



Review Article

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### Flame atomic absorption Spectroscopy (FAAS)

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#### Abstract

The role of the aerosol in atomic absorption spectroscopy is considered and theories of the production of aerosols by pneumatic and ultrasonic devices are outlined. The predicted droplet size is related to sensitivity and interference by Al and Si in the estimation of Mg. Experiments using pneumatic and ultrasonic (70-kHz and 115-kHz) nebulizers at sample flow rates from 0.05 ml/min to 3.5 ml/min and with spray chambers of 100-cm<sup>3</sup> to 500-cm<sup>3</sup> capacity are reported. The results obtained indicate that ultrasonic nebulizers must be operated at high frequency (>500 kHz) and high power to generate fine aerosols (~5-μm) at sample flow rates of 1–5 ml/min if they are to be an improvement in sensitivity and interference on the pneumatic nebulizer.

**Keywords:** flame atomic absorption spectroscopy, sensitivity, nebulizer, flow rate.

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### 1. Introduction

The optical methods of chemical analysis make up a large group. From this group we will only deal with optical spectroscopy. In optical spectroscopy the light is resolved to components which have different wavelengths. The methods in this group can be divided into two categories: atomic spectroscopy and molecular spectroscopy. Methods in the first category are capable for the elemental analysis of substances, while with methods belonging to the latter category molecular composition can be determined.

### 2. Development of atomic spectroscopy

Flame coloring was used for the identification of sodium and potassium as far back as 1758 by Margrave. The investigation of the spectrum of the sun was a milestone in the development of atomic spectroscopy. Wollaston was the first who noted the presence of black lines in the spectrum of the sun in 1802, but he did not know the reason of it. It was Fraunhofer who could explain the presence of these lines in 1815, whom after they are called fraunhofer

lines. The best known of them is the yellow D line of sodium. In 1822 Hershel noted that the spectrum of the flames containing some salts can be used for the identification of the salts. It was the beginning of spectroscopy. Bunsen and Kirchhoff in their common article in 1859 explained the structure of spectrum of colored flames: when we transfer energy to the atoms of certain gases, they emit a characteristic spectrum consisting of lines. Furthermore these atoms can absorb light having the same wavelength as the wavelength of the emitted ones. These findings led to the discovery of new elements such as Cs, Rb, He. The first flame spectrograph was built in 1928; which could be used for the quantitative determination of elements. The real advance was the emerge of the atomic absorption spectrophotometer in 1957 equipped with electric parts and proper light source based on the results of Welch's and coworkers.

#### Flame spectrometry includes three methods:

##### a) Flame emission spectroscopy (FES):

We measure the intensity of molecular bands or atomic or ionic lines emitted by excited molecules, excited atoms or even by excited ions.

##### b) Flame atomic absorption spectroscopy (FAAS):

We let through the fire a light beam with such a wavelength that can be absorbed by ground state atoms and thus we measure the decrease of light intensity.

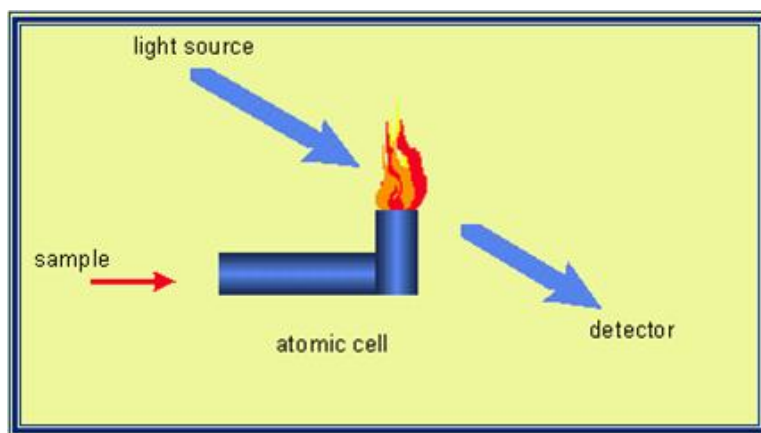
##### c) Atomic fluorescent spectroscopy

We irradiate the ground state atoms with an external light source, however we measure the intensity of emitted light at the characteristic wavelength instead of the decrease of light intensity due to the absorption of light.

