

Atomic Spectroscopy

These methods deal with the absorption and emission of radiation by atoms.

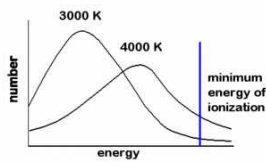
The methods deal with free atoms

Line spectra are observed

Specific spectral lines can be used for elemental analysis - both qualitative and quantitative.

Effect of temperature

Our source must have a stable temperature as this can dramatically affect the number of atoms that are ionized.



Note, this is a measure of the kinetic energy.

Absorption methods


Atomic absorption spectroscopy (AA)

A quantitative method of analysis based on the absorption of light by atoms in the free atomic state.

The method relies on the Beer-Lambert relationship - calculations are the same as with molecular absorption methods.

Atomic absorption

Basis of method
 With electrical or flame excitation, most atoms remain in the unexcited state.



Atomic absorption

Advantages over emission

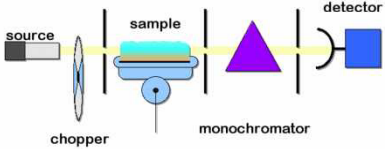
- Fewer interferences
- Less dependent on temperature
- Most elements exhibit better sensitivity and accuracy - ppb range with +2% accuracy.

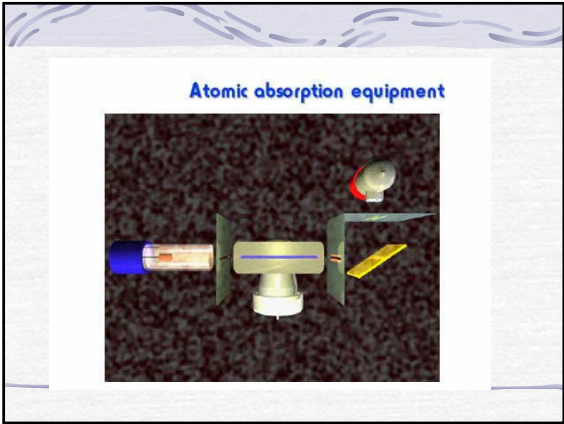
Disadvantages over emission

- Metals only - most other elements form oxides to rapidly.
- Quantitative analysis only.

Atomic absorption equipment

In its simplest form, an AA resembles a single beam spectrophotometer.





Sources

A molecular spectrophotometer relies on a broad band light source.

With atomic absorption, a line source is required to reduce interferences from other elements and background.

Two basic types

- Hollow cathode lamp - HC
- Electrodeless discharge lamp - EDL

Hollow cathode lamp

This source produces emission lines specific for the element used to construct the cathode.

The cathode must be capable of conducting a current for it to work.

Hollow cathode lamp

The lamp is filled with an inert gas like argon or neon.
When a potential is applied, it causes the gas to become excited and it is driven towards the cathode.

Metal atoms are then sputtered off the surface of the cathode.

Hollow cathode lamp

Repeated bombardment of the metal atom by the gas causes it to be excited. It ultimately relaxes, producing specific atomic emission lines.

Hollow cathode lamp

An HC lamp will only produce the emission lines for the cathode element.

Multi-element HC lamps are available but are limited.

Not all metals will make suitable cathodes

- Metal is too volatile
- A good cathode can't be produced
- The metal may not be good conductors

Electrodeless discharge lamp

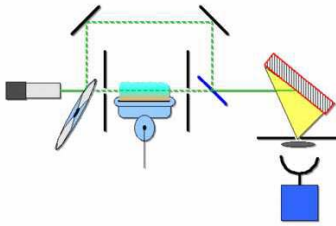
An alternative to the hollow cathode lamp.

A salt containing the metal of interest is sealed in a quartz tube along with an inert gas.

An RF field is used to excite the gas which in turn causes the metal to be ionized.

Light intensity is about 10-100 times greater but are not as stable as HC lamps.

Signal modulation



Atomization source

We need to be able to convert our sample to free atoms. Two approaches are used.

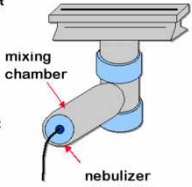
Flame atomization
liquids and gases

Flameless atomization
graphite furnace
liquids and solids



Flame atomization

A flame atomizer will usually have a long, narrow burner head that serves as a sample path (b).
 Sample is introduced via aspiration.
 The nebulizer controls sample flow, producing a mist.
 The mixing chamber assures that the sample mixes with the oxidant and fuel prior to entry into the flame.



The diagram shows a cross-section of a flame atomizer. On the left, a tube labeled 'nebulizer' has a small opening where a sample is aspirated. This tube leads into a larger 'mixing chamber'. From the top of the mixing chamber, a long, narrow tube labeled 'burner head' extends to the right. Red arrows point to the nebulizer and mixing chamber labels.

Flame atomization

The most common fuel to use is acetylene.
 Either air or nitrous oxide are used as oxidants, with N_2O producing a hotter flame.

	Temperature, °C
C_2H_2/Air	2100 - 2400
C_2H_2/N_2O	2600 - 2800

N_2O also tends to produce a noisier flame.

Flame atomization

Flame atomization tends to produce stable signals in the ppm range for most metals.

It is a dynamic method
 Sample is constantly being consumed.
 Large sample size (>1 ml).
 Your sample must be a fluid.

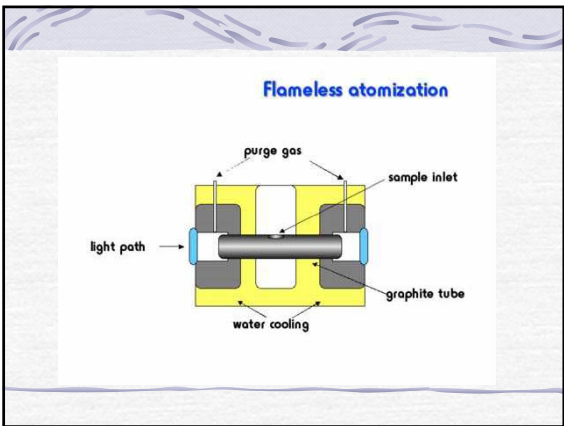
The detection limits are relatively high since only a small portion of your sample is present in the flame at any given time.

Flameless atomization

Samples are placed in a carbon tube which is heated electrically - graphite furnace

Sample residence time is greater so you have improved detection limits and sensitivity.

Solid samples can also be assayed.



Flameless atomization

You can't simply heat your sample to atomization temperatures or the sample will splatter.

We use a temperature program to ensure reproducible atomization.

A three stage program is the most common.

Flameless atomization

Dry
A fixed temperature and time used to remove your solvent (50-200°C).

Char
A second temperature/time used to decompose your matrix (200-800°C).

Atomization
A rapid increase to 2000-3000°C for just a few seconds - when you collect your data.

Flameless atomization

Argon is often used as a purge gas to:

- ✓ Remove excess material during the dry and char phases and after atomization
- ✓ Reduce oxidation of the tube.
- ✓ Provides a protective blanket during atomization since high temperature carbon will react with nitrogen to produce cyanogen - you should always vent to a hood anyway.

Monochromator and detector

A high resolution, holographic grating is used to resolve your lines. It is not designed to be used in 'scan' mode.

The typical detector is a photomultiplier tube.

An additional component that is very common is a method of background correction.

AA methods

For each element, you must consider:

- Which λ and slit width to use
- Determines sensitivity and linear range.

For flame AA

- Flame type
- Method of sample mixing

For flameless AA

- Optimum temperatures to use

AA methods

Fortunately, AA is a reasonably well worked out technique.

Standard conditions for all elements that can be measured by AA are available

If you have a computer based system, it will even help set up the proper conditions

Flame AA example - Mn

λ	Relative Noise	Sensitivity (mg/l)	Linear range (mg/l)
279.5	1.0	0.052	2.0
279.8	0.77	0.067	3.0
280.1	0.88	0.11	5.0

Other conditions

- Air/C₂H₂ flame - lean, blue
- Slit width of 0.2 nm
- Flow spoiler

0.2% CaCl₂ can be added to overcome interference from presence of Si.

Flameless AA example - Mn

Matrix	Aqueous
λ	279.5 nm
Slit width	0.2 nm
Temperatures	
Maximum Char	1100°C
Optimum Atomization	2700°C
Sensitivity	4 μ g / 0.0044A
Linear range	200 μ g

REFERENCES:

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<http://ull.chemistry.uakron.edu/analytical/>
