Basics of Atomic Absorption Photometer

Hitachi High-Technologies Corporations

1. Atomic Absorption Photometer

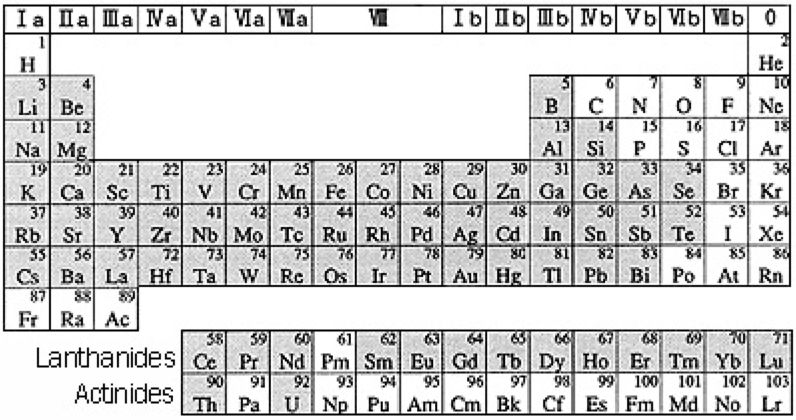
Q “What does an atomic absorption photometer measure?”

A: It is a system which mainly measures the concentration of metallic elements (quantitative analysis).

Q “What are metallic elements?”

A: They are elements corresponding to metallic elementary substances. For example, calcium, which is an ingredient in our bones, or sodium and potassium, which are contained in alkali drinking water are metallic elements.
The metallic elements which can be measured are shown in the following periodic table.

- Sixty-nine elements can be analyzed.
- The elements which can be measured are shaded.
- The peripheral equipment which needs to be prepared varies by element.
  Please refer to the supplemental data for details.



Q “What concentrations can it measure?”

A: It can measure from ppm to ppb.

Q “Just a moment. What are ppm and ppb?”

A: These are units indicating concentration, similar to percent. The ‘m’ and ‘b’ in ppm and ppb stand for million and billion, respectively.
That is, 1% means 1/100, ppm means 1/million and ppb means 1/billion.
To illustrate simply, 1% would mean one person in 100 people, while 1 ppm would be one person in one million people.
Do you understand?
Please see the following concentration conversion table.

Generally a measurement sample is a solution specimen.
Solution concentration units

1% ＝ 1/100 ＝ 10^{-2}
1 ppm ＝ 1/1,000,000 ＝ 10^{-6} ＝ 0.0001%
1 ppm ＝ 1 mg/L＝ 1 μg/mL

1 ppb ＝ 0.001 ppm ＝ 10^{-9}
1 ppt ＝ 0.001 ppb ＝ 10^{-12} = 1/trillion

1 ppb ＝ 1 μg/L ＝1 ng/mL
1 ppt ＝ 1 ng/L ＝1 pg/mL

2. Application Fields

Q: "Where is it used?"

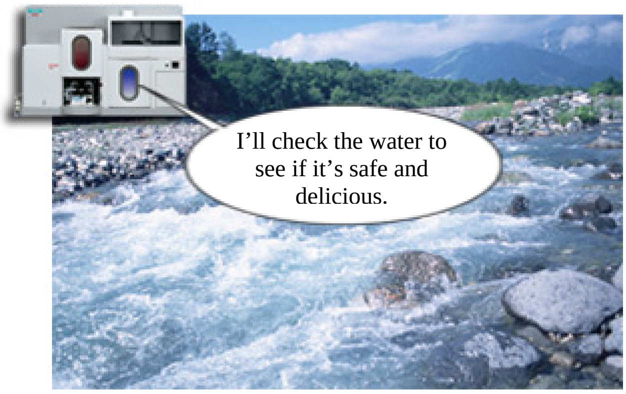
A: The concentrations of mineral ingredients are indicated on commercial water. An atomic absorption photometer is used for measuring these concentrations. (Foods)

The concentrations of contained metals may determine the safety or flavor of groundwater. The atomic absorption photometer is also used for measuring these concentrations. (Environment)

It is said that the concentration of aluminum in serum is related to Alzheimer's disease, etc. An atomic absorption photometer is used for measuring aluminum concentration. (Medicine)

In addition, this system is widely used in the chemistry and metal fields.

Atomic absorption photometer

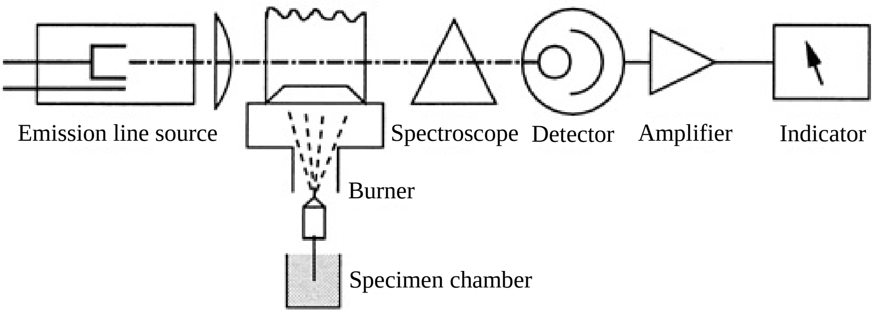


3. Outline of the System

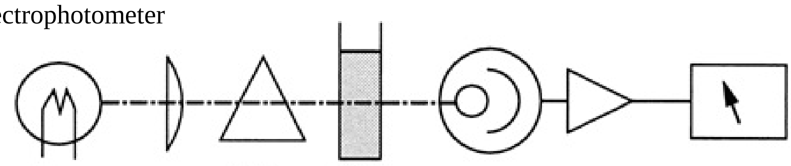
Q: How does an atomic absorption photometer work?"

A: An atomic absorption photometer works like a spectrophotometer. Shown below are diagrams of a spectrophotometer and an atomic absorption photometer. Please compare these diagrams for similarities and differences.

Atomic absorption photometer



Spectrophotometer



Differences between a spectrophotometer and an atomic absorption photometer

(1) Different light sources are used.
Spectrophotometer: Continuum source
Atomic absorption photometer: Emission line source (the meaning of the term, 'emission line' will be explained later.)

(2) The structures of the specimen chambers are completely different.
Spectrophotometer: Only injects a specimen into a cell.
Atomic absorption photometer: Burns a specimen using a burner, etc as shown in the diagram.

(3) Different locations for the spectroscope
Spectrophotometer: In front of the specimen chamber
Atomic absorption photometer: Behind the specimen chamber

Q: "Why is there such difference?"

A: The answer to this question will become clear, if the principle of the atomic absorption photometer is understood.