The greatest importance is credited to FAAS. FES can be applied at a much smaller application field. Although AFS is rather sensitive, the potential of the method compared to FAAS only for a few elements is comparable, thus it is relatively less popular. Recently flameless atomization (graphite furnace atomic spectroscopy, GFAAS) keeps getting more and more significant since it has small sample volume demand, high sensitivity and good detection limits.

#### Principle:

The technique of flame atomic absorption spectroscopy (FAAS) requires a liquid sample to be aspirated, aerosolized, and mixed with combustible gases, such as acetylene and air or acetylene and nitrous oxide. The mixture is ignited in a flame whose temperature ranges from 2100 to 2800 oC. During combustion, atoms of the element of interest in the sample are reduced to free, unexcited ground state atoms, which absorb light at characteristic wavelengths, as shown in figure 3.



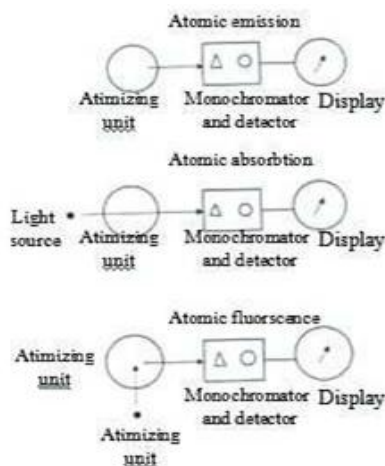
**Figure 3:** Operation principle of an atomic absorption spectrometer.

The characteristic wavelengths are element specific and accurate to 0.01-0.1nm. To provide element specific wavelengths, a light beam from a lamp whose cathode is made of the element being determined is passed through the flame. A device such as photomultiplier can detect the amount of reduction of the light intensity due to absorption by the analyze, and this can be directly related to the amount of the element in the sample.

### 3. Construction of flame spectrometers

Most parts of flame spectrometers are very similar or the same, thus the commercial flame atomic absorption spectrometers can be used as flame emission spectrometers as well (Fig 1). In case of FES the delaminated particles (excited atoms) are produced by the flame itself. For FAAS and AFS measurements to excite ground state atoms external light source is needed. In FAAS the light of the light source (to be more precise that part of the light which is not absorbed) gets directly to the light resolving unit, the monochromator (the light source, the flame and the

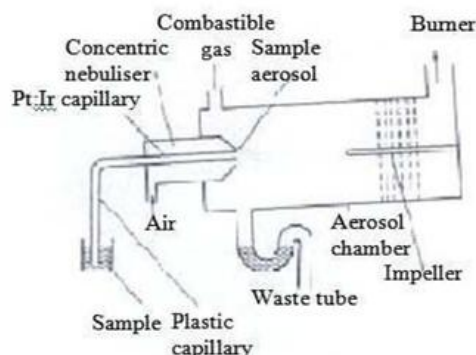
monochromatic are arranged in such a way that they are in one line). Although in AFS the light of the light source cannot get to the monochromator thus we measure only the intensity of secondarily emitted light. In newer instruments the light resolving unit (monochromator) is the diffraction grid, the detection of the light is attributed to the photomultiplier. The signal processing/displaying unit of the photometers can be very different (analog/digital displays, graphical recorders), but the modern spectrometers are equipped with computers.



