrode gap and is excited by a low voltage spark discharge.

Hollow cathode discharge :

- 0.06-10 ppm for solid samples and from 0.2-1 ppm for solutions.

The electromagnetic radiation is resolved with a spectrograph and the spectra are recorded photographically or measured with an array detector. Solid state Nd glass laser, a spark source, a mirror and focusing lens to direct the laser beam on to the surface of the sample constitute the instrumentation.

A laser pulse with 0.1 – 1.0 J and a duration of 2 µsec produces a crator of 25 – 250 µm. The detection limit is 10^{-9} – 10^{-11} g.

PLASMA SOURCES

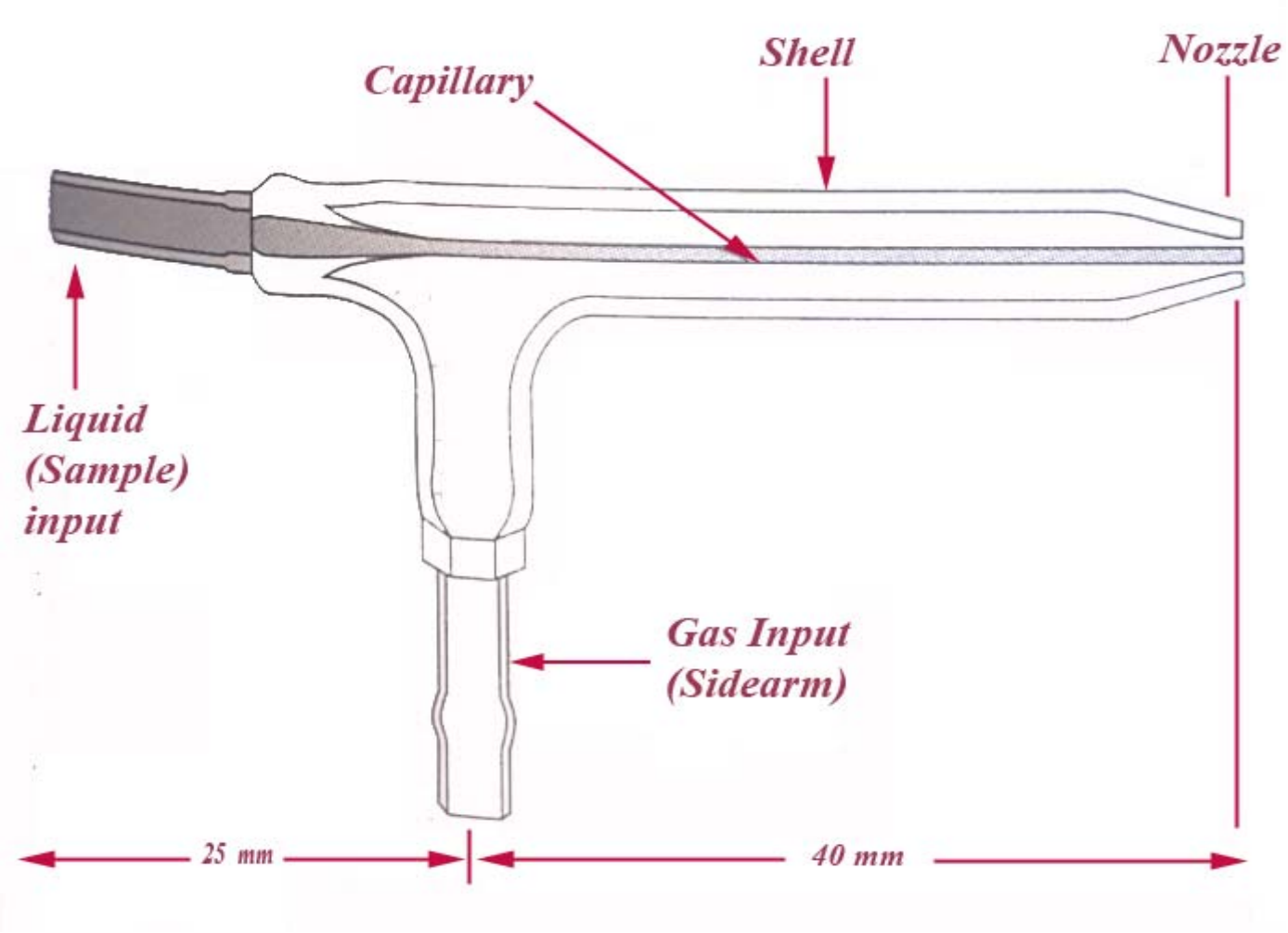
High temperature plasmas generated from electrical power sources where collisions are induced by electrical currents are useful for the analysis of solid, liquid and gaseous samples. They are Direct Current Plasma (DCP), Inductivity Coupled Plasma (ICP) and Microwave Induced Plasma (MCP).

A DC plasma source consists of a DC arc discharge between two electrodes in which argon is introduced. Gas is introduced in a tangential flow so that the resultant gas is constricted, resulting in increased current density and higher temperature. The DC plasma is operated at a current 5 - 30 A^0 and gas flow rates up to 70 litres/minute. Temperatures in the plasma range from 4700-11000 K.

The sample is introduced as an aerosol by means of a neubulizer positioned between the electrodes (anodes). The optical measurement region is located near the base of the confluence to eliminate high background from the arc plasma.

It is useful for analysis of solutions containing 45% of the total dissolved solids. The advantage is that it is a low cost DC power supply. However continuous operation for longer periods is not possible because the electrodes erode. Consequently electrodeless plasma sources such as inductively coupled plasma are common in ICP – AES.

PLASMA TORCH



INDUCTIVELY COUPLED PLASMA

The energy to form the plasma is generated by a high frequency magnetic field. It is analogous to that of a transformer in which primary winding is an induction coil with an oscillatory current from a RF generator. The secondary winding (or load) is the ionized argon gas which is coupled inductively to the radio frequency source. The plasma torch consists of two concentric quartz tubes with Ar gas flowing tangentially between the inner and outer tubes to provide cooling and a water cooled induction coil near the periphery of the outer tube. Argon gas flowing through the smaller tube interacts with the magnetic field when sufficient external energy is applied to ionize the gas. Initial ionization can be provided by a Tesla discharge and the plasma is sustained by ionized argon formed in the high temperature plasma.

The sample is directed into the plasma through a capillary tube mounted in the centre of the torch assembly. An RF generator of 1-5 kw at 3-100 MHz will sustain an argon plasma which produces 5000 – 10000 K depending upon the power, gas flow rate and composition and coupling efficiency. Optimum viewing heights vary with the analyte and which is usually a compromise of 3 -10 mm range in multi-element analysis.

ICP is an extremely versatile source for AES. Sample solutions are nebulized into a chamber and the aerosol is directed into the plasma using a carrier gas. Standard calibration curves for most elements are linear over 5-6 orders of magnitude in concentration and detection limits range from 0.1 to 200 ppb.

MICROWAVE INDUCED PLASMA

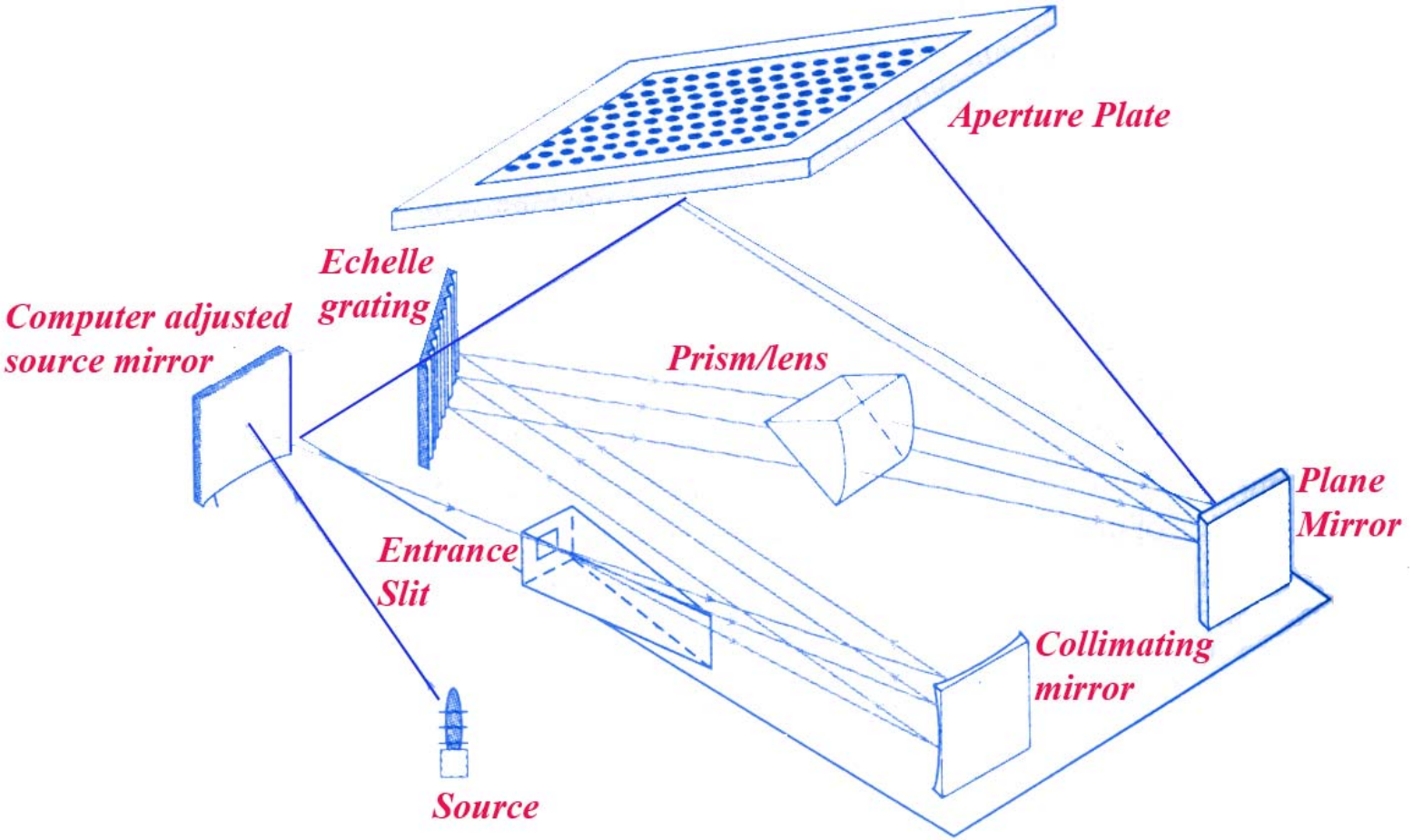
The plasma source consists of a microwave resonator or a cavity inductively coupled to a high frequency generator by means of a coaxial waveguide. It provides 200-500 W of power at a frequency of 2 - 45 GHz. Power is transferred to the microwave cavity by means of a coupling loop.