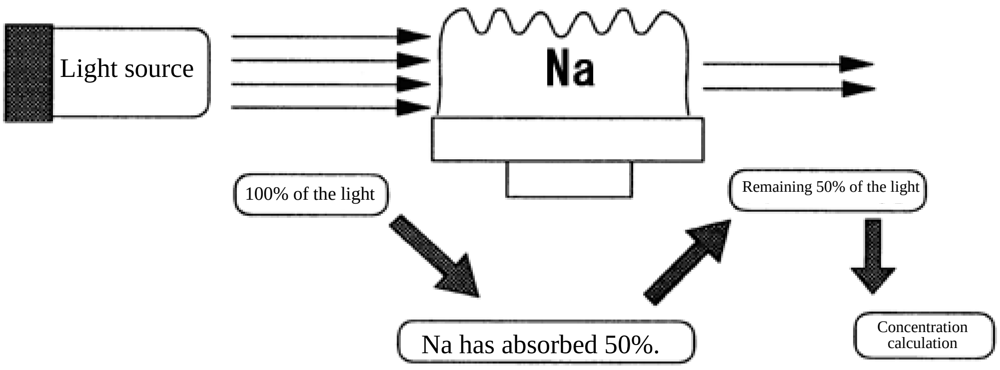
4. Principle of the Atomic Absorption Photometer

Q: "What does an atomic absorption photometer use to analyze?"

A: Like a spectrophotometer, an atomic absorption photometer measures how much light is absorbed when the light flux from a light source passes through a material to be measured.

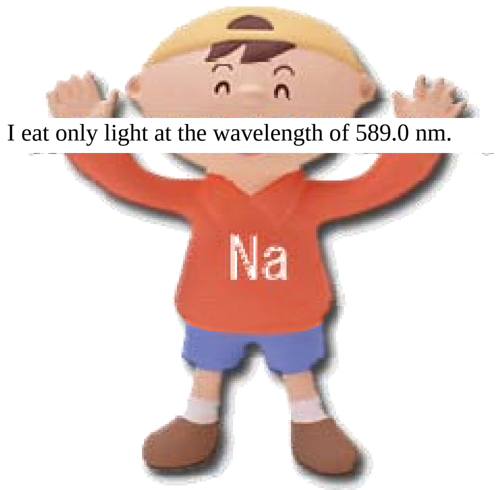
The fundamental difference from a spectrophotometer is the condition of the material to be measured.

That is, an atomic absorption photometer analyzes using atomic absorption, while a spectrophotometer analyzes using molecular photoabsorption.

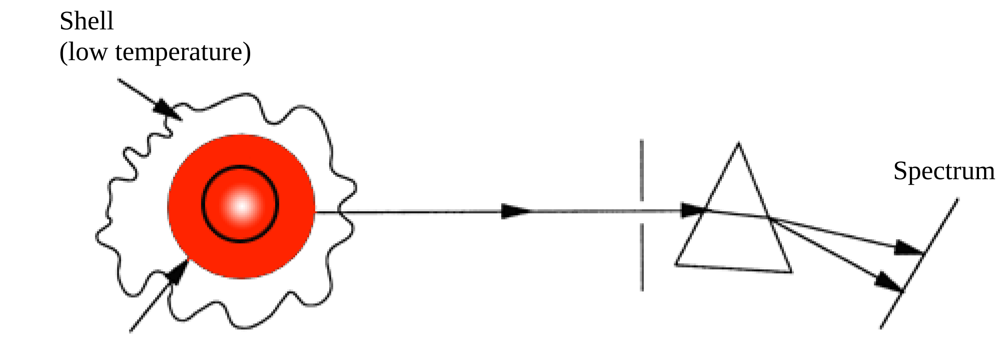


Q: "What is atomic absorption?"

A: It means that an atom absorbs (eats) a particular wavelength.
For example, Na eats only light at the wavelength of 589.0 nm.



As for discovery of atomic absorption,
A long time ago…in the early 19th century,
a man named Fraunhofer observed the spectrum of sunlight and found dark lines in it.
These lines were named Fraunhofer lines after the discoverer of the dark lines.
In the middle of the 19th century, Kirchhoff inferred that Fraunhofer lines might be due to absorption by atoms.



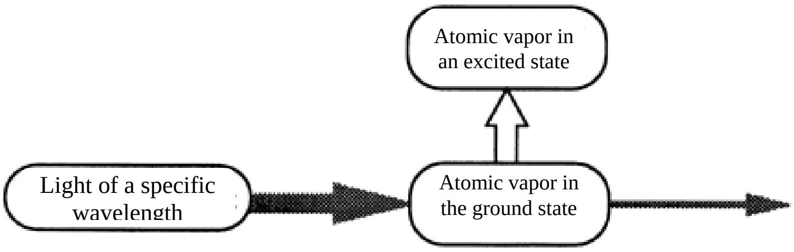
Observation of Fraunhofer lines

Q: "Why does atomic absorption take place?"

A: An atom usually exists in its lowest, stable energy level (the ground state).

However, ...

An atomic vapor in the ground state will be converted into an atomic vapor in an excited state by irradiation of light at a particular wavelength. A part of the irradiated light will be consumed. This is called atomic absorption.



(Absorption)

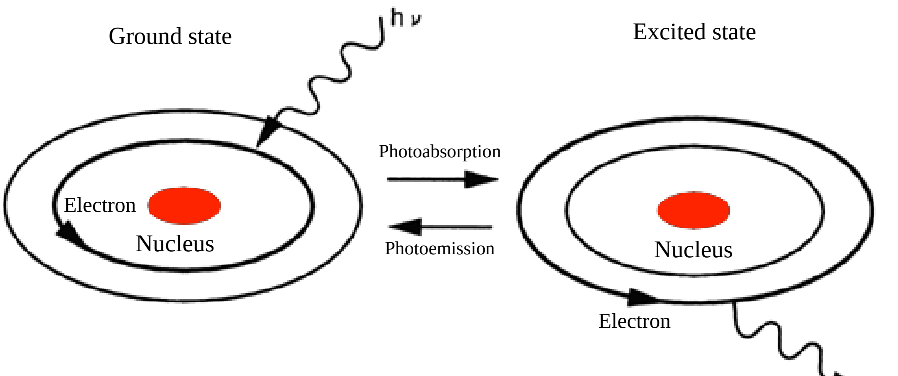


Diagram of atomic absorption and emission

Simple diagram showing atomic energy levels.