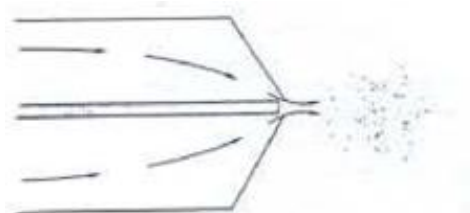
**Figure 1:** Principles of instruments used for atom spectrometric methods

### 3.1 Sample introduction

The aim of sample introduction is to introduce samples (mostly liquids) to the flame with good reproducibility and with high efficiency so that the interfering effects should remain minimal (the liquid must be introduced as fine aerosol). The sample introduction is most often spraying the liquid. The small droplets formed in the mobilization transform gradually while going through the high temperature zones of the flame. It is an important aspect that the particle size of the droplets ( $<5\mu\text{m}$ ) should be possibly in similar size ranges in order the particles to be desolated and to be further transformed in the same region of the flame for the mobilization of solutions the indirect pneumatic mobilization is the most frequently used method which has a sample introduction efficiency about 10%. In Fig. 2. the structure of a typical pneumatic system used for premixed flames can be found. The sample gets into the nebulizer through a plastic capillary. In the nebulizer shown in Fig. 3 the sample leaving the capillary is surrounded by the gas (air) feeding the flame. After this high speed gas comes out through the tight emergent hole of the nozzle pressure decrease is established in the capillary which results the take up of the liquid. By the way the high speed gas breaks the uptake liquid into small drops thus aerosol is formed. The latter phenomenon is called Ventura effect (Fig. 4.)

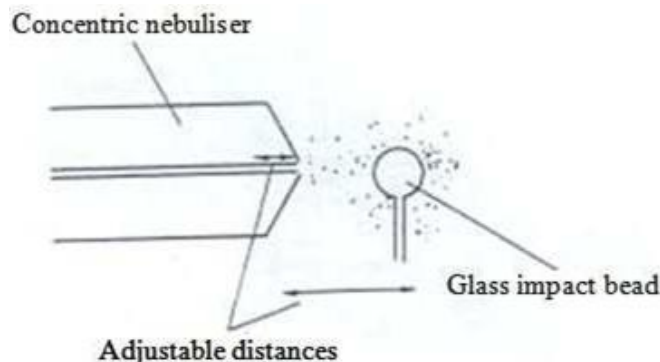


**Figure 2:** Structure of concentric pneumatic mobilization system



**Figure 3:** Ventura effect

The position of the nebulizer's capillary can be adjusted by a screw and by this way the sample take up speed and the aerosol size distribution can be optimized. The size distribution of the formed primer aerosol is further refined by a glass impact bead placed in front of the nebulizer (secondary aerosol is formed). The larger drops of the aerosol hit the impact bead, however, the smaller ones can go round of it without precipitating.



**Figure 4:** Role of impact bead in the development of secondary aerosol

### 3.2 Types of burners and flames

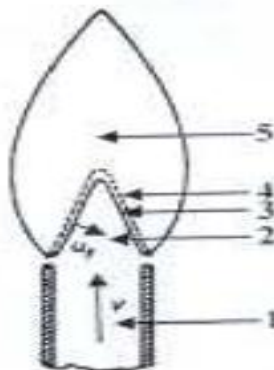
In the first spectrometers meeker burners were used. These burners are actually such tubes that are covered from one end with a plate containing several holes. The application of this burner is appropriate for flames with slow burning speed. Nowadays burners with slots are the most frequently used burner types. The 10 cm long slot is favorable especially for the absorption measurements in air/acetylene flame. In the design of slotted burners the width and the length of the slot, and the heat conducting property of the material of the burner is of great importance. The temperature of the most commonly used burners is in the range of 2200-3300 °C (table 1.). In this temperature range only the spectrum lines having higher excitation energy than 4.5 eV can be excited.

The emitted light of the flame is sophisticated. In case of the most commonly used air/acetylene flame the emission spectrum consists of the followings:

- From the background radiation of flame (excited radicals of solvent and flame gases)
- From molecular bands and spectral lines of excited atoms in the flame

Table 1: Gas mixture composition	°C
Hydrocarbon (methane, propane-butane) – air	1900
Acetylene - air	2300
Hydrogen - oxygen	2700
Acetylene - dinitrogen-oxyde	3000
Dicyanide - oxygen	4500
Carbon sub nitride – ozone	5300

The flames can be categorized from several points of view. One is based on the mixing way of the combustible gases and the combustion feeding gases. When the gases are mixed before the combustion as in the case of Bunsen burner (Fig. 5.), we can speak about premixed flame. When the oxygen feeding the combustion gets to the flame from air, the flame is called diffusion flame as in the case of the flame of a candle.