MIP is used to determine a wide variety of gases such as C, H, N, O, F, Cl, Br, S. Detection limits range from 1 - 50 ppb and calibration curves are linear over 3 - 4 orders of magnitude.

B. SEPARATION OF EM RADIATION

Electromagnetic radiation can be separated into its components by a variety of instruments and techniques. Grating instruments are commonly used. For high resolution spectroscopy the incident radiation can be separated in two dimensions by an Echelle grating and separating multiple orders with a prism. Fourier transform spectroscopy has been developed that extends the wavelength range to ultraviolet region.

ECHELLE GRATING

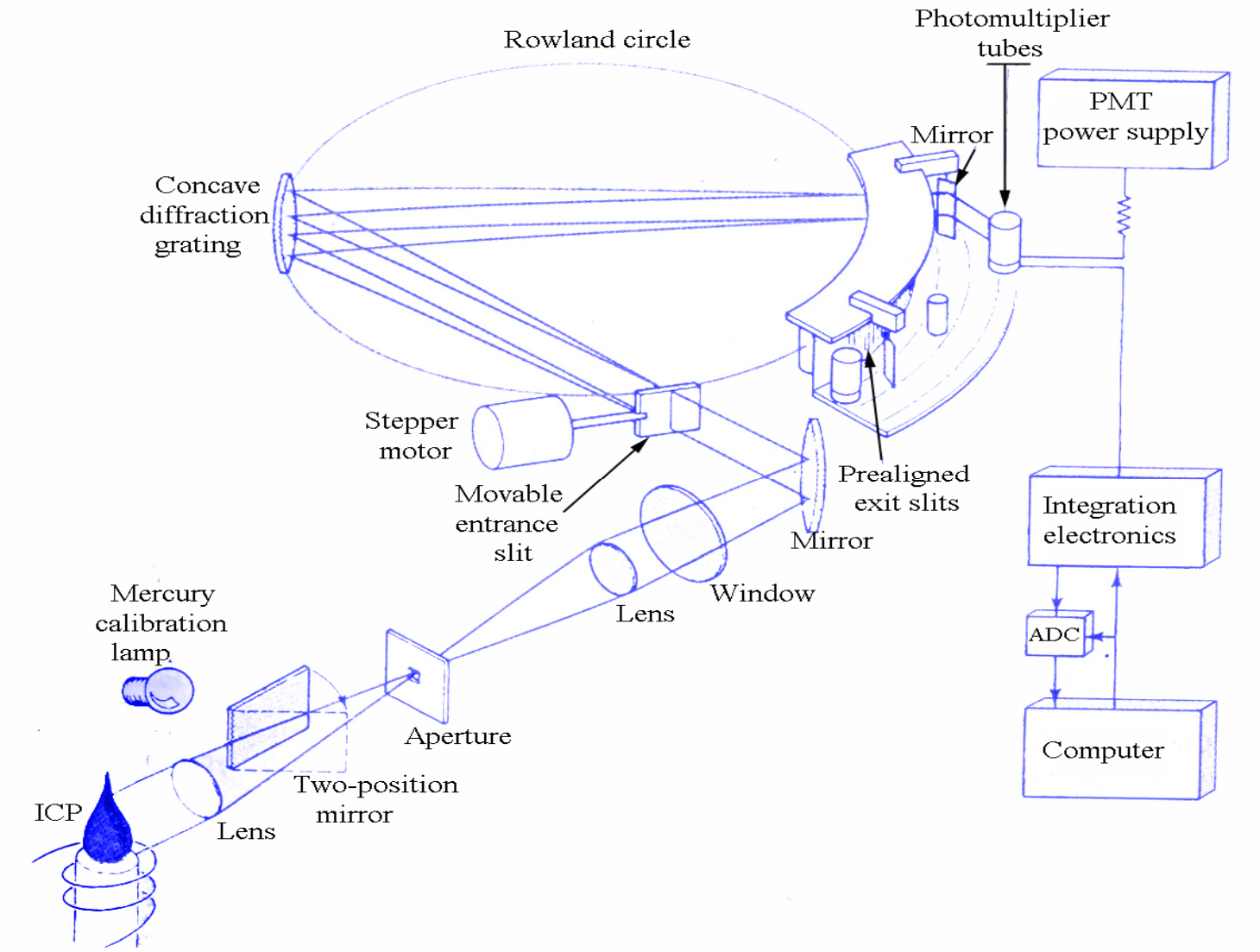


CONCAVE GRATINGS

In Rowland mounting, the grating and the detector are attached to a rigid bar that moves relative to a fixed entrance slit. The angle of diffraction remains constant and the angle of incidence varies. The detector is always kept in a position normal to the grating. Under these conditions, the dispersion is linear over a broad wavelength range.

In Abney mounting, grating and detector are fixed and the slit moves along the axis of the Rowland circle. This is slightly cumbersome because light source and external optics also need to be repositioned when the angle of incidence is changed.

ROWLAND MOUNTING



In Eagle mounting, slit and detector are mounted on the same side of the grating normal to all components on the Rowland circle. This is a compact arrangement.

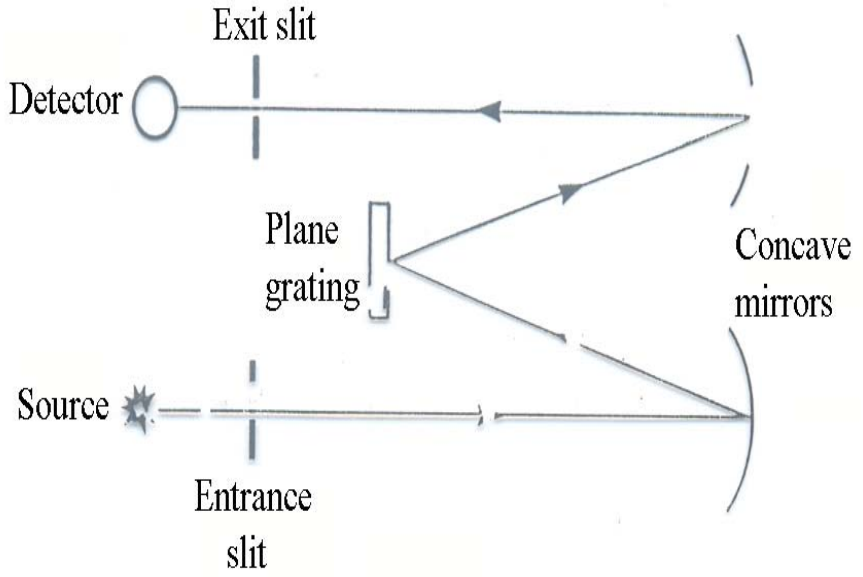
The Paschen – Runge mounting has slit ,grating and detector at fixed positions on the Rowland circle. Most of the commercial direct reading instruments are of this type.