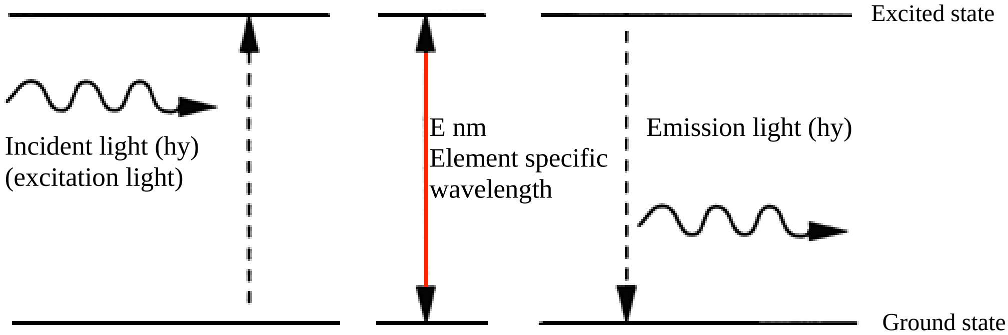


Photo-absorption and emission (spontaneous emission)

Do you now understand atomic absorption?

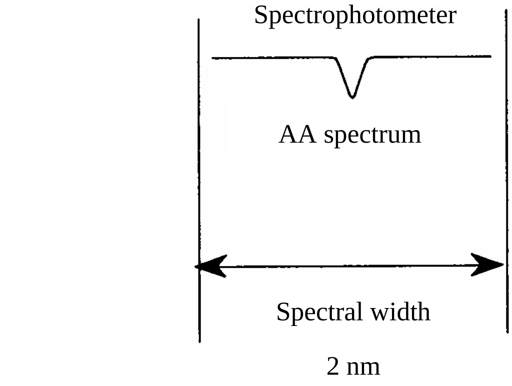
To induce atomic absorption in a system and measure its amount ...

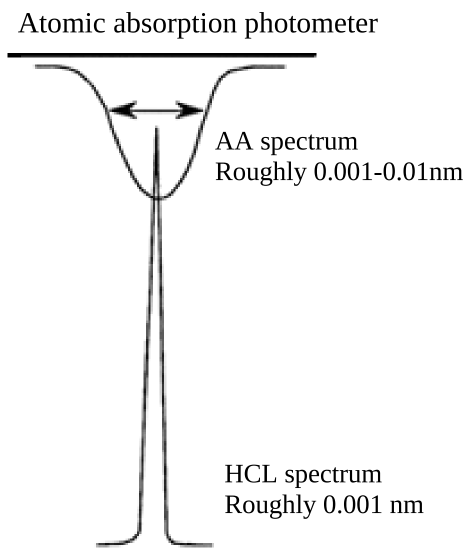
1. Light source ...

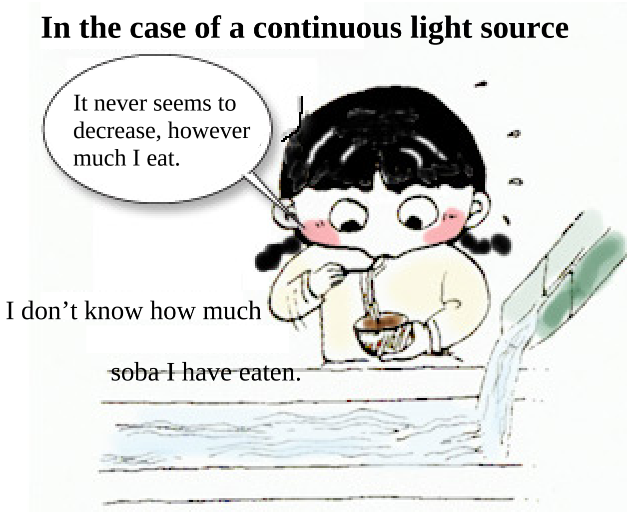
- The spectral width of an atomic absorption spectrum is very narrow (usually about 0.01 nm).
- To measure atomic absorption, a light source with narrower spectral width is necessary.
- The spectral width of the light source of the spectrophotometer is as wide as 1-2 nm.

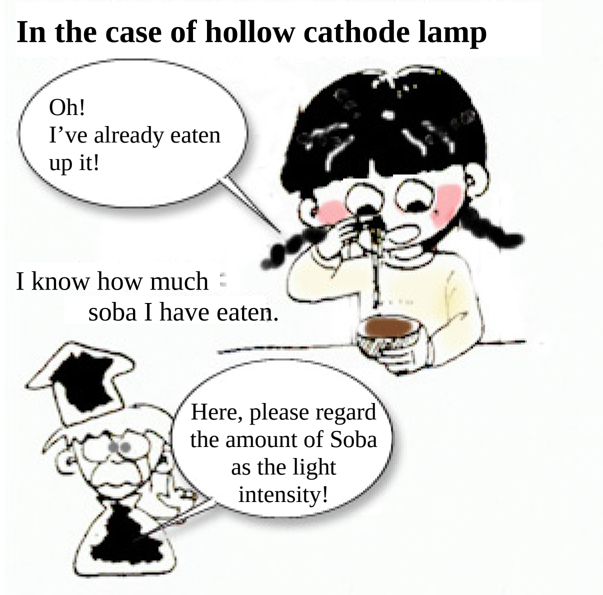
Therefore, an atomic absorption cannot be measured with a continuum source.

In an atomic absorption photometer, a hollow cathode lamp (HCL) is used.
The spectral width of an emission line (bright line) of a hollow cathode lamp is even narrower than a line in an atomic absorption spectrum.









2. Specimen chamber...

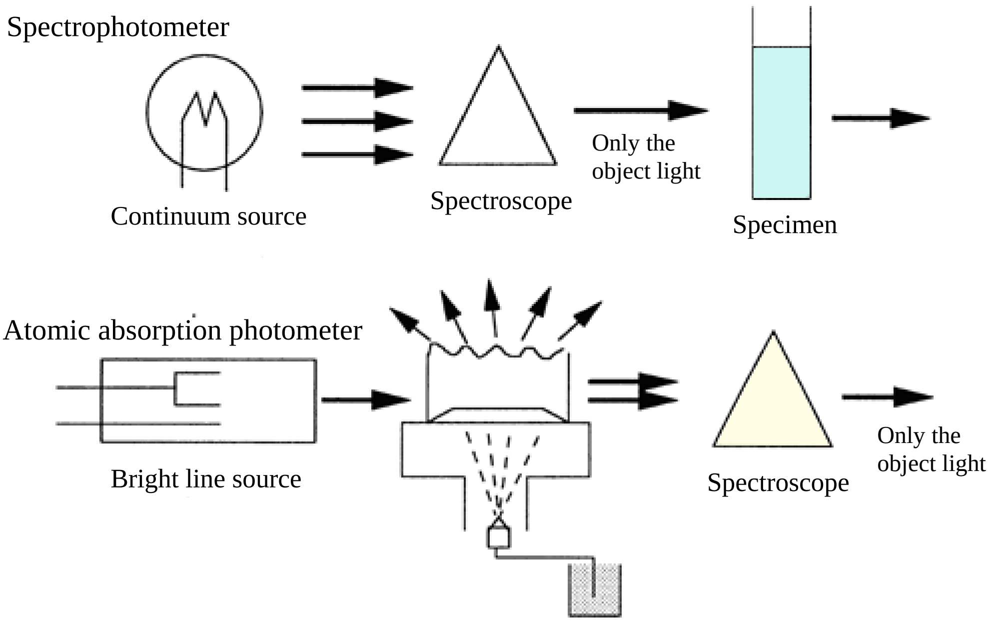
A specimen has to be changed to an atomic state to perform atomic absorption. However, metallic elements do not exist in the atomic state in the specimen. In order convert the specimen into the atomic state, an outside force is necessary.
So, the specimen is burned, changing it into the atomic state, using a burner, etc. (absorption cannot be measured simply by injecting the specimen into a cell, as with a spectrophotometer, because the specimen is not atomized only by injection.)

Atomization by an external force such as heat

Here is the answer to why the spectroscope is located behind the specimen chamber (atomization section).

In a spectrophotometer, a spectroscope is located in front of a specimen chamber, to let only the object light of the continuous light transmit.

On the other hand, in an atomic absorption photometer, the spectroscope is located behind the specimen chamber to remove the light component (luminescence component) of the flame generated in the atomization section.



The method using a burner (flame method) is not the only means of atomizing (atomization method).

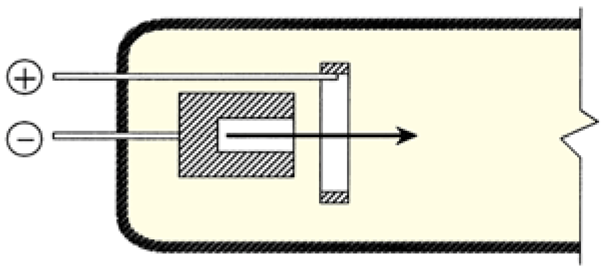
The various types will be explained, later.

5. Structure and Principle of Emission of the HCL

Q: "What about the inside (structure) of the HCL? How does it emit light?"

A: Let's begin with the inside (structure)...

It is a discharge tube consisting of a hollow cylindrical cathode and an anode, enclosing a small amount of noble gases such as neon.



Principle of emission

Voltage is applied between the electrodes to cause discharge.

→ The filler gas is ionized.

→ Ions collide with the cathode.

→ The vapor of cathode material is jetted (the vapor is in the ground state).

→ The atoms, electrons, ions, etc in the filler gas collide with the vapor to bring it to an excited state.

→ The atomic vapor in the excited state emits light to return to the ground state.

The wavelength of the emitted light depends on the cathode material.
If the cathode is made of copper, an emission line with a wavelength peculiar to copper will be emitted.
Since the cathode is hollow, ions enter the hollow intensely, leading to efficient (high luminance) emission.

In an atomic absorption photometer, an HCL which emits a wavelength with which atomic absorption by the metallic element to be measured is possible is selected.
For example, an HCL dedicated to copper is used to measure copper.
(One element - one lamp)

6. Atomization Method

Some atomization methods are described below.

(1) Flame method ... Atomizes with flame.

(2) Electric heating furnace method ... Atomizes with current.

(3) Hydride generation method ... Application of the frame method (uses a chemical reaction to vaporize the specific element)

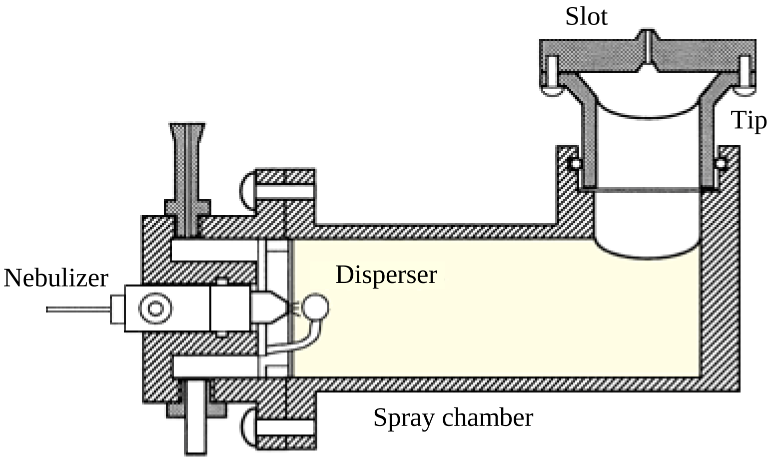
(4) Reduction-vaporization method ... Atomizes using an element’s easy-to-evaporate nature.

1. Flame Method

Function of burner

A specimen is introduced into the flame to atomize the elements contained in it.
Note that it is necessary to nebulize the specimen.
The flame will be extinguished without nebulization.

Nebulizer: Creates a fine mist of (nebulizes) the specimen.
Disperser: Supplies small particles of the nebulized specimen to the flame. The whole is made of glass.
Burner head: Supplies a stable flame to atomize the elements in the specimen. In order to secure an optical path length, it has a structure to generate a long flame. Since it looks like the tail of a fish, it is called a fishtail burner.



There are two kinds of burner heads: a standard burner, and a high temperature burner.
The following table shows a comparison between the two.

Comparison of standard burner and high temperature burner

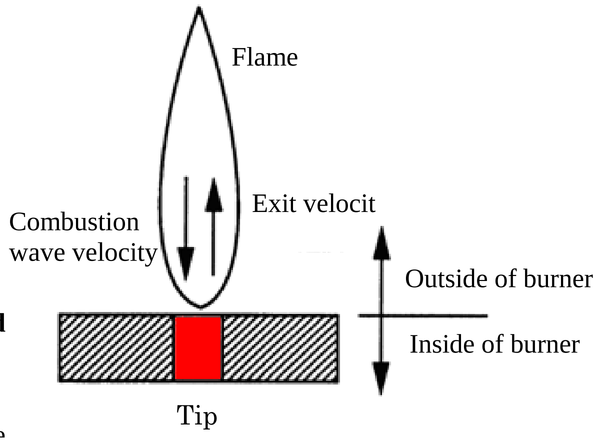
	Standard burner	High temperature burner
Gas system	Air-acetylene: 2000°C Air-hydrogen: 2000°C Argon hydrogen: 1600°C	Dinitrogen oxide-acetylene : 2900°C
Tip size	0.5 mm × 100 mm	0.4 mm × 50 mm
Measured elements	Pb, Cd, Fe, Cu, Mn, Cr, Au, K, Ag, Zn, Na, Ca, Mg, etc.	Al, B, Ba, Be, Ge, Si, Ti, V, W, etc.