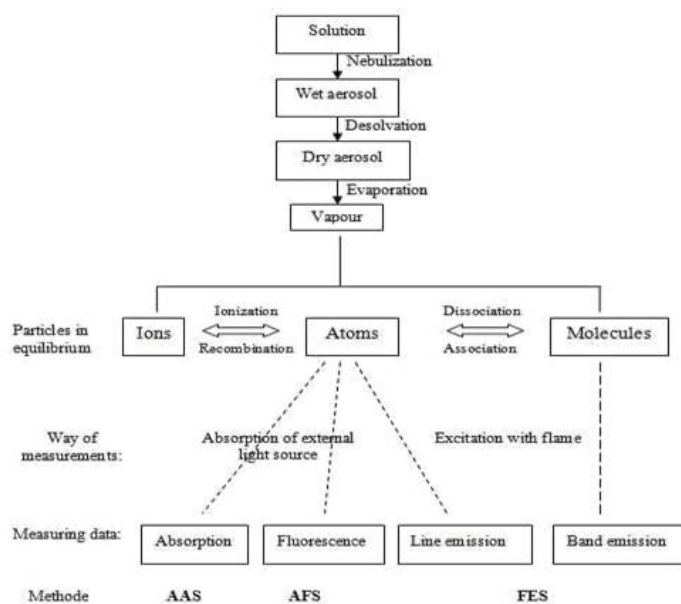
**Figure 5:** Schematics of Bunsen flame

1 open end of the burner; 2 preparing zone; 3 reaction zone; 4 inner combustion zone; 5 outer combustion zone;  $v$  is the flow rate of the gas mixture;  $o_f$  is the rate of combustion of the flame

We make difference between the flames on the basis of the flow rate of the components and the rate of the burning, thus flames that have smaller Reynolds number ( $Re$ ) than 2300 are called laminar flames. In case of higher Reynolds number that is at higher combustion rate the flame is turbulent. Stationary, standing flame is established when the flowrate of the flame ( $v$ ) is the same as the rate of burning in the opposite direction ( $o_f$ ). When  $v > o_f$  of the flame is blown off, and when  $v < o_f$ , the flame „burns back”

### 3.3 Processes occurring in flame

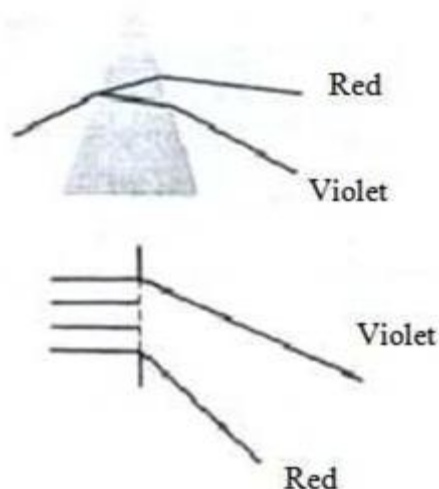
From the liquid drop the solvent evaporates first, and solid aerosol particles (micronized crystals of salts) are formed, in the next step it loses its crystalline water (if possessed) then the crystals melt and evaporate that is molecule vapour forms. In the higher regions of the flame the thermal dissociation of the molecules occurs: ground state atoms are formed (for atomic absorption measurements only these particles are useful). Of course, when the temperature of the flame makes it possible, the thermal processes go further, by the side of the ground state atoms excited atoms, even ions will be present in the flame (these excited particles are useful only for emission measurements).