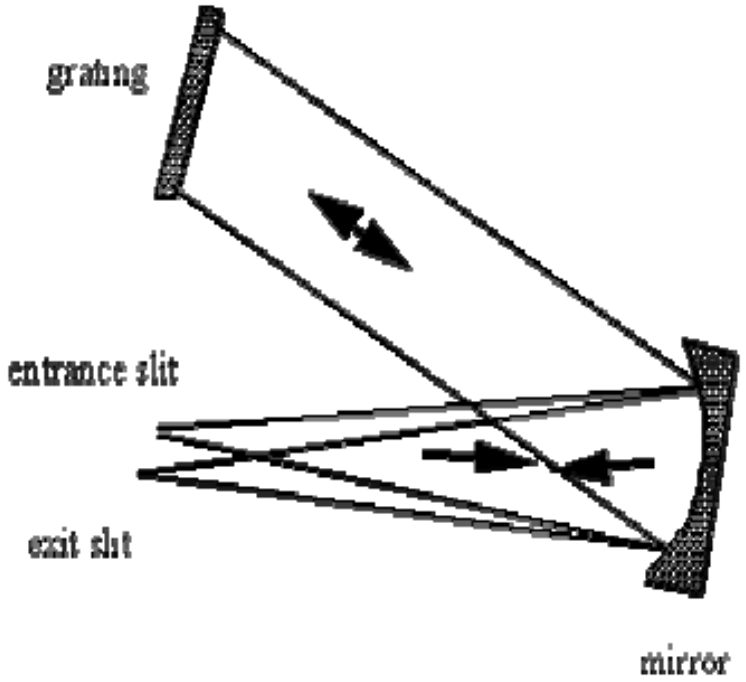
In Wadsworth mounting, a spherical mirror is used to collimate the incident beam which illuminates the grating with a parallel light. When the wavelength region is changed, the detector to grating distance must be changed to maintain proper focus of the diffracted light.

PLANE GRATINGS

The Ebert – Fastie and Czerny turner mountings utilize a plane grating in combination with a spherical mirror to collimate the incident beam and to focus the diffracted light on the exit slit or detector. The incident beam passes over the grating and the diffracted light passes under the grating. Since the detector is near normal to the grating plane, the dispersion is approximately linear.

The Czerny –Turner mounting differs from the Ebert – Fastie in that the spectrometer has two spherical mirrors. These are used in combination with array detectors which have replaced photographic emulsions for the measurement of spectra.





Czerny – Turner mounting

C. DETECTION OF ELECTROMAGNETIC RADIATION

The PMT is the preferred mode of measurement. It consists of a photo cathode, a series of dynodes and an anode in an evacuated tube. The amplification is nearly 1 million. The line image is focused on the slit and directed to PMT by means of a refractor plate.

PHOTOGRAPHIC DETECTOR

This is the most sensitive and versatile technique. A densitometer is used for measuring and identifying elements. It consists of a photoplate or film holder assembly and a light source and associated photo detector to measure the quantity of light passing through a photographic emulsion. The photoplate is moved in a direction normal to the light beam and can be positioned to measure any segment on the photoplate. The image is magnified and displayed on a screen. A reference spectrum with spectral lines of known elements is displayed adjacent to the sample spectrum.

THE ICP SOURCE

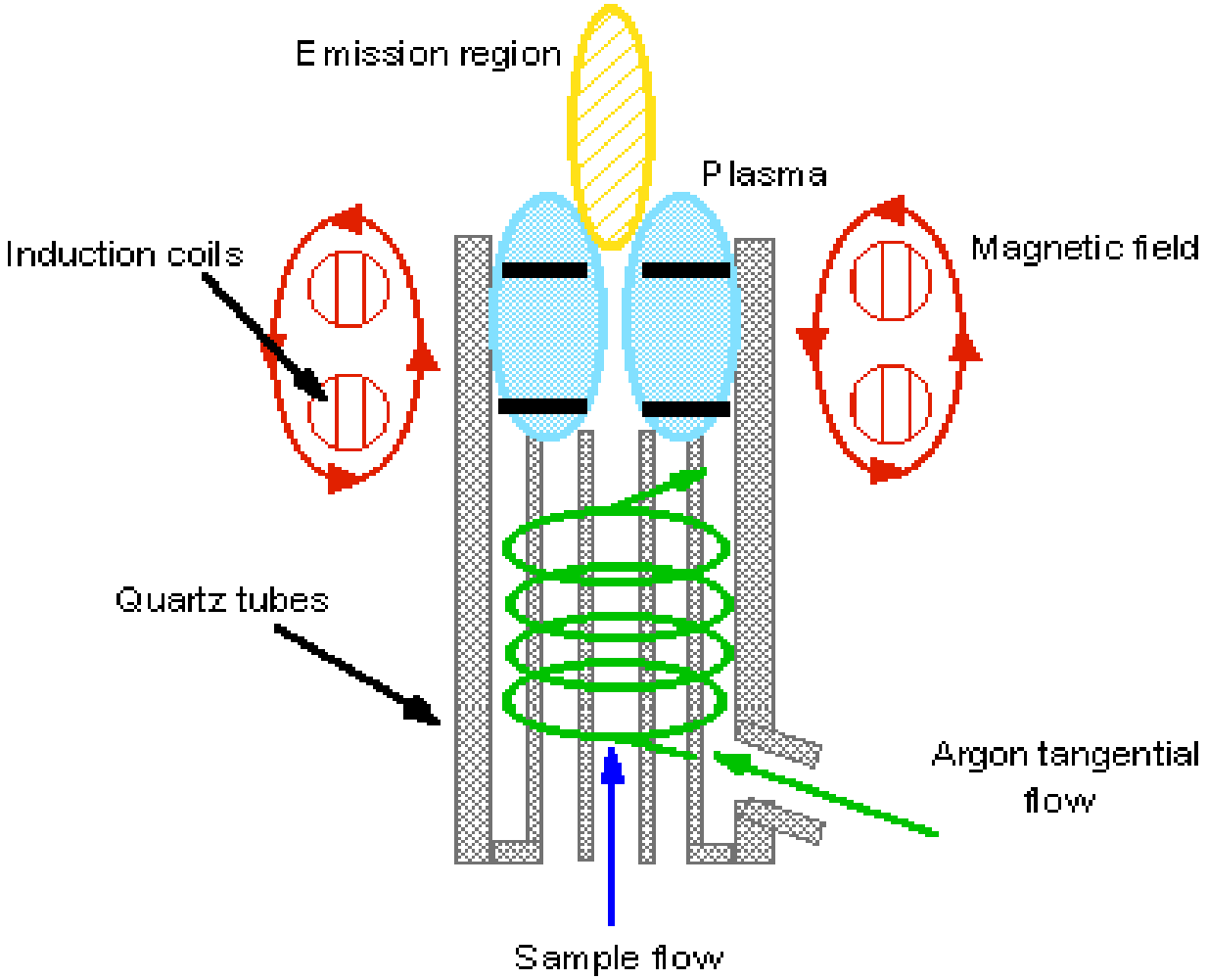
A typical ICP source is called a torch. It consists of three concentric quartz tubes through which streams of argon flow at a total rate of 5-20 L/min. the inner diameter of the tube is about 2.5 cm. The top portion of this tube is an induction coil that is powered by a radio frequency generator which radiates 0.5 – 2 kW of power at 27.12 MHz or 40.68 MHz at this voltage a spark from the Tesla coil ionises the argon.

The resulting ions and their associated electrons interact with the fluctuating magnetic field produced by the induction coil. This interaction causes the ions and electrons within the coil to flow in the closed annular paths. The resistance of the ions and electrons causes ohmic heating of the plasma.

The temperature of the plasma reaches 4000-6000 K, which requires thermal isolation of the outer quartz cylinder. This is achieved by argon flowing tangentially around the walls of the tube and entering the plasma radially.

In most of the instruments the torch is positioned at 90^0 and aligned axially with the spectrometer system. The radiation emitted from the plasma is used for analysis.

TYPICAL DESIGNS OF ICP TORCHES



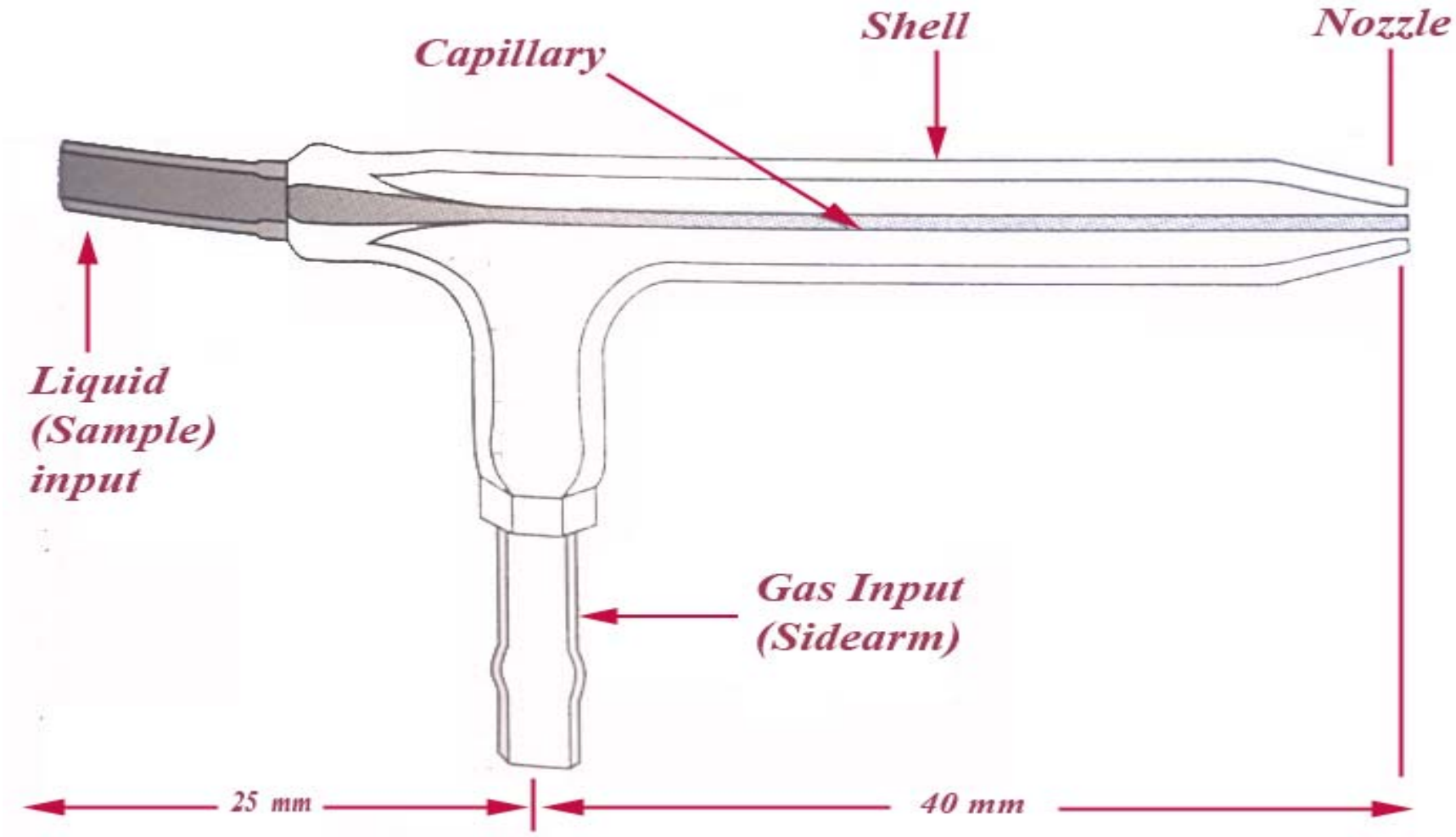
SAMPLE INTRODUCTION

The most common means of sample introduction is through the Bernoulli effect. High velocity moving gas flowing around a capillary sucks the sample and delivers it at the tip where the liquid breaks up into fine droplets before entering the plasma.

Another way of introducing the sample is to pump it through the capillary using a peristaltic pump. At the tip, high velocity argon flows across at right angles causing the same Bernoulli effect.

It is also possible to atomize the sample in a graphite tube and introduce the vapour into the plasma.

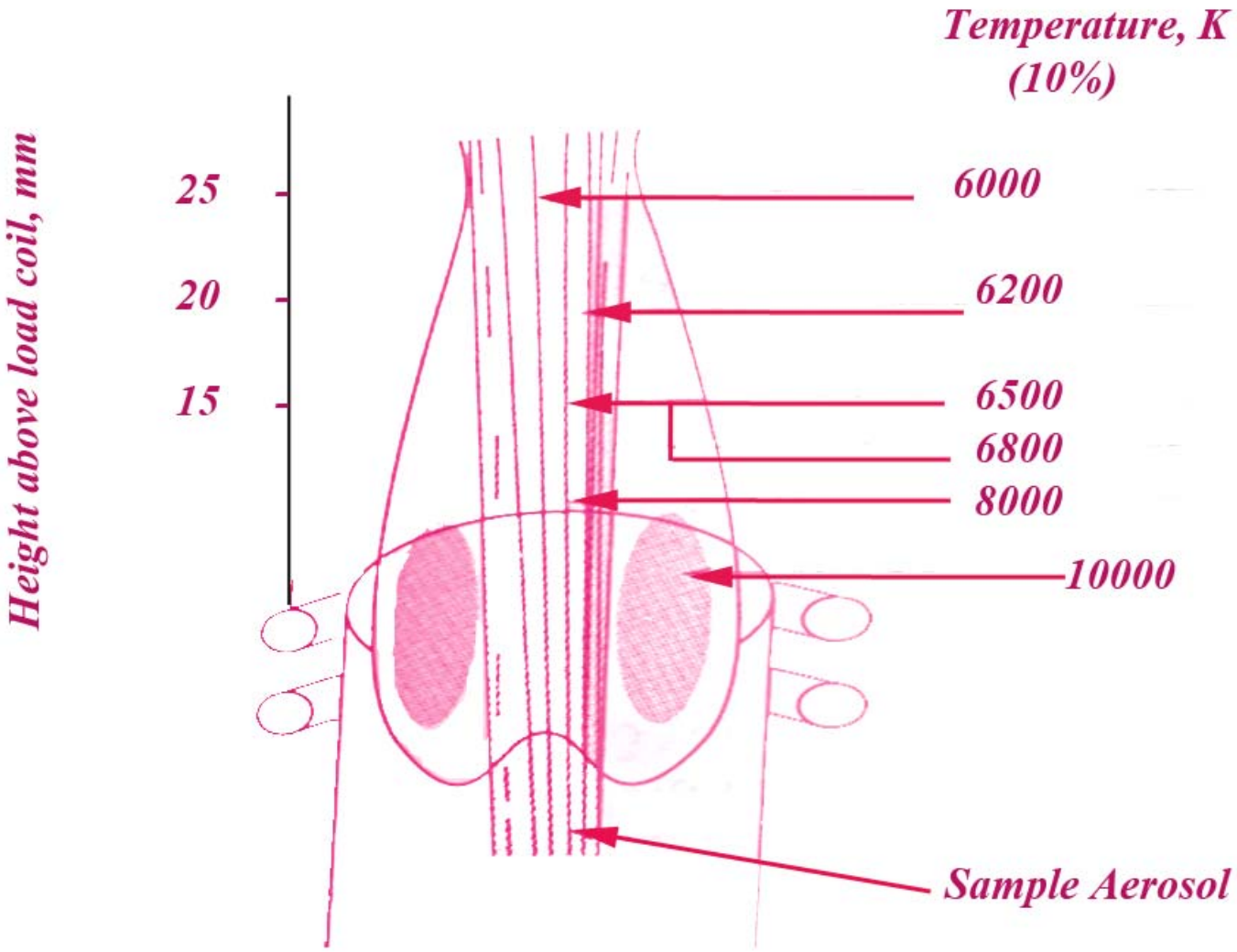
MEIN HARD NEBULIZER



A typical plasma appears as very intense white flame. It has a non-transparent core topped by a flame like tail. The core extends a few millimeters above the tube and produces the atomic spectrum of argon superimposed on a continuum spectrum. The continuum spectrum is typical of charged ions and electrons interaction and known as "bremstrahlung".

10-30 millimeters above the core the continuum fades and the plasma is optically transparent. Hence spectral observations are generally made a 15-20 millimeters above the induction coil where temperature of 6000-6500 K prevail. In this region the background radiation is remarkably free from the argon lines but those of Ca^+, Cd^+, Cr^+, Mn^+ etc., remain.

TEMPERATURE VARIATION IN THE PLASMA



ADVANTAGES OF PLASMA SOURCE

- ✓ High temperatures ensure complete atomization. Hence fewer interferences are found in ICP.
- ✓ Atomization occurs in a chemically inert environment.
- ✓ The temperature cross section is more uniform. Therefore self absorption or self reversal do not occur. Therefore calibration curves are linear over several orders of magnitudes of concentration.
- ✓ Since the plasma produces significant ionization, it is an excellent source for ICPMS.

PLASMA SOURCE SPECTROMETERS

- High resolution 0.01 nm or $\lambda/\Delta\lambda > 100{,}000$.
- Rapid signal acquisition and recovery.
- Low stray light.
- Wide dynamic range ($> 10^6$).
- Accurate and precise wavelength identification and selection.
- Precise intensity readings (< 1% relative standard devn).
- High stability with respect to environmental changes.
- Computerized data handling.

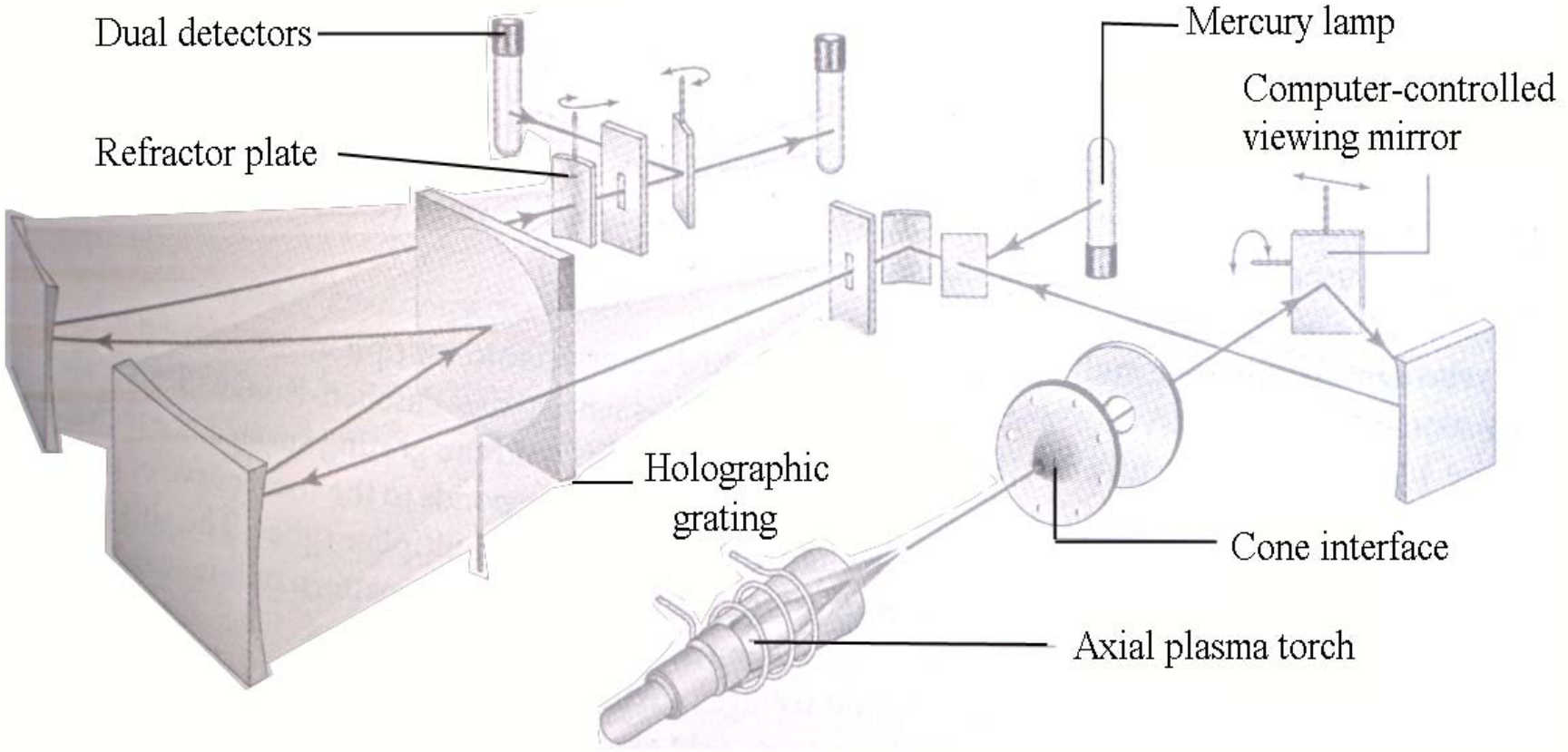
SEQUENTIAL ICP INSTRUMENTS

Such instruments use a holographic grating monochromator of 2400 or 3600 grooves/mm. Scanning is accomplished by rotating the grating with a digitally controlled stepper motor so that precise wavelengths are focused on the exit slit.

In some designs the grating is fixed and the slit and photomultiplier tubes are moved along the focal plane. For ultraviolet and visible range, separate sets of slits and PMTs are used. The switch between the two is effected by the movement of a plane mirror located between the two transducers.

The scanning of spectra is controlled by a computer in a series of small steps of 0.01 to 0.001 nm. Usually whenever there is no emission, the spectra is scanned quickly and slows down near a peak. Such an arrangement is known as slew scan spectrometer.

OPTICAL SCHEMATIC DIAGRAM OF ICP



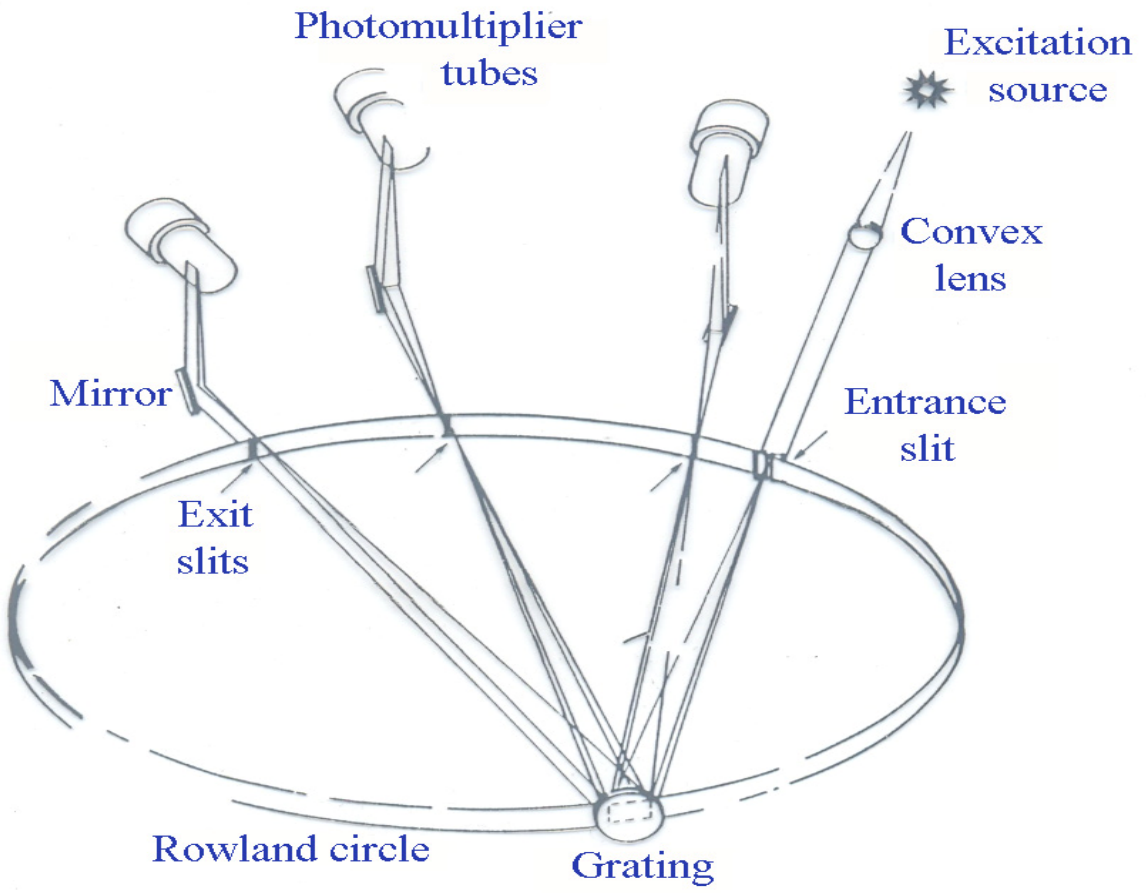
MULTICHANNEL INSTRUMENTS

In multichannel instruments the entrance slit, exit slits and the grating surface are located around the circumference of a Rowland circle which corresponds to the focal curve of the concave grating.