Why a high temperature burner is necessary...
Some elements are not atomized at the temperature of a standard burner.

In order to obtain a high-temperature flame,
Dinitrogen oxide (nitrous oxide) - acetylene gas is necessary.
In order to supply a stable flame, the following relationship must be satisfied;

[Gas exit velocity] > [Combustion wave velocity of mixed gas]

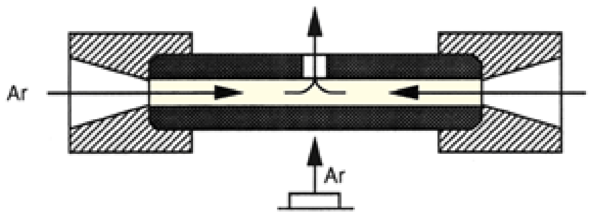
If this relationship fails, the flame may escape into the inside (backfire).



As for the gas system, since the combustion wave velocity of the dinitrogen oxide-acetylene combustion system is high, backfire will be generated with a standard burner head.
So, a high temperature burner head with a narrow tip, increasing the gas exit velocity, is used.

2. Electric Heating Furnace Method

A large current is applied to a carbon tube to generate Joule heat for atomizing the elements in a specimen.
Energization and measurement are carried out in an inert-gas atmosphere of argon (Ar), etc in order to protect the carbon tube.
A high-capacity power supply is necessary.
(Single-phase 200V/30A)
Upon getting hot, the polar zone is water cooled.



Advantages compared with the flame method

(1) High sensitivity
(2) Requires no pretreatment of the specimen
(3) Capable of measuring a small amount of the specimen

Disadvantage compared with the flame method

(1) Long measurement time
(2) Poor reproducibility because of intermittent measurement.

3. Hydride Generation Method

High sensitivity analysis (at a level of several ppb) of arsenic (As), selenium (Se), and antimony (Sb) is possible.

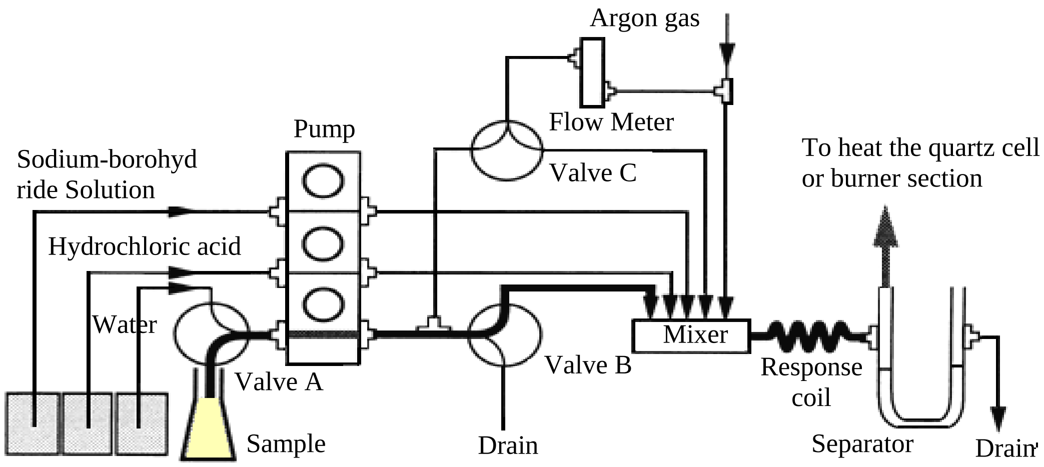
<<Measurement method>>

Generate gas hydrides by reaction of hydrogen and metallic elements.

Introduce the generated gas into an atomization section.

Atomize by heat decomposition.

The hydrogen used at this time causes an acid (hydrochloric acid etc.) and a reductant (sodium borohydride) to react. The generated hydride gas is carried to the atomization section using argon gas.



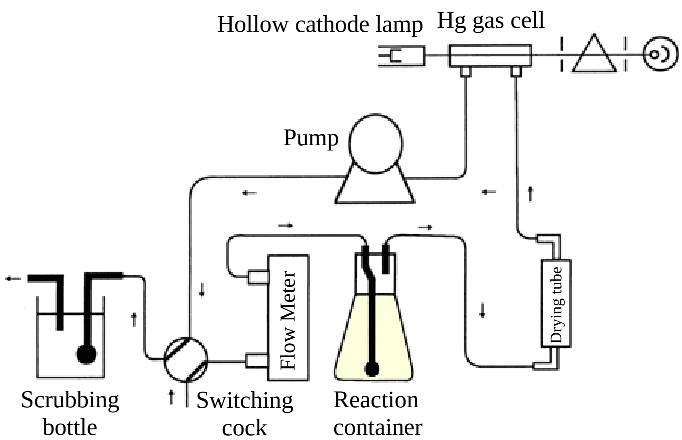
Hydride generation apparatus channel drawing

4. Reduction-vaporization Method

This method applies only to the measurement of mercury (Hg), which can be in the atomic state at room temperature.

<<Measurement method>>

When a specimen is added to the reaction chamber and a reagent (sulfuric acid and stannous chloride (6N HCl solution) is added, the mercury will evaporate and exit from the container (being reduced and exiting). The vaporized mercury is led to a mercury cell with an air pump to be measured (not requiring thermal decomposition). Commonly known as the flameless method.

