Flame Emission Spectroscopy

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To understand the relationship of these techniques to each other, it is important to understand the atom itself and the atomic process involved in each technique.
Practically, the ratio of the excited to ground state atoms is extremely small. Therefore, the absorption spectrum is usually only associated with transitions from the ground state to higher energy states.

Boltzmann equation explains the relationship between the ground and excited state atoms:

\[ \frac{N^*}{N} = Ae^{-\frac{E_a}{KT}} \]

- \(N^*\): No. of excited atoms
- \(N\): No. of ground state atoms
- \(E_a\): Excitation energy
- \(A\): Constant for particular element
- \(K\): Boltzmann constant
- \(T\): Temperature in kelvin
The process of excitation and decay to ground state is involved in the two techniques of atomic spectroscopy.

We measure the energy absorbed or emitted and use it for quantification process.
**Principle:** Flame photometry is based upon those particles that are electronically excited in the medium.

**Flame**: is the source of excitation energy. (low energy source).

**Uses:**
Flame photometry is used mainly for the determination of alkali metals and easily excited elements (Na, K, Li, Ca, etc.) particularly in biological fluids and tissues.
Spraying a solution of the sample in a hot flame

Solvent evaporation

Formation of Mist

Vaporization

Residual solid particles

Ground state atoms

$\text{Na}^\circ$

Emission and return to $G^\circ$

Excited atoms

$\text{Na}^*$

Excitation

Free atoms

$\text{Na}^\circ$

Dissociation

Residue in to neutral atom

Events occur in FES
Instrument components

Flame Structure

Interzonal region

Fuel-oxidant mixture

Primary combustion zone

Secondary combustion zone

Flame

Monochromator

Detector
Functions of Flame

1. To convert the constituents of liquid sample into the vapor state.

2. To decompose the constituents into atoms or simple molecules:

\[ M^+ + e^- \text{ (from flame)} \rightarrow M + h\nu \]

3. To electronically excite a fraction of the resulting atomic or molecular species

\[ M \rightarrow M^* \]

<table>
<thead>
<tr>
<th>Oxidant - Fuel</th>
<th>Max. temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air- propane</td>
<td>1725</td>
</tr>
<tr>
<td>Air- acetylene</td>
<td>2400</td>
</tr>
<tr>
<td>Oxygen- acetylene</td>
<td>3100</td>
</tr>
<tr>
<td>Nitrous oxide-acetylene</td>
<td>3000</td>
</tr>
<tr>
<td>Air-hydrogen</td>
<td>2000</td>
</tr>
<tr>
<td>Oxygen-hydrogen</td>
<td>2700</td>
</tr>
<tr>
<td>Air + argon-hydrogen</td>
<td>1577</td>
</tr>
</tbody>
</table>

The flame is composed of:

- a fuel gas and oxidant gas
Factors affecting intensity of flame emission:
1. The concentration of the analyte in solution
2. The rate at which excited atoms are formed in the flame.
3. The rate at which the sample is introduced into the flame.
4. Temperature of the flame.
5. Composition of the flame.
6. The ratio of fuel to oxidant in the flame.
7. Solvent used to dissolve the sample.

The flame temperature is the most important factor. Increase in flame temperature causes an increase in emission intensity. This is controlled by composition of the flame.

High temperature flames should not be used for elements that ionized easily e.g. Na, K, Li or Ce. However, high temperature flames are generally favored for transition elements and alkaline earth metals.
Effect of the solvent used to dissolve the sample; if the solvent is water the process is slow and if it is organic solvent the process is fast and emission intensity is increased.

It is therefore very important that calibration curves be prepared using the same solvent.

The stochiometric ratio of fuel to oxidant in the flame must be used, in which both fuel to oxidant are totally consumed.
The nebulizer-burner system

To convert the test sample into gaseous atoms

Nebulizer produce an aerosol of the test solution
Burner in which the mixing between fuel and oxidant

Types of burner system

1. Pre-mix or laminar flow burner

Advantages

1. Homogenous flame
2. Suitable for AAS and AES as the pathway could be increased

Disadvantages

Suffers from explosion hazards
2. Total consumption burner

3 concentric tubes, the sample, fuel and oxidant only mix at the tip of burner

Used mainly for FES (short bath)

Advantages
1. Simple to manufacture
2. Allows a total representative sample to reach the flame
3. Free from explosion hazards

Disadvantages
1. Aspiration rate varies with different solvents
2. Suitable only for AES
In the burner

The combustion of fuel occurs producing the necessary heat for atomization and excitation but not ionization.

The temperature of the flame produced depends on fuel-oxidant ratio and kind.
Non Flame Atomizers

For example: Heated Gravite Furnace

Sample evaporation → time and temp. controlled drying and ashing

Advantages

1. small samples are analysed
2. 1000-fold more sensitive than flame
3. Oven is adaptable to determination of solid samples

Disadvantages

1. Low accuracy          2. Low precision
2. More ionic interferences due to very high temp.
Monochromators

Detectors

Analytical technique

As in UV

Films or photomultipliers

1. **Choice of the wavelength:** of max. sensitivity and min. spectral interferences
2. **Sample preparation:**
   a. It is very important to obtain the sample in a form of solution, where the spectral and chemical interferences are absent
   b. Demineralized dist. Water and very pure reagents are to be used because of the high sensitivity of the technique
   c. Because of the instability of the very dil. Solution, it is advisable to dilute the soln just before use.
   d. Several elements can be determined in blood, urine, cerebrospinal fluid and other biological fluids by direct aspiration of the sample after dilution with water.
**Interference:**
Same interferences occur in FES and Flame AAS but to different extents, 4 general classes

A) **Background absorption:** is caused by the large number of species present in the flame (metal oxide, OH radical, H₂, fragments of solvent mol etc)
- incident radiation is absorbed by these species as well as by the analyte atoms

**Correction:**
1) “blank” solution (solution devoid of analyte) can be used to correct the measurement from sample solution (in practice it is difficult to prepare exact blank)
2) use of a continuous source of radiation in conjunction with hollow-cathode line source
- resonance line of the hollow cathode is absorbed by both free analyte atoms and interfering species in the flame.
- radiation from the continuous source is absorbed over the entire wavelength (due to the component of the background) and is a measure of the background
- background correction is then made at the same wavelength as the resonance line used for AAS determination
3) Pulsed hollow cathode lamp background correction.

- two absorption measurements are made one with the lamp run at a normal low current and a second with the lamp pulsed to a large current
- the first measurement indicates the absorbance due to both analyte atoms and background, whereas the second measurement indicates primarily background, because large current eliminates the resonance line
- subtraction of these two absorption measurements yields a corrected value for atomic absorption

B) Spectral Line Interference:

- arise when the absorption or emission of an interfering species either overlaps or lies so close to the analyte band that resolution by the monochromator become impossible

- in AAS amplitude modulation of the radiation source can minimize this interference
C) Vaporization Interference:

- arise when some component of the sample alters the rate of vaporization of salt particle that contain the analyte
- hotter flame minimizes vaporization interference (acetylene/nitrous oxide flame as compare to cooler acetylene/air flame for refractory phosphate, sulphate etc)
- pretreatment of sample also helps

D) Ionization Interference:

- atoms with low ionization potential become ionized reducing the population of both the ground state and excited state free atoms
- by adding an excess of easily ionized element (viz. K, Cs or Sr), ionization in the sample and calibration solution can be suppressed
- more easily ionized atoms produces a large concentration of electrons in the vapor and, by mass action, suppresses the ionization of analyte atoms
**Chemical interferences:** can often be overcome by simple dilution with a suitable reagent solution e.g. serum is diluted by EDTA solution for the determination of calcium in order to prevent interference from phosphate.

3. **Standard curves**

Deviations from linearity may occur.
3. **Qualitative analysis**

Flame photometry are useful mostly for the detection of elements in group I and II of the periodic table. The presence of certain elements can be detected by the use of a filter or monochromator.  

**Advantages and disadvantages**

The method is not as reliable as other atomic emission spectroscopic methods, but it is fast and simple.

4. **Quantitative analysis**

To perform quantitative analysis, the sample is introduced into the flame and the intensity of radiation is measured. The concentration of the emitting substance is then calculated from a calibration curve or using standard addition method.
Application of flame photometry in pharmaceutical analysis

1. Metals are major constituents of several pharmaceuticals such as dialysis solutions, lithium carbonate tablets, antacids and multivitamin - mineral tablets.

2. The elements Na, K, Li, Mg, Ca, Al and Zn are among the most common elements subjected to pharmaceutical analysis using flame emission technique.

3. Sodium and potassium levels in biological fluids are difficult to analyze by titrimetric or colorimetric techniques. Their analysis is very important for control of infusion and dialysis solutions which must be carefully monitored to maintain proper electrolyte balance.

Advantages and disadvantages

1. Flame emission is the simplest and least expensive technique.

2. The analysis may be carried out without prior separation as other components such as dextrose, do not interfere.
THANK YOU....