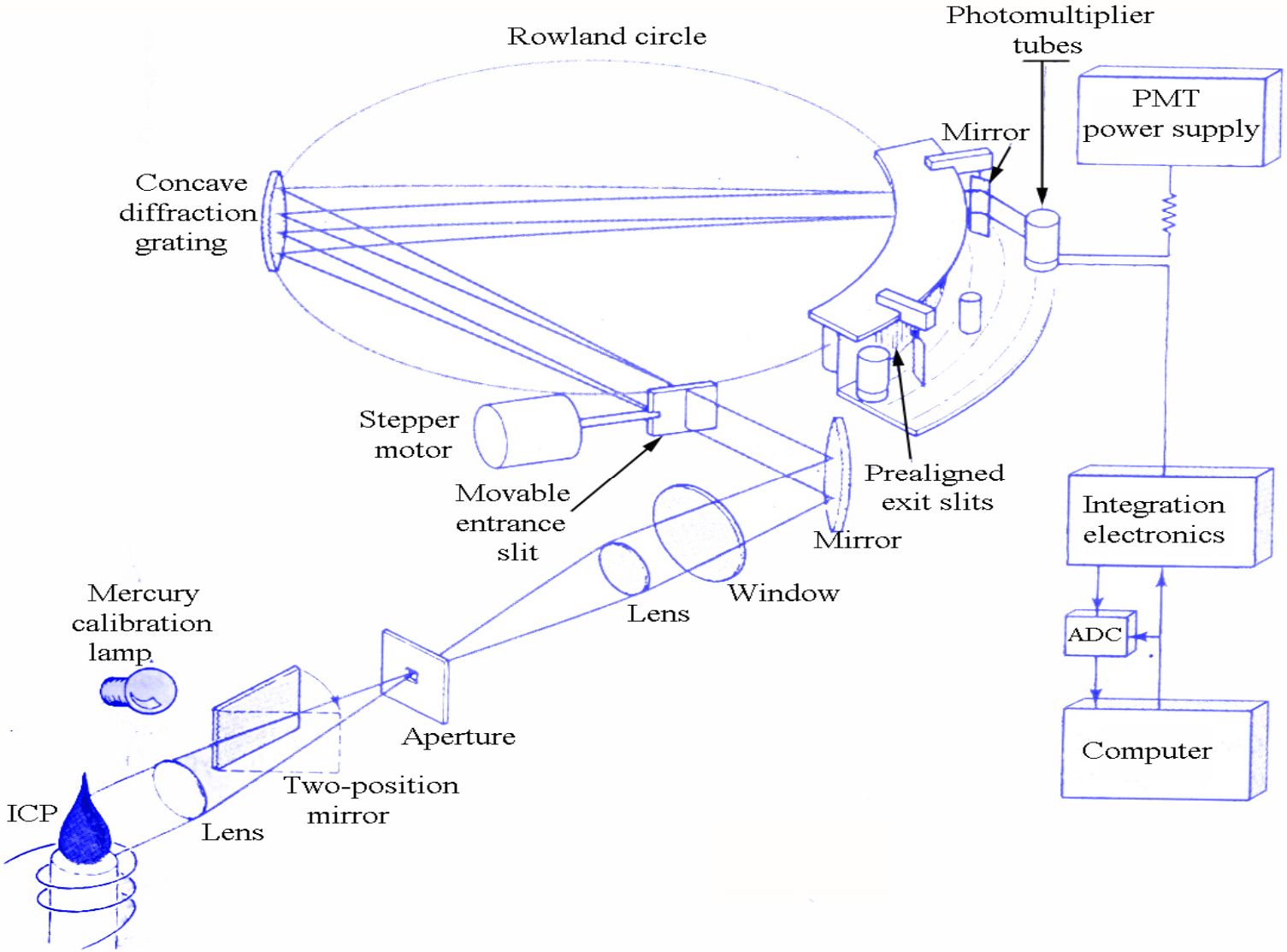
Radiation from each of the fixed slits impinges on the PMTs. The slits are factory configured to transmit lines for selected elements. The signals are integrated , the output is digitized and converted into concentrations.

For rapid analysis such instruments are quite useful.

MULTICHANNEL ARRANGEMENT 1



MULTICHANNEL ARRANGEMENT 2



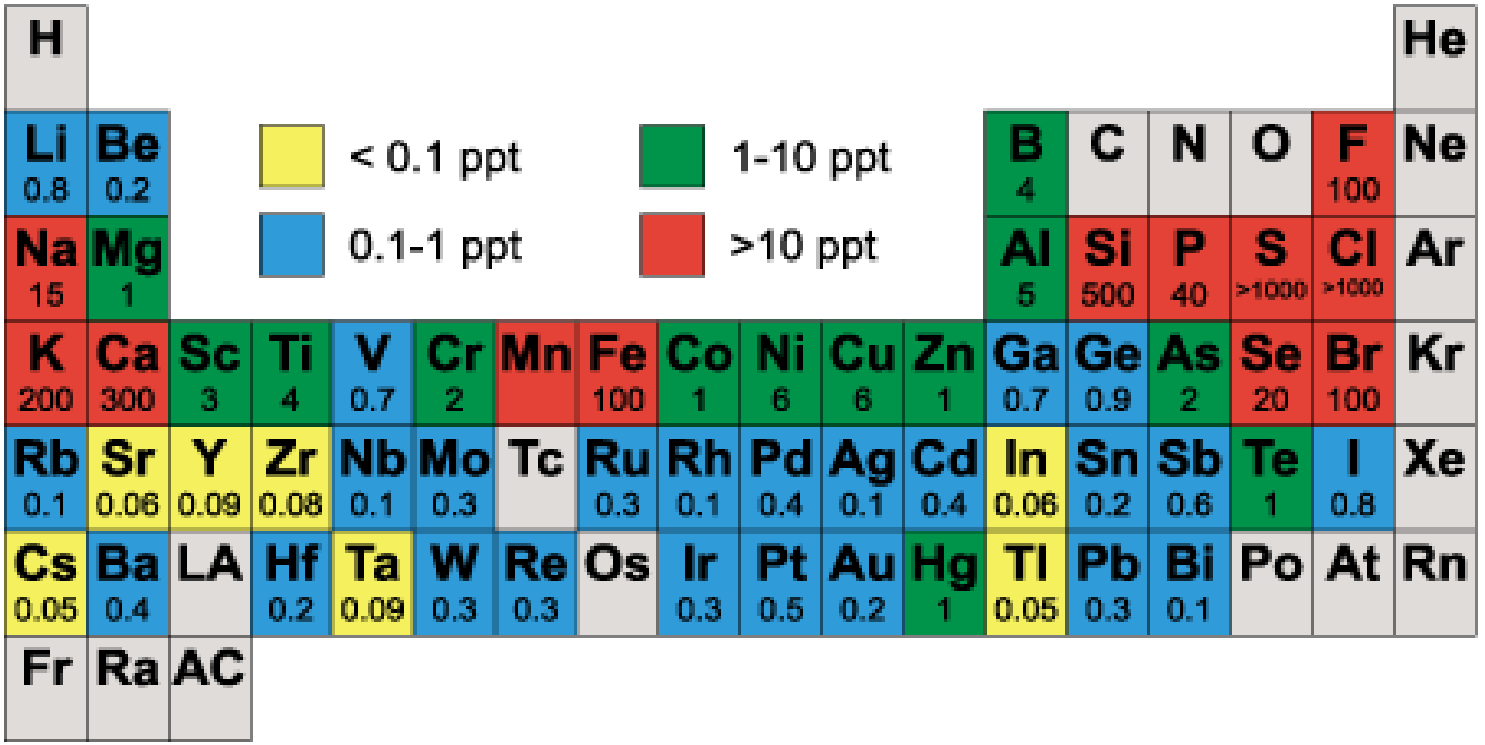
APPLICATIONS OF PLASMA SOURCES

- **Useful for qualitative and quantitative elemental analysis. The samples must be dissolved in aqueous or organic solvents.**

- **In principle all metallic elements can be determined by ICP. For B, N, S and C, vacuum spectrometer is necessary as their emission wavelengths are less than 180 nm.**

- **Li, K, Rb and Cs lines are located at near IR lines which lead to detection problems.**