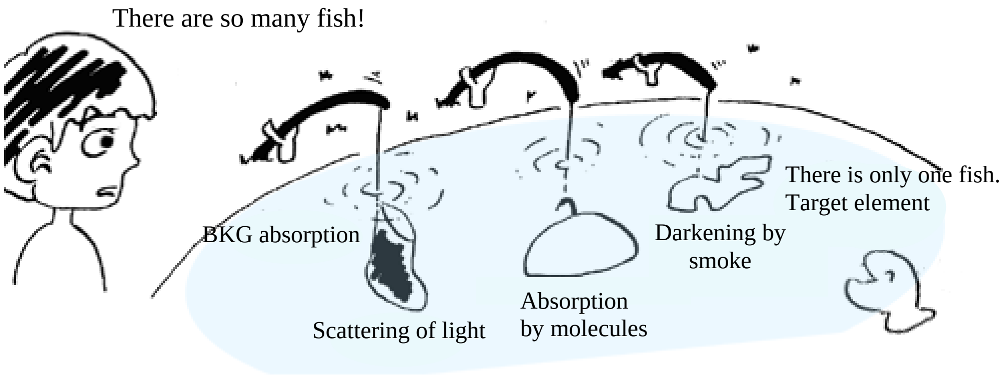


Tubing diagram

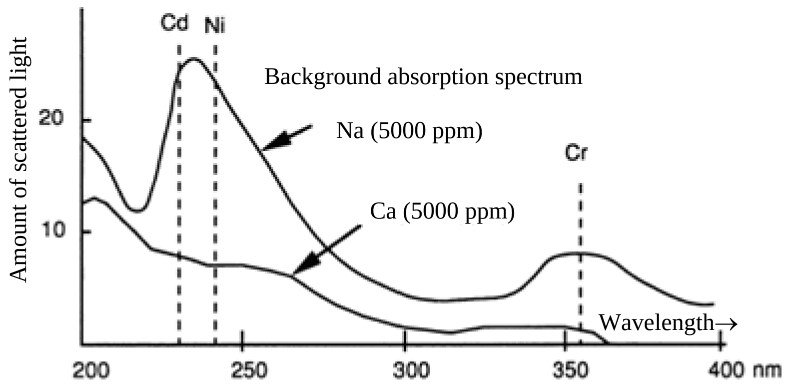
7. Background (BKG)

Q: “What is background?”

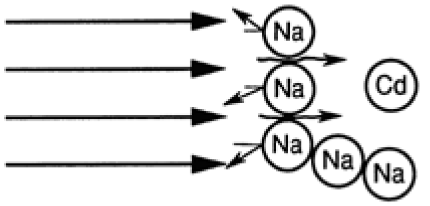
A: In a photoabsorption measurement, an analytical line may be darkened due to causes other than absorption by a target metallic element.
This darkening is called background.



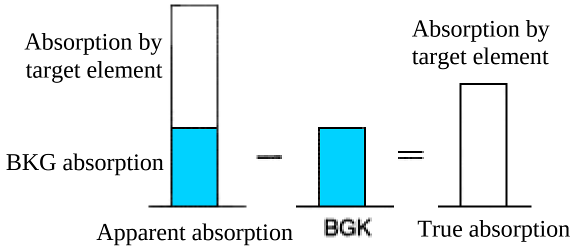
For example, in the case of sodium chloride (NaCl) in sea water, the wavelengths absorbed by Na, cadmium (Cd), and nickel (Ni) are overlapped.



For a specimen containing a large quantity (several percent) of NaCl, like sea water, a trace amount of (ppm) Cd or Ni cannot be measured accurately. If the background absorption is not corrected accurately, the measurement result will be ruined.



Scattering of light



BKG correction method of atomic absorption photometer

(1) Polarized Zeeman method
(2) D_2 correction method
(3) HCL self absorption method

8. Background Correction Method (BKG)

Let's see how BKG is corrected, in principle.

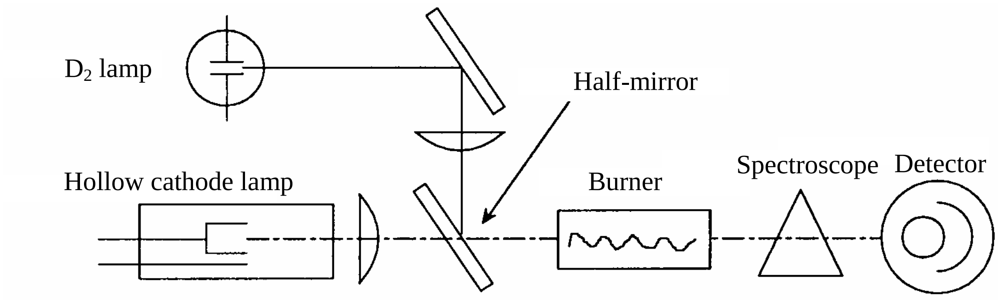
However, before that...
"How to measure only the background absorption" is the point.

1) D_2 (deuterium lamp) correction method

A hollow cathode lamp and a D_2 lamp are used as light sources (The following diagram shows the optical system).

Please imagine that there are two photometers, one using an HCL as its light source, and one using a D_2 lamp as its light source.

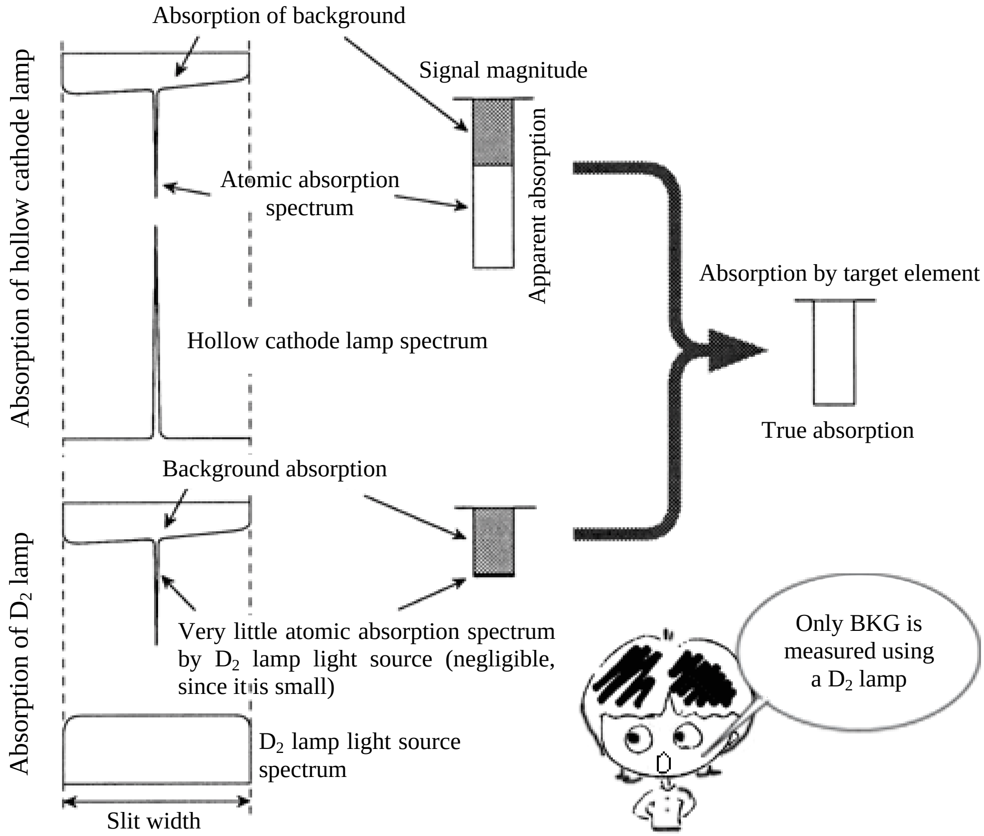
The signals from the two photometers are electric signals which are processed and distinguished.