### 3.4 The resolution of light

The light leaving the flame is led to the detecting unit with a proper optical device. Due to the background radiation of the flame and the emission of the other metals present in the flame with direct measurements we cannot get proper results. By the help of an optical device we try to eliminate the interfering radiations and we let only the almost monochromatic, to the investigated metal characteristic light to the detector. While formerly this function was tried to be fulfilled with color filters, nowadays nearly there are only monochromators in use. The monochromators are capable for the separation of small wavelength ranges with 0,01-1 nm width in a wide (190-800 nm) spectrum. The two major type of monochromators are prisms and optical (diffraction) grids. The desired wavelength is set by rotating the prism or diffraction grid. Although by increasing the size of the slit, the intensity of the light increases, however, the purity of the spectrum decreases. The material of the prism in UV range is quartz while in UV visible range glass. The advantage of the prism type monochromators is that they provide a spectrum with high light intensity although it has a disadvantage too: the resolution is low

The diffraction grid is such a glass, quartz or secular metal surface, on which there are parallels scratches near to each other at a same distance (1000-4800 crutch/mm). The intermediate space between the scratches are transparent to light while the scratches themselves do not let the light through. Owing to the high number of scratches the deflection interference pattern we get contains sharp maximums (Huygens principle). A grid irradiated with white (that is blended) light diffracts the different wavelength (that is different coloured) light beams in different direction, thus it acts like a prism. Thus the grid splits up white light into homogeneous colours. In Fig. 7. the light pathway of some component of dispersion and diffraction spectrum can be seen produced by prism and diffraction grid. Table 2. shows the wavelengths related to different colors.



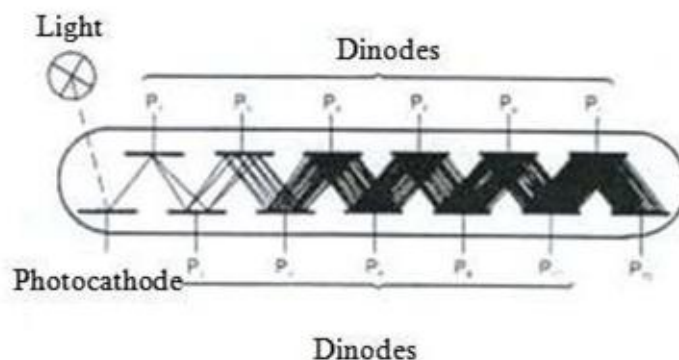
**Figure 7:** Light pathway of some components of dispersion and diffraction spectrum produced by prism and diffraction grid

**Table 2:** Wavelengths related to different colors

Shade of colour	Wavelength (nm)
Red	721
Reddish orange	656
Orange	600
Yellow	589
Green	495
Bluish green	490
Blue	410
Violet	396

### 3.5 Detectors

The light intensity passed through the detector can be measured with different measuring devices. In the beginning of flame photometry photographic light measurements were used, but nowadays instead of them solely photocells or photomultipliers are in use. The multiplying factor of photomultipliers might be as well 10<sup>10</sup>. The principle of photomultipliers (Fig. 8) is the following: Photons impacted to K photosensitive cathode produce electrons which flow towards the P1 dynode due to the potential between P1 dynode and K cathode. Electrons impacting to P1 dynode create a secondary electron emission of which intensity is larger than the primer electron current. This process is repeated on the following (P2-P11) dynodes until the anode. The number of electrons increases exponentially with the number of dynodes.



**Figure 8:** Schematics of photomultiplier

## 4. Flame emission spectrometry (FES)

Flame emission spectrometry is the quantitative application of the well known flame coloring probes. As we mentioned it earlier, even the alchemists knew that some materials change the color of a colorless (spirits of wine) flame. The atoms of some elements in form of volatile compounds are excited, ionized even in the few hundred °C temperature gas flame. The absorbed thermal energy is emitted in form of light with characteristic wavelength

(characteristic color). Especially the alkali metals and alkaline earth metals have this property, the atoms of other elements get atomized at more higher temperature- even at several thousand degrees. When we moisten a solid substance with hydrochloric acid and carry it on an O-shape ended platinum wire and put it into a colorless flame, we can observe a flashing light. We can make our measurement more precise when we detect the colored light instead of with our eyes with a simple spectroscope. In this case the wavelength of the colorful lines appearing in the visible spectrum (400-800 nm) can be determined as well.

The theoretical bases of flame emission measurements are that when an atom absorbs an energy quantum it is converted to excited state. When the excited atoms return to ground state, photon is emitted. For example when we heat a piece of glass in a flame, the observed yellow color of the flame is credited to the presence of sodium atoms in the glass. The frequency or the wavelength of the emitted light can be calculated from the energy of the light:

$$E = h\nu = \frac{hc}{\lambda}$$

Where h is the Planck constant ( $6.62 \cdot 10^{-34}$  Js),  $\nu$  is the frequency of the light,  $\lambda$  is the wavelength, c is the speed of light in vacuum ( $3 \cdot 10^8$  s)

The excitation energy and the wavelength of the emitted light is characteristic to the atom. The number of atoms in excited state grows exponentially with the temperature. The atoms stay in excited state for about  $10^{-8}$  sec than the atom emits a photon spontaneously. In flame emission spectrometry the sample is introduced to the flame and the intensity of the emitted light is measured. We measure the light intensities in case of known concentration samples and with the help of this calibration curve we can determine the concentration of unknown samples.

Flame emission spectrometry is a rapid and cheap method which can be used for the analysis of readily excitable alkali and alkaline earth metals. The other elements cannot be excited due to the relatively low temperature of flame. Nowadays this method is used mostly in medical diagnostics for the determination of sodium and potassium level in blood and other bodily fluid. The application field can be significantly expanded by using higher temperature flame (dinitrogen-oxide/acetylene flame).

### 5. Flame atomic absorption spectrometry

Flame atomic absorption spectrometry is a quantitative analytical method based on measuring the light absorption of free, ground state atoms. The ground state atoms are excited by electromagnetic radiation (light), while absorbing photons having equivalent wavelength with the excitation energy. The absorption spectrum of atoms (similarly to emission spectrum) is line spectrum. The lines are present at exactly determined wavelengths and they have a very small, approximately 0,001 nm FWHM (full width at half maximum). This type of absorption spectrum of atoms gives the high selectivity of atomic absorption spectrometry. At the best line of a given element the probability of absorption of other elements is very low thus complex systems containing several elements can be analyzed without the separation of elements. This procedure has great advantage to molecule absorption spectrometry methods where there is a higher probability of optical interfering effect due to the band absorption and usually the analysis of complex systems is possible only after the application of separation techniques. With atomic absorption we measure the concentration of free atoms in the atomizing unit. The relationship between the decrease of light intensity at the wavelength of the examined metal and the concentration of free atoms in a unit of volume is described by Lambert-Beer law as follows:

$$A = \log \frac{I_0}{I} = a \cdot c \cdot l$$

Where A=absorbance

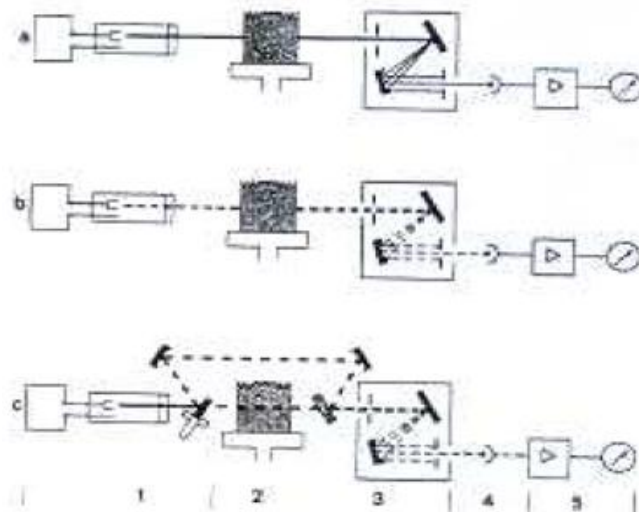
$I_0$  = initial light intensity before absorption  $I$  = Light intensity after absorption

a = absorption coefficient (constant depending on material properties)

c = number of free ground state atoms in the atomizing unit (flame) l = length of way passing the light in the atomizing unit

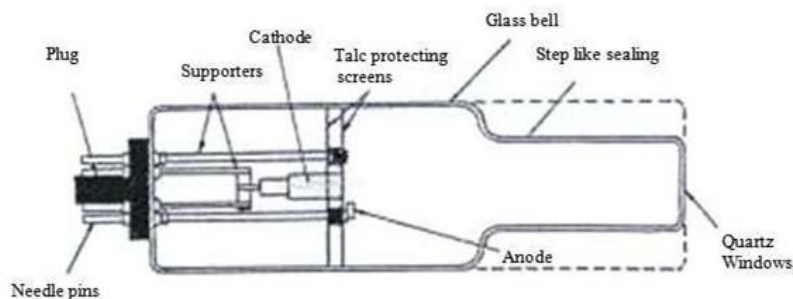
Thus the absorbance is directly proportional to the number of free, ground state atoms in a unit of volume. Furthermore the number of free atoms in the flame is proportional to the concentration of analyze in the solution. When the concentration is doubled, the number of ground state atoms in the atomization unit is doubled as well. (Of course only when the parameters of analysis of sample and calibrating solutions are the same.). In order to perform atomic absorption measurements the light of the light source producing characteristic, sharp spectrum of the element

to be measured should be led through the flame where the aerosol is present in form of fine spray. The narrow range of the spectrum containing the resonance line of the element is separated from the other part of spectrum with a monochromator. The selected resonance line gets to the light sensing detector (like photomultiplier), of which signal is amplified. To exclude the emitted light of the flame, the light of the light source is chopped with a chopper and in the detector it gives alternating current, while the background radiation of the flame gives direct current. Based on the implementation of it, there are single beam (Fig. 9. a and b.) and double beam photometers (Fig. 9. c.).



**Figure 9:** Arrangement of single beam (a, b) and double beam (c) atomic absorption spectrophotometers (1 light source; 2 flame; 3 monochromator; 4 detector; signal processing and displaying unit).

For atomic absorption measurements light sources providing intensive line spectrum are needed and the FWHM of the emitted lines should be small. The hollow cathode lamp (HCL) is such a light source which is a special discharge tube (Fig. 10). The cathode is made from the material of the examined element and it has a cylindrical shape. The discharge is established due to the 300- 400 V potential put between the cathode and anode resulting the electron emission of the cathode. Accelerating the electrons in the electric field gives rise to the avalanche-like ionization of the filling gas of the HCL. Noble gas ions travelling at high speed impact to the cathode and metal atoms are torn out from the surface of the cathode (cathode atomization). The free atoms of the examined elements are produced by this way. These atoms collide with the noble gas ions travelling at high speed and a line spectrum characteristic to the desired element is emitted. HCLs are usually monoelements thus lamps are need to be changed when turning to the measurement of a new element.



Each elements those have resonance line in that range of the spectrum which can be measured by the detector can be determined with AAS. Most of the instruments can be used in UV and visible range (190-800 nm). Noble gases, halogens and C, H, S, O, N, P cannot be determined since the resonance line of these elements is under 190 nm. The elements of which oxides do not decomposes in flame or which produce oxides or hydroxides in flame can be determined difficultly.

## 6. Conclusion

Flame atomic absorption spectroscopy is used for absorption of elements and excitation of energies. Also absorption of elements like heavy metals and other light emitted energies and elimination of light sources in noble gases and accelerating the electrons in the electric field and it is the most wanted advanced technology. Other technology coming is flame agitation absorption spectroscopy. Flame atomic absorption spectroscopy we can determine the wavelength and the light absorption with the droplets present in the excitation of energies.



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