TYPICAL DETECTION LIMITS IN ICP

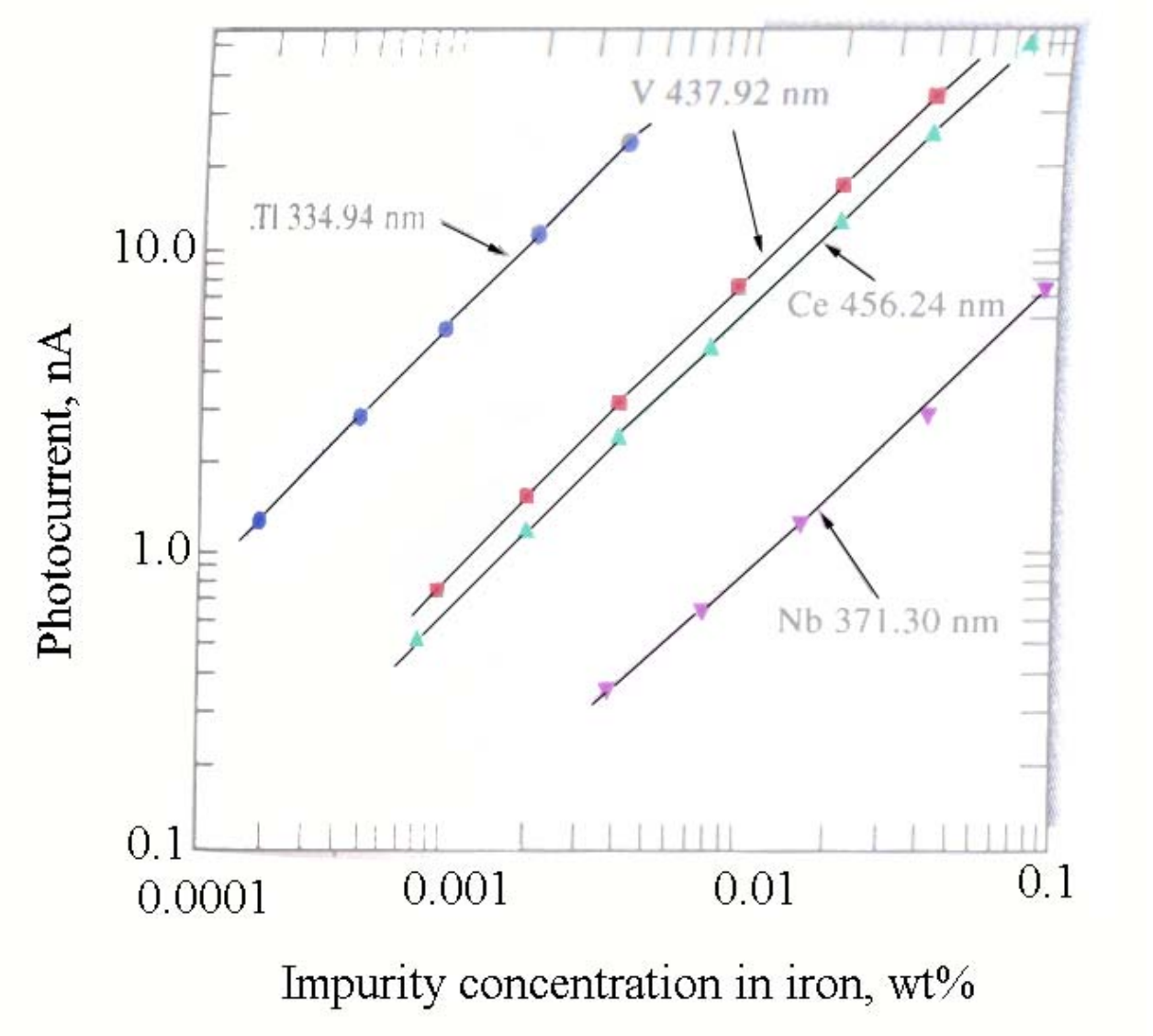


CHEMICAL ANALYSIS WITH ICP

Typical calibration curves in ICP consist of electrical signals in the form of counts (intensity) versus analyte concentration . More than 70 elements have been determined by ICP at various wavelengths and the data is recorded to three decimal places with appropriate intensity. The information is available in several data bases and standard publications. Thus a suitable wavelength for any element can be found easily.

Usually the selection of an analytical line depends upon the intensity. However other concomitant elements present in the matrix should not be emitting at the same wavelength. Calibration plots are usually linear over several orders of magnitudes of concentration. Therefore log-log plots can also be used.

TYPICAL CALIBRATION CURVES IN ICP-AES



Departures from linearity often occur especially when large concentrations are covered.

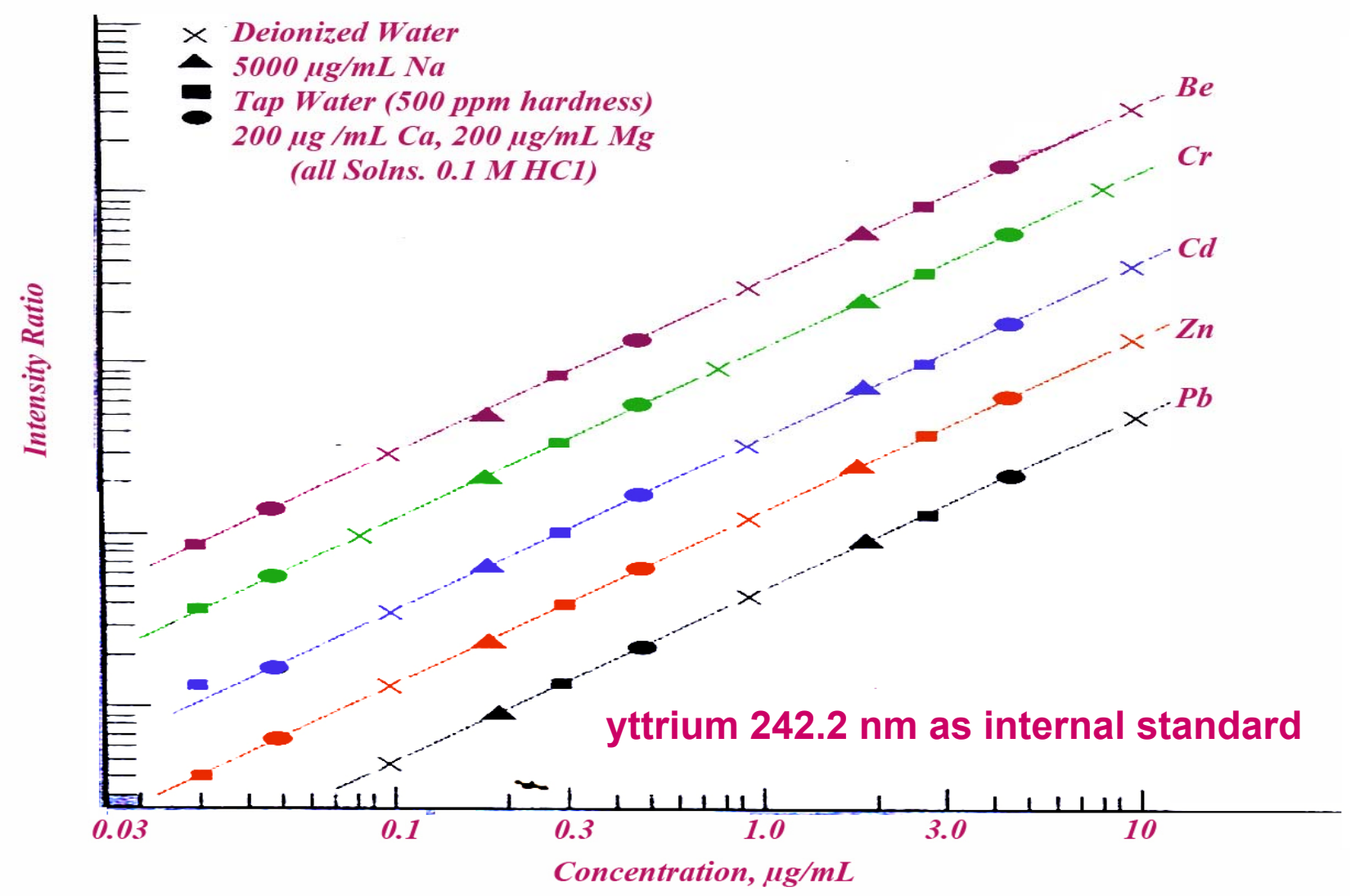
Self absorption becomes evident only at high analyte concentrations and causes the calibration curves to bend towards the horizontal axis.

Nonlinearity also arises from erroneous background correction, from ionization and from nonlinear detector responses.

INTERNAL STANDARD

In ICP work an internal standard is often used. In this case, the vertical axis of the calibration curve is the ratio or the log ratio of the detector signal for the analyte and that of the internal standard. Thus the intensity improves to a considerable extent.

INTERNAL STANDARD CALIBRATION CURVES IN ICP



INTERFERENCES

Chemical and matrix interferences are significantly lower with plasma sources compared to other atomizers. However at low analyte concentrations the background emission due to recombination of argon ions with electrons is significant. For both single channel and double channel instruments, this correction is made by taking an average of the background readings on either side of the emission peak. Nowadays instrument software accomplishes this task automatically or at the discretion of the operator.

Spectral interferences are always possible in ICP analysis because emission spectra of many elements are rich in lines. Therefore it is preferable to have a knowledge of the other matrix elements in the sample and their emission lines to choose a noninterference analytical line.

The software for ICP instruments has powerful routines for wavelength selection, calibration, spectral analysis and deconvolution of overlapping lines. Additionally, integrated data bases of spectral lines of other elements make spotting and correcting for interferences an integral part of the analytical process.

DETECTION LIMITS

In general, detection limits in ICP-AES are comparable to or better than flame AAS and electrothermal AAS. The following table is illustrative.

	Number of Elements Detected at Concentration of				
Method	<1 ppb	1-10 ppb	11-100 ppb	101-500 ppb	>500 ppb
ICP emission	9	32	14	6	0
Flame atomic emission	4	12	19	6	4
Flame atomic fluorescence	4	14	16	4	3
Flame atomic absorption	1	14	25	3	14

DETECTION LIMITS OF ICP

JY 24, 2 SIGM DETECTION LIMITS FOR AQUEOUS SOLUTIONS OF SINGLE ELEMENTS

ELEMENT	DETECTION LIMIT ppb	ELEMENT	DETECTION LIMIT ppb
Ag	1.2	Na	5*
Al	4.7	Nb	5.3
As	[illegible]	Nd	6.7
Au	2.0	Ni	2.7
B	1.1	Os	0.13
Ba	0.7	P	13
Be	0.13	Pb	10
Bi	7.4	Pd	6.0
C	50	Pr	6.0
Ca	0.07	Pt	4.7
Cd	0.6	Re	3.3
Ce	9.3	Rh	17.0
Co	2	Ru	6.7
Cr	1.0	S	20.0
Cu	0.9	Sb	7.4
Dy	1.0	Sc	0.4
Er	0.7	Se	14
Eu	0.33	Si	3.3
Fe	1.0	Sm	6.7
Ga	7.4	Sn	6.7
Gd	2.0	Sr	0.07
Ge	6.0	Ta	5.3
Hf	3.3	Tb	5.3
Hg	4.7	Te	6.0
Ho	1.3	Th	5.4
I	–	Ti	0.4
In	17	Tl	12.0
Ir	6.0	Tm	1.3
K	20.0*	U	17
La	1.5	V	0.8
Li	0.8*	W	5.3
Lu	0.35	Y	0.5
Mg	0.07	Yb	0.3
Mn	0.20	Zn	0.5
Mo	1.3	Zr	2.5

Table 1. DETECTION LIMITS FOR AIR-ACETYLENE FLAME

Element	Symbol	Wavelength (nm)	Type	LOD-AES (ppb)	LOD-AAS (ppb)
Aluminum	Al	308.2153	I		700
		309.2710	I		500
		396.1520	I	NA	600
Antimony	Sb	206.833	I	NA	50
		217.581	I	NA	40
		231.147	I	5000	40
		259.805	I	NA	
Arsenic	As	193.759	I	10,000	140
Barium	Ba	455.403	II	NA	
		553.548	I	NA	
Bismuth	Bi	223.061	I	3000	25
Boron	B	249.677	I	NA	
Cadmium	Cd	228.8022	I	500	1
		326.1055	I	NA	NA
Calcium	Ca	393.366	II		5000
		396.847	II		5000
		422.673	I	0.5	0.5

Table 1 …

Cesium	Cs	455.5276	I	NA	
		852.1122	I	NA	8
Chromium	Cr	357.869	I	NA	3
		425.435	I	NA	200
Cobalt	Co	240.725	I		4
		352.685	I	NA	125
Copper	Cu	324.754	I	NA	1
		327.396	I	NA	120
Gallium	Ga	287.424	I		50
		294.364	I	NA	50
		417.204	I	NA	1500
Germanium	Ge	265.1172	I	7000	
Gold	Au	242.795	I	NA	6
		267.595	I	NA	90
Indium	In	303.936	I	NA	30
		325.609	I	NA	20
		451.131	I	NA	200
Iodine	I	183.038	I		8000
		206.163	I	2,500,000	

(continued)

Table 1 …

Element	Symbol	Wavelength (nm)	Type	LOD-AES (ppb)	LOD-AAS (ppb)
Iridium	Ir	208.882	I		600
		263.971	I		2500
Iron	Fe	248.3271	I		5
		371.9935	I	NA	700
Lead	Pb	217.000	I		9
		283.3053	I	NA	240
		368.3462	I	NA	
Lithium	Li	670.776	I	NA	0.3
		451.857	I		NA
Magnesium	Mg	279.553	II		NA
		280.270	II		NA
		285.213	I	NA	NA
Manganese	Mn	279.482	I	NA	2
		403.076	I	NA	600
Mercury	Hg	253.652	I	NA	140

Table 1 …

Molybdenum	Mo	313.259	I		20
		379.825	I	80,000	900
		390.296	I	100	1600
Nickel	Ni	232.003	I		2
		352.454	I	NA	350
Niobium	Nb	309.418	II		NA
Osmium	Os	290.906	I	NA	1200
Palladium	Pd	244.791	I		20
		247.642	I		20
		340.458	I	NA	660
		363.470	I	NA	300
Phosphorus	P	213.547	I		30,000
Platinum	Pt	214.423	I		350
		265.945	I	NA	50
Potassium	K	766.490	I	NA	1
Rhenium	Re	346.046	I		800
Rhodium	Rh	343.489	I	NA	2
		369.236	I	NA	70
Rubidium	Rb	420.180	I	NA	
		780.027	I	NA	0.3

Table 1 …

Element	Symbol	Wavelength (nm)	Type	LOD-AES (ppb)	LOD-AAS (ppb)
Selenium	Se	196.09	I	NA	50
		203.98	I	50,000	10,000
Silver	Ag	328.068	I	NA	1
		338.2068	I	NA	70
Sodium	Na	330.237	I		NA
		588.9950	I	NA	1
		589.5924	I	NA	0.2
Strontium	Sr	407.771	II	NA	400
		421.552	II		NA
		460.733	I	NA	2
Sulfur	S	180.7311	I		30,000
Tellurium	Te	214.281	I	500	30
		238.578	I		NA

Table 1…

Thallium	Tl	276.787	I	NA	30
		377.572	I	NA	1,200
		535.046	I	NA	12,000
Tin	Sn	224.605	I		10
		235.484	I	2,000	600
		283.999	I	NA	1,000
		326.234	I	NA	
Tungsten	W	255.135	I		3,000
		400.875	I	90,000	
Uranium	U	591.539	I	NA	
Vanadium	V	318.540	I	NA	
		437.924	I	300	
Ytterbium	Yb	398.799	I		80
Zinc	Zn	213.856	I	7,000	1
Zirconium	Zr	351.960	I		NA

[a]NA means that FAES or FAAS was observed but no detection limit was reported; a blank space indicates that no observation was made.
Source: From Refs. 16 and 17.

Table 2. DETECTION LIMITS FOR NITROUS OXIDE ACETYLENE FLAME

Element	Symbol	Wavelength (nm)	Type	LOD-AES (ppb)	LOD-AAS (ppb)
Aluminum	Al	308.2153	I	NA	
		309.2710	I	NA	20
		396.1520	I	3	900
Barium	Ba	553.548	I	1	8
Beryllium	Be	234.861	I	100	1
Boron	B	208.891	I		NA
		208.957	I		24,000
		249.677	I		700
		249.773	I		1,500
Cadmium	Cd	326.1055	I	800	
Calcium	Ca	422.673	I	0.1	1
Cesium	Cs	455.5276	I	600	
		851.1122	I	0.02	
Chromium	Cr	425.435	I	1	

Table 2 …

Cobalt	Co	352.685	I	200	
Copper	Cu	324.754	I	30	
		327.396	I	3	
Dysprosium	Dy	353.170	II		800
		404.597	I	20	500
		421.172	I		50
Erbium	Er	337.271	II		100
		400.796	I	20	40
Europium	Eu	459.403	I	0.2	30
Gadolinium	Gd	368.413	I		2000
		440.186	I	1000	
Gallium	Ga	417.204	I	5	
Germanium	Ge	265.1172	I	400	50
Gold	Au	267.595	I	500	
Hafnium	Hf	307.288	I		2000
Holmium	Ho	345.600	II		3000
		405.393	I	10	400
		410.384	I		40

Table 2 …

Element	Symbol	Wavelength (nm)	Type	LOD-AES (ppb)	LOD-AAS (ppb)
Iron	Fe	371.9935	I	10	
Lanthanum	La	408.672	II		7500
		550.134	I	4000	2000
Lead	Pb	368.3462	I	0.2	
Lithium	Li	670.776	I	0.001	
Lutetium	Lu	261.542	II		3000
		451.857	I	400	
Magnesium	Mg	285.213	I	1	
Manganese	Mn	403.076	I	1	
Mercury	Hg	253.652	I	10,000	
Molybdenum	Mo	313.259	I	10	25
		379.825	I	300	
		390.296	I	10	
Neodymium	Nd	463.424	I		600
		492.453	I	200	700

Table 2 …

Nickel	Ni	352.454	I	20	
Niobium	Nb	334.906	I		1000
		405.894	I	60	5000
Osmium	Os	290.906	I		80
		442.047	I	2000	NA
Palladium	Pd	363.470	I	40	
Phosphorus	P	177.499	I		30,000
		213.547	I		29,000
Platinum	Pt	265.945	I	2000	2000
Potassium	K	766.490	I	0.01	
Praseodymium	Pr	495.137	I	500	2000
Rhenium	Re	346.046	I	200	200
Rhodium	Rh	343.489	I		700
		369.236	I	10	1400
Rubidium	Rb	780.027	I	8	
Ruthenium	Ru	372.803	I	300	
Samarium	Sm	429.674	I		500
		476.027	I	50	14,000

(continued)

Table 2 …

Element	Symbol	Wavelength (nm)	Type	LOD-AES (ppb)	LOD-AAS (ppb)
Scandium	Sc	391.181	I	10	20
Selenium	Se	196.09	I	100,000	
Silicon	Si	251.6113	I	3,000	20
		288.1579	I		NA
Silver	Ag	328.068	I	2	
Sodium	Na	588.9950	I	0.01	
		589.5924	I	0.01	
Strontium	Sr	460.733	I	0.1	50
Tantalum	Ta	271.467	I		800
		474.016	I	4,000	
Terbium	Tb	432.643	I	NA	600
Thallium	Tl	377.572	I	50	
		535.046	I	2	
Thorium	Th	324.4448	I		181,000
		491.9816	II	10,000	
Thulium	Tm	371.791	I	4	10
Tin	Sn	224.605	I		3,000
		235.484	I		90
		283.999	I	100	

Table 2 …

Titanium	Ti	334.941	II		NA
		364.268	I	NA	10
		365.350	I	30	500
Tungsten	W	255.135	I		500
		400.875	I	200	7,500
Uranium	U	358.488	I		7,000
Vanadium	V	318.540	I	200	20
		437.924	I	7	100
Ytterbium	Yb	398.799	I	0.2	5
Yttrium	Y	410.238	I		50
Zinc	Zn	213.856	I	10,000	
Zirconium	Zr	351.960	I	1,200	
		360.119	I	3,000	1,000

[a]NA means that FAES or FAAS was observed but that no detection limit was reported; a blank space indicates that no observation was made.
Source: From Refs. 16 and 17.