(1) Photometer using HCL as its light source: Measures atomic vapor absorption + BKG absorption.

(2) Photometer using D_2 lamp as its light source: Measures only BKG absorption.
This is the point. When a D_2 lamp is used as the light source, the wavelength interval is dependent on the slit width of a spectroscope, which is much larger than the atomic absorption lines (refer to 'Principle of Atomic Absorption Photometer'). Thus, most of the absorption by atomic vapor is hardly observed (Actually, there is very little absorption).

From (1) - (2), true atomic absorption can be measured.



2) Self-absorption correction method

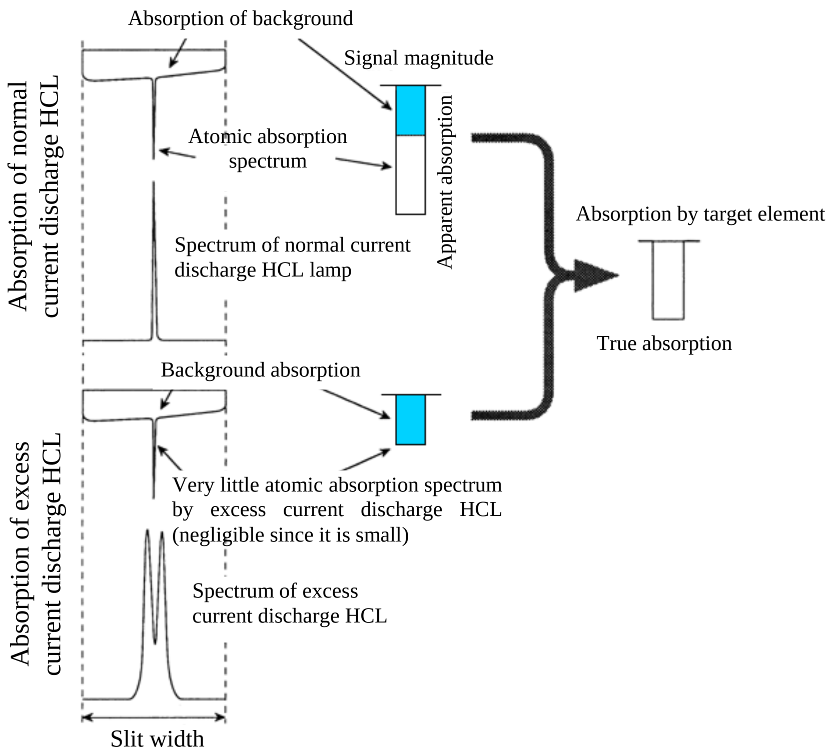
A lighting method for a hollow cathode lamp (HCL) is devised.

(1) It is normally lit for a certain period. Then, it is lit for a short period with an excess current. This is repeated several tens of times per second.

(2) Repeatedly, the following spectra can be obtained.

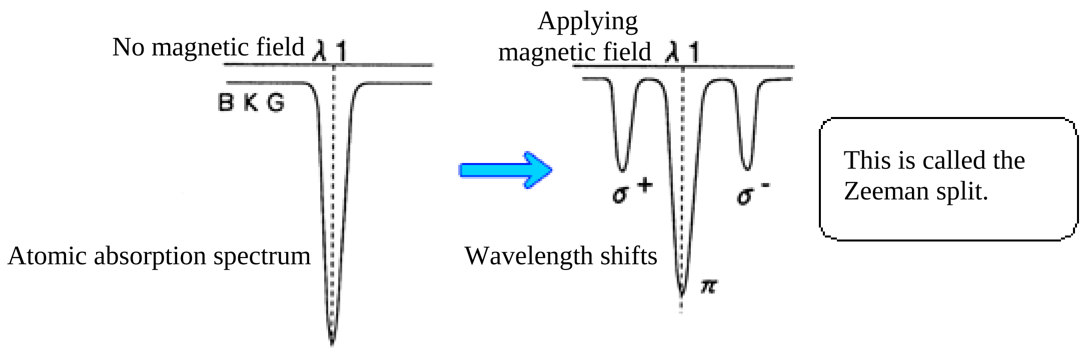
Spectrum of normally lit HCL lamp   Spectrum of HCL lit by excess current

The self-absorption correction method uses the spectrum obtained by lighting with an excessive current instead of the D_2 lamp light source spectrum of the previous section.



3) Polarized Zeeman correction method

When a magnet is set in an atomization section to apply a magnetic field to the atomic vapor, the absorption spectrum of the atomic vapor will be split, showing the polarization property. On the other hand, the background (BKG) is not affected by the magnetic field, showing neither a split nor the polarization property. It is the Zeeman correction method which uses this phenomenon.

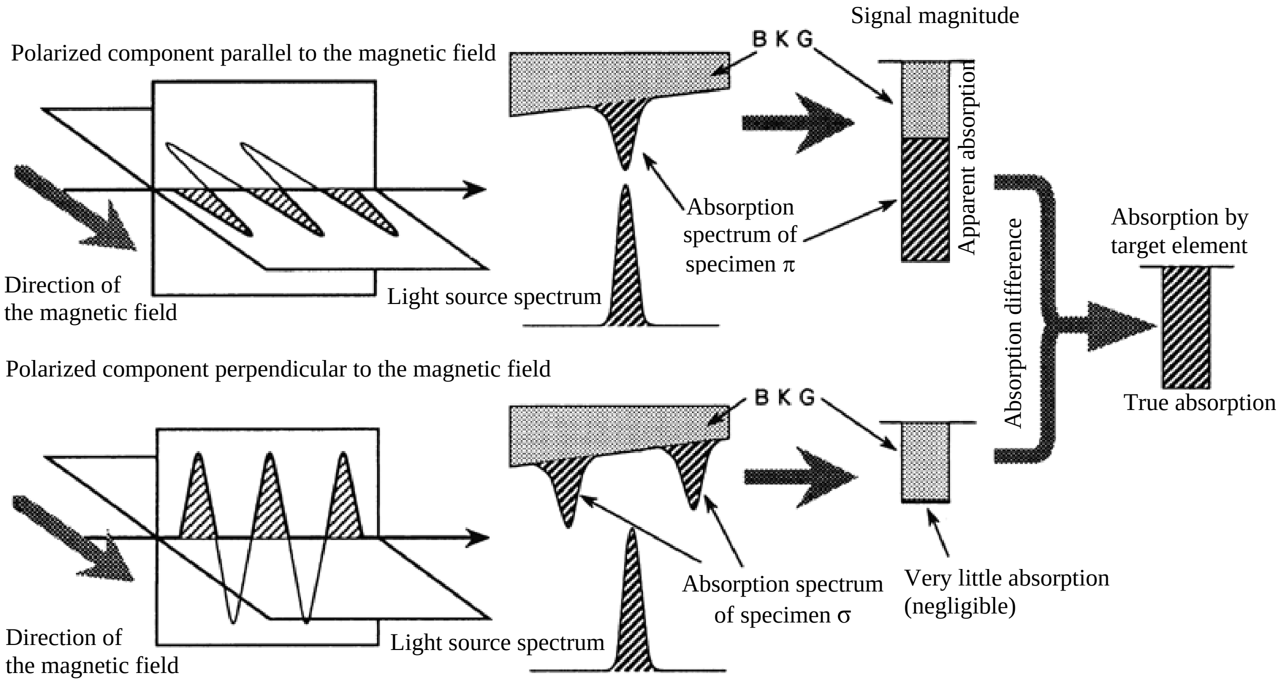


When a magnetic field is applied the atomic vapor, it is split into

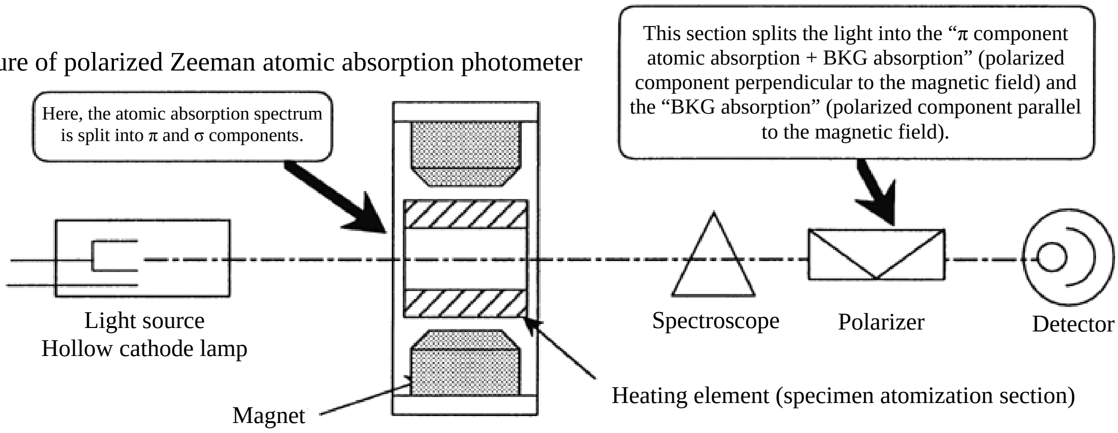
- Atomic absorption spectrum polarized parallel to the magnetic field <π> , and
- Atomic absorption spectrum polarized perpendicular to the magnetic field

For the component of the light source polarized parallel to the magnetic field, "π component atomic absorption + BKG absorption" is observed. However, only "BKG absorption" is observed for the component polarized vertically to the magnetic field.

(Since the σ component, which causes atomic absorption is shifted from the measurement wavelength, it does not cause atomic absorption.)



Structure of polarized Zeeman atomic absorption photometer

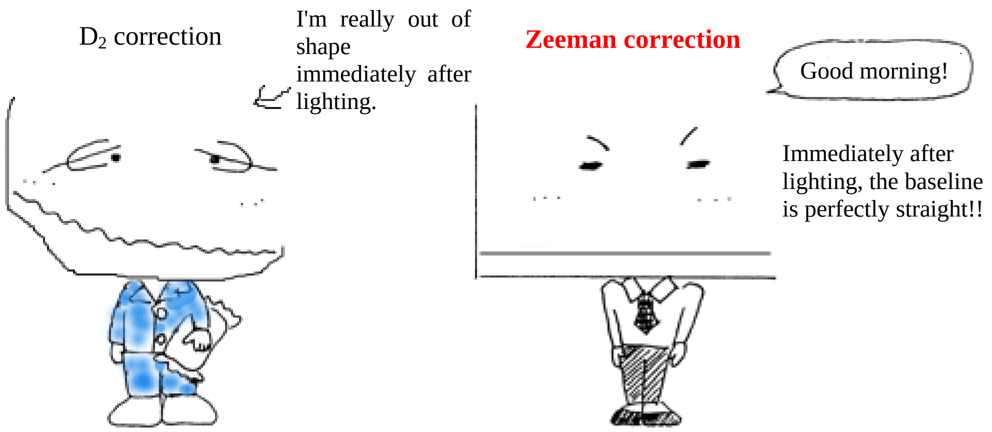


A. "What are features of the Zeeman correction method?"

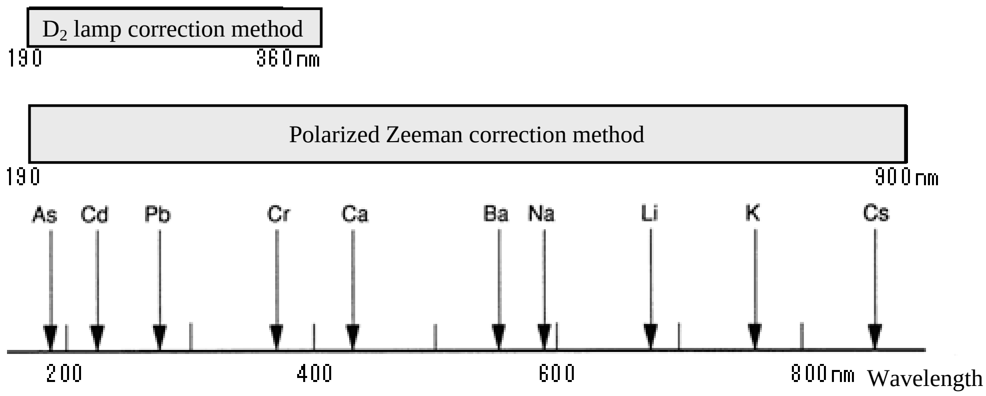
(1) Since t is a double beam measurement system in which the light parallel to the magnetic field (apparent atomic absorption line) and the light perpendicular to the magnetic field (BKG absorption line for subtraction) traverse the same optical path (one beam is split into two, with the polarizer), there are no drifts, leading to a stable baseline.

The D_2 (deuterium lamp) correction method and the self-absorption method measure two kinds of beams with different characteristics. Accordingly, the system is called a single beam measurement system.

Since this system does not measure two kinds of beams under the same conditions, the baseline may drift.



(2) The Zeeman correction method can cover the whole wavelength region.



D_2 correction method	1) Only the ultraviolet region can be corrected.
	2) The electric heating furnace atomization method features poor performance.
Self absorption method	1) Some elements cannot be measured.
	2) Since the hollow cathode lamp is lit irregularly, deterioration is promoted.