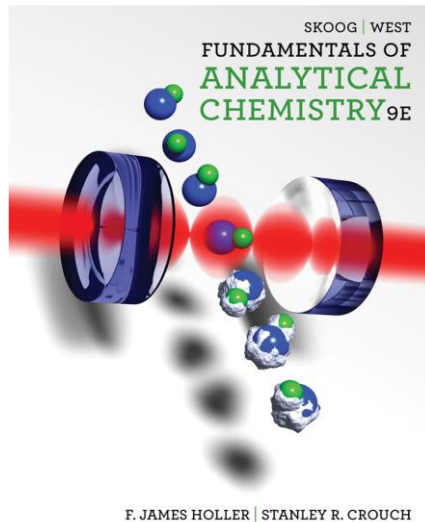


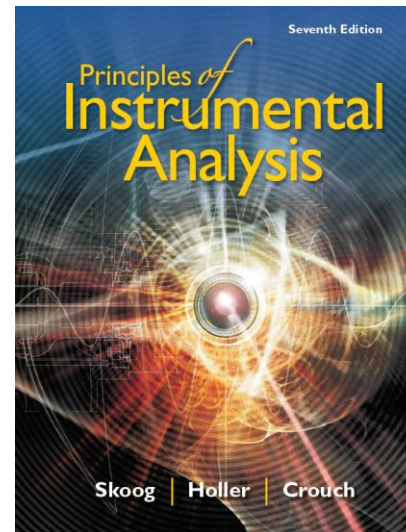


These materials have been prepared by H. Elif Kormalı Ertürün for educational purposes only (as lecture notes) using the following resources. Responsibility for reproducing any part of these materials in any form or by any means or stored in a retrieval system for different purposes, rests with the third person performing the action.

1.



2.



3.

ATAKOL's lecture notes

1. Skoog, D.A., West, D.M., Holler, J.F., Crouch, S.R. 2013. Fundamentals of Analytical Chemistry (9E). Cengage Learning, Belmont, USA.
2. Skoog, D.A., Holler, J.F., Crouch, S.R. 2016. Principles of Instrumental Analysis (7E). Cengage Learning, Boston, USA.
3. Prof. Dr. Orhan ATAKOL's lecture notes.

LOD, LOQ and Calibration in AAS Methods

The relationship between the analyte concentration and absorption is directly proportional and is expressed as $A = \epsilon l C$ (Lambert-Beer Law).

A = absorption intensity

ϵ = molar absorption coefficient

l = length of the pathway

C = analyte concentration

Atomic Absorption spectroscopy is based on at high temperature atomized analytes absorbing light from a source producing light specific to that analyte.

For this reason, AAS is classified according to the high temperature method which using for atomization. Elevation to high temperature is mainly in 2 ways:

1- Analyte solution is sprayed homogeneously into a flame (FAAS)

2-The analyte solution (or it may be in solid form) is atomized by electrically heating in a furnace (ETAAS or GFAAS)

Other than these, there are methods of atomizing with electric arc, but their use are limited. In the early 1960s, hydride-generation systems began to be developed, but hydride-generation systems are a different application of FAAS.

The higher the number of electrons that switch to orbital at the upper energy level during absorption, the more intense the absorbance is. In this case, the ability to determine the absorbance value at lower concentrations with higher accuracy means that the limit of detection is lowered. The number of electrons passing to the upper energy level conforms to the Maxwell-Boltzmann distribution formula:

$$(N_e / N_0) = (P_e / P_0) \times e^{- (E / kT)}$$

N_e = the number of excited atoms,

N_0 = the number of atoms in the ground state,

P_e = the number of atomic states in the excited state,

P_0 = the number of atomic states in the ground state,

E = the energy of light used in excitation,

k = Boltzmann constant, 1.38×10^{-23} J / (atom.K),

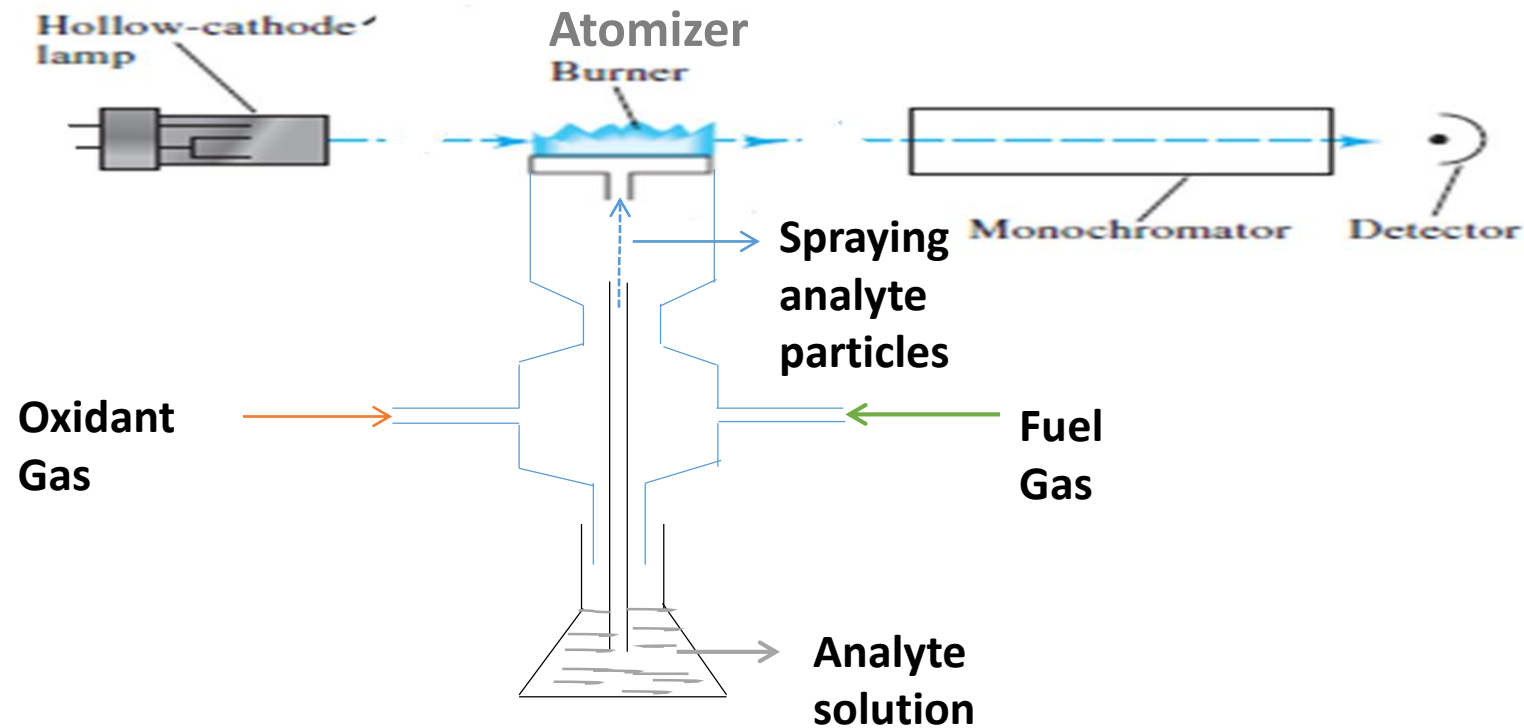
T is the absolute temperature.

TYPES OF ATOMIZATION

- 1- Flame Atomization (FAAS)
- 2- Electrothermal (ETAAS) or Graphite Furnace (GFAAS) Atomization
- 3- Atomization with Electric Arc
- 4- Hydride Generation Atomization (HGAAS)
- 5- Cold Vapor Atomization (CVAAS)

Flame Atomization (FAAS)

In the FAAS method, the flame is a long or thin flame with a length of 10 or 5 cm and a thickness of 0.5-1.0 mm. The flame is placed in the longitudinal full light path and the analyte solution is sprayed into this flame as nebulized. Nebulizing is carried out by dragging the liquid with the help of the gases used. Glass or teflon parts that make nebulizing are usually called nebulizers.



As shown in the figure, both fuel and oxidant gases are delivered to the flame head and its ratio is important for analysis. The result of the analysis at a certain fuel / oxidant ratio and the analysis at a different rate may not overlap. Because this ratio determines the flame temperature. The type of gases used affects the flame temperature.

Flame is not a stable environment. First and foremost, it fluctuates with a breeze in the air. It is also a complex matrix environment. For this reason, the limit of detection (LOD) in the analyzes carried out by flame atomizer is in ppm levels. A further disadvantage of the method is that the sample must be in solution form.

Electrothermal (ETAAS) or Graphite Furnace (GFAAS) Atomization

Due to some disadvantages of flaming atomization, graphite cuvette method has been developed as a more stable and less material containing medium. Graphite cuvettes are cylindrical containers made of graphite with 3-5 cm length and 5-6 mm diameter and 0.2-0.5 mm wall thickness.

Since graphite is carbon, it is conceivable why it does not catch fire at 2000 °C. During drying and ashing, continuous Ar gas is passed through the graphite furnace to avoid contact with