

Atomic spectroscopy

Atomic spectroscopy may be divided into two classes optical atomic spectroscopy and atomic mass spectroscopy.

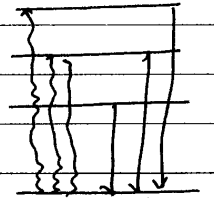
Optical atomic spectroscopy is subdivided into three classes (a) Atomic absorption spectroscopy (b) atomic fluorescence spectroscopy and (c) Atomic emission spectroscopy

(a) Atomic absorption spectroscopy:- an external source of energy radiation impinges on the analyte vapour and if the external source of radiation is of appropriate frequency, it can be absorbed by the analyte vapour of atoms and promote them to excited states. For example sodium vapour absorbs radiation of 285, 330 and 590 nm to excite 3s electron to 5P, 4P and 3P respectively.

(b) Emission spectroscopy:- analyte atoms are excited by external source of energy in the form of heat or electrical energy. For example, atomic sodium exhibits three emission spectral lines of wavelength 285, 330 & 590 nm. The partial energy level diagram of sodium shows that thermal or electrical energy promote 3s electrons to 3P, 4P & 5P

orbitals and after a few nano seconds, the excited atoms relax to ground state, giving up their energy as photons of visible and UV radiation of wavelength 590, 330 & 285 nm.

A transition to or from the ground state called a resonance transition, and the resulting spectral line is called resonance line.



Fluorescence Spectroscopy

In atomic fluorescence spectroscopy, an external source is used just as in atomic absorption and emitted radiation from the excited atom is measured at the right angle of incident radiation. Atomic fluorescence is often measured at the same wave length as the source wavelength.

Width of spectral lines:- Atomic spectral lines have finite widths and the factors that contribute to atomic spectral line widths ~~are~~ includes:-

a) Natural broadening:- The natural line width of an atomic spectral line is determined by the life time of the excited

state and Heisenberg's uncertainty principle
The shorter the life time the wider the spectral lines and vice versa.

The one form of uncertainty principle may be written as $\Delta E \cdot \Delta t = h$

where Δt may be considered as life time of an excited atom. Thus shorter lifetime results broader lines. Generally typical radiative life times of atoms are on the order of 10^{-8} s, which leads to natural line widths on the order of 10^{-5} nm

Collisional broadening:— Collisions between atoms and molecules in the gas phase causes deactivation of excited state and thus broadening of the spectral line. The extent of broadening increases with increasing concentration i.e. pressure i.e. pressure of the collision partners. As a result collisional broadening also called pressure broadening collisional broadening also increases with increasing temperature. Collisional broadening highly dependent on the gaseous medium and collisional broadening greatly exceeds the natural broadening of the spectral line. For Na atoms, in flame, such broadening can be as great large as 10^{-3} nm.

Doppler broadening— Doppler broadening results from the rapid motion of atoms as they emit or absorb radiation. Atoms moving toward the detector wavelengths that are slightly shorter than the wave length emitted by the atoms moving right angles of the detector.

The effect is reversed for the atoms moving away from the detector. The net effect is an increase in the width of emission line

For the same reason, Doppler effect causes the broadening of absorption lines.

Doppler broadening increases with increasing temp, as because increase of temperature increases the velocity of atoms. Doppler broadening can be a major contributor to overall line widths. For Na, in flames, the Δ Doppler broadening of lines is in the order of 4×10^{-3} - 5×10^{-3} nm

Advantages of atomic spectroscopy:—

- i) Atomic spectroscopy could be used both for qualitative and quantitative determination of more than 70 elements
- ii) This method can detect minute quantity of sample and detection limit is parts-per-million to parts-per-billion. In some cases it can detect even lesser concentration
- iii) The method is very rapid, convenient and usually of high selectivity.
- iv) Spectroscopic determination of atomic species can only be performed on a gaseous medium, so they are well separated from one another and interaction among them is negligible
- v) Atomisation is a crucial step and has large influence on sensitivity, precision and accuracy of the method

Effect of flame temperature:— Both absorption & emission spectra are affected by flame temperature in a complex way.

- i) Higher temperature increases the total atom population and thus sensitivity. But in many cases, increase of atom population is more than off-set by the loss of atoms by ionisation.
- ii) Flame temperature also determines the relative population of excited and unexcited atoms. For example, in air-acetylene flame, excited and unexcited population ratio is 10^{-8} to 10^{-8} and that for oxygen-acetylene flame is 10^{-6} . Number of unexcited atoms in a typical flame exceeds the number of excited atoms by a factor of 10^3 to 10^{10} or some cases even more. Thus, absorption method shows lower detection limits than emission method.

The relationship between the ground state and excited state population may be obtained from Boltzmann distribution law:—

$$\frac{N_i}{N_0} = \frac{g_i}{g_0} e^{-\Delta E/kT}$$

Thus the ratio depends on ΔE and Temperature. g_1/g_0 is ratio of statistical weights for ground state and excited state.

Advantages of absorption spectroscopy over emission:-

i) Absorption spectra of most elements are simple in nature as compared to atomic emission spectra.

Emission spectra is complex because emission spectra may occur many different ways like $E_3 - E_2$, $E_3 - E_1$, $E_2 - E_1$ etc.

ii) Only a small fraction of atoms is excited and ground state mostly populated thus atomic absorption spectra is process is more sensitive than atomic emission ~~emission~~ ^{spectroscopy}. Though

iii) wave length of resonance line is a critical factor, and elements whose resonance lines are associated with relatively low energy values are more sensitive (as far as flame emission spectroscopy is concerned) than those whose resonance lines are associated with high energy values.

Interference:-

(i) Spectral interference:- Spectral interference some time occurs due to overlap between the frequencies of selected resonance lines with lines emitted by other elements.

Some spectral interference ~~occurs~~ may occur from the emission band spectra of produced by molecules or molecular fragments.

present in the flame gases.

ii) Chemical interference:-

a) Stable compound formation - Stable compound formation leads to incomplete dissociation of the substances or it may arise due to it may occur due to the formation of refractory compound within the flame and that fails to dissociate ~~it~~ into constituents.

Few examples of such refractory compounds include: $CaSO_4$, $CaPO_4$, Ti , V & Al oxide etc.

Stable compound formation could be overcome

by (i) increasing flame temperature

(ii) Adding releasing agents like EDTA &

(iii) Extracting analyte or removing ~~interfe~~ interfering chemicals.

b) Ionisation of ground state gaseous atoms will reduce the intensity of emission lines.

This can be minimised by selecting appropriate temperature and adding ionisation suppressant (solution containing a cation having lower ionisation potential, like potassium).

c) Matrix effect:- Physical factors like viscosity, density etc.

d) Molecular absorption: