**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.

**Atomic spectroscopy**

General concerns and considerations.

Atomic spectra have narrow lines.

Anything that causes broadening of the lines can cause problems.

The two largest problems are

Doppler broadening

Pressure broadening

**Doppler broadening**

During atomization/ionization, our species may move towards or away from the detector.

This will result in a Doppler shift in the resulting line.

Spectral lines that should be about 1-5nm can end up being 100 times wider.

There is not much you can do about it except recognize that is occurs.

**Pressure broadening**

The effect arises from the collision of our sample atoms with other species causing some energy to be exchanged.

The effect is greater as the temperature increases.

**Effect of temperature**

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

![Graph showing number of ions vs. energy with two curves, labeled 3000 K and 4000 K]

Note: this is a measure of the kinetic energy.

**Atomic emission**

A group of techniques that are typically classified based on the excitation source.

- Flame photometry
- Atomic fluorescence
- Electrical excitation - arc and spark
- Plasma emission

We can conduct both qualitative and quantitative analysis with these methods.
**Qualitative analysis**
Methods rely on the presence of specific emission lines.

<table>
<thead>
<tr>
<th>Element</th>
<th>Major emission line, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>3281</td>
</tr>
<tr>
<td>Cu</td>
<td>3248</td>
</tr>
<tr>
<td>Hg</td>
<td>2537</td>
</tr>
<tr>
<td>K</td>
<td>3447</td>
</tr>
<tr>
<td>Zn</td>
<td>3345</td>
</tr>
</tbody>
</table>

**Quantitative analysis**
Based on measuring the intensity of an emission line.

\[
\text{intensity} = K \cdot c \]

Best for metals, sensitivity $\geq 0.001%$

Large relative error, $\pm 1 - 5%$

Sensitivity and error are highly dependent on the element and line being used.

**Excitation Sources**

**Electrical**
Relies on a pair of high purity carbon electrodes.

- **Arc** - continuous electrical excitation.
- **Spark** - short burst of excitation.

Temperature: 4000 - 8000°C for a spark
Voltage: 15,000 - 40,000 V

**Flame excitation**
This method of excitation is of relative low temperature:

- $\text{Air/H}_2$ 2100 °C
- $\text{O}_2/H_2$ 2700 °C
- $\text{N}_2\text{O}/\text{C}_2\text{H}_2$ 3050 °C

This results in only a very small percentage of the atoms being ionized ($\leq 1%$). One option is to go to higher $T$ - **Plasma emission**.
**Plasma**

Similar to flame photometry.

An RF field is used to excite an inert gas (typically argon) which in turn ionizes our sample.

Higher temperatures (≥10,000K) are achieved so we obtain better sensitivity than with a flame.

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**Inductively coupled plasma source (ICP)**

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**Three electrode DC plasma source**

- Cathode
- Anode
- Viewing area
- Sample + Ar

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**Microwave plasma source**

- Reagent gas
- Vent
- Water in
- Water out
- Sample
- Microwave cavity
- Plasma
- Window

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**Monochromator system**

Because emission lines are very narrow (< .01 nm), high resolution grating are required.

One common approach is to use a curved grating.

This approach disperses the lines with focal points based on the curvature of the grating - **Rowland’s circle**.
Several approaches can be used.

**Eye**
May be used with simpler arc emission sources.
You move the ocular around the Rowland’s circle to look for lines.
A calibrated strip indicates the wavelength you are looking at (and possibly the element).
Used mostly for qualitative work.

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Film can be used as a detector
Qualitative - position of lines
Quantitative - degree of exposure

**Photomultiplier Tube**
A PM tube provides a means of obtaining quantitative data.
Typically, it is easier to move the tube. Moving the grating will alter the position of the Rowland’s circle.
Multielemental work requires several PM tubes or recalibration after tube movement.

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The monochromator/detector system for a flame photometer is much simpler than with the other types of systems.
We have fewer species to look at.
These systems are similar in layout to molecular filter photometers or single beam spectrophotometers.
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.

Even with plasma emission, this is still true but not as large a problem.

If we can look at the free atoms, we can potentially develop a more sensitive method of analysis.

Atomic absorption

As the temperature increases, more atoms are excited. Most are still in the atomic state.

Minimum energy for ionization

\[ T_1 < T_2 < T_3 \]

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.

Source | Sample | Monochromator | Detector
---|---|---|---

Chopper
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

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

The cathode must be capable of conducting a current.

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.

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.

Chopper

A chopper is used to provide signal modulation in conjunction with a lock-in amplifier.
Its not practical to have two separate cells, so the light is simply split, with half being sent around the atomization source.
This reduces some noise from the atomization source and accounts for instrumental variations.

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

Signal modulation

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.
Flame atomization

The most common fuel to use is acetylene. Either air or nitrous oxide are used as oxidants, with N₂O producing a hotter flame.

Temperature, °C

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₂/Air</td>
<td>2100 - 2400</td>
</tr>
<tr>
<td>C₂H₂/N₂O</td>
<td>2600 - 2800</td>
</tr>
</tbody>
</table>

N₂O also tends to produce a noisier flame.

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.

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

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.

Background correction

Modulation of your signal (using a chopper) is an easy way to account for instrumental variations and 'flame flicker'.

It is not very good at accounting for background absorption or emission.

Two approaches that are commonly used are D₂ or Zeeman correction

Background correction

These methods rely on
Atomic lines being very narrow.
Background is typically molecular so is broad band.

Background correction

D₂ background correction
A continuous-source correction method.

Light from both the AA source lamp and a D₂ lamp alternately pass through the sample.

Because the spectral slit width is significantly larger than the AA source line, the D₂ lamp sends a much broader band of light through the sample.
Background correction

With the HC, we measure absorption of our element and background over a very narrow bandwidth.

With the D₂ lamp, we measure absorption over a much larger bandwidth. Because the elemental line is so narrow, we mostly measure background.

Limitations of D₂ correction

Either undercorrection or overcorrection can occur based on sample.

Background may vary around line

Composition of background can differ based on position in flame - requires good alignment of HC and D₂ lamps.

D₂ output is not very good at > 350 nm

Example showing our elemental line occurring near the maximum of some sort of molecular absorption from the background

In this example, D₂ correction would tend to overcorrect.

An alternate approach is to make use of the Zeeman effect.

When an atomic vapor is exposed to a strong magnetic field (1 - 10kG), there is a splitting of the atoms electronic energy levels.

This essentially moves our absorption away from the emission lines.

The magnetic field is applied to the sample.
Background correction

Using this method of correction, we can measure at a fixed and narrow wavelength.

At regular intervals, we simply move our sample component out of the way.

This allows us to directly measure background.

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

<table>
<thead>
<tr>
<th>λ</th>
<th>Relative Noise</th>
<th>Sensitivity (mg/l)</th>
<th>Linear range (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>279.5</td>
<td>1.0</td>
<td>0.052</td>
<td>2.0</td>
</tr>
<tr>
<td>279.8</td>
<td>0.77</td>
<td>0.067</td>
<td>3.0</td>
</tr>
<tr>
<td>280.1</td>
<td>0.88</td>
<td>0.11</td>
<td>5.0</td>
</tr>
</tbody>
</table>

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 pg / 0.0044A
Linear range 200 pg

Atomic fluorescence

A modification of the normal AA setup will permit atomic fluorescence to be done.

The HC lamp is placed at a right angle to the detector.

Any atoms that fluoresce can be measured.

Not as common as AA or plasma emission.
**Atomic fluorescence**

Most AA instruments permit the measurement of emission.

Any element that can be sufficiently excited by the flame will produce spectral lines when they relax - flame photometer.

If no HC is present (or turned off) and emission mode is selected, normal flame emission can be conducted.

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**X-rays**

We can also use the high energy end of the EM spectrum to conduct elemental analysis.

X-rays can be used for measurement of Absorption, Diffraction and Emission/Fluorescence

The principles of the methods are basically the same but the components vary quite a bit.

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**Production of X-rays**

If an inner electron is ‘knocked out’ of an atom, an outer electron will fall into the hole that is produced.

The energy difference is emitted as an X-ray.

Since this difference is a function of the type of atom, the energy of the X-ray is a function of the atom’s atomic number.

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**X-ray emission**

Emission of X-rays is independent of chemical form - only depends on Z. The I of the emission can be used to identify the element for Z ≥ 20.
X-ray absorption

Atoms can also absorb X-rays where:

\[
\text{Absorption } \propto \frac{Z^4}{\text{atomic weight}}
\]

Wavelength

K edge

L edges

The source of the X-rays must have a higher atomic number than the sample

X-ray equipment

The arrangement of the various components in an X-ray system is dependent on the type of method to be used.

Let's start by reviewing some of these components since they are different than what we've dealt with so far.

X-ray source

An electron beam is used to produce X-rays from a target metal.

Common metals are Cu, W and Mo. Z must be greater than the elements you plan on working with.

The collimator is a series of metal plates with holes in the middle.

It is designed to absorb all X-rays not traveling in the proper direction

The filter is a metal with an atomic number one greater than the element of interest.

Filter absorption

source emission
**Monochromator**

Normal gratings or prisms cannot be used with X-radiation. It would either pass through or be absorbed - no dispersion.

If one is required, it is typically constructed of NaCl and works by diffraction of the X-rays by the ions.

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**Detector**

Three types - two classes

- Non-discriminating
  - Gas filled - GM tube
- Discriminating - can resolve the energy.
  - Scintillation - NaI(Tl)
  - Solid State - Si(Li)

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**GM tube**

An argon filled tube with a potential difference of 1000V or more.

At this voltage, you get the maximum number of ionizations per radiation event.

Each event causes a total avalanche of ions resulting in a single, large pulse.

It does not discriminate.

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**Scintillation Detectors**

**NaI(Tl)**

- Very common material used for γ and X-ray detection.

  - When an X-ray interacts with a NaI(Tl) crystal, light is produced.
  - You get one photon for each 200 eV.
  - The number of photons is proportional to the energy of the X-ray

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**Scintillation Detectors**

When exposed to X-rays, the crystal will produce a burst of photons. The intensity of the light is proportional to the energy.

- NaI(Tl) crystal

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**NaI(Tl) detector**

- Diagram of NaI(Tl) crystal
**Nal(Tl) detector**

- An aluminum 'shield' covers the crystal to prevent contamination and keep water out - can destroy the crystal.
- The inner surface is reflective to direct light towards the photomultiplier tube.

**Si(Li)**

- Silicon doped with lithium
- A solid state device that can detect X-rays

**Si(Li)**

- When a small voltage difference is applied to the crystal, you create a positive, negative and a depleted zone.
- This is similar to a transistor (np type).
- negative - electrons
- positive - + holes

**Si(Li)**

- These regions are relatively small.
- Once created, there is no net movement of charge.
- n-layer 0.01-0.10 cm
- intrinsic region 0.1-2.00 cm
- p-layer

**Semiconductor detectors**

- When ionizing radiation passes through the detector, it leaves behind a trail of + and - charges in the depletion zone.
- Detection is based on the current required to re-establish the depletion zone.

**X-ray diffraction**

- This approach is used to find the dimensions and shape of a crystal unit.
- It can be used to:
  - Deduce the structure of a new material
  - Identify a substance
  - Tell structure of a polymer
  - Elemental analysis
**X-ray Diffraction**

Film can be used for detection of the patterns. It is now more common to rotate the crystal and detect the x-rays with a fixed position detector. This way, you have data that can be processed by a computer.

**X-ray Absorption**

This is a common approach for measuring the quality of metal casts and welds. Its major use is in medicine and dentistry.

**X-ray Fluorescence**

When a sample is exposed to X-rays, secondary x-rays are produced.

Both qualitative and quantitative data can be obtained (Z ≥ 11).

In addition, this is a multi-elemental, non-destructive form of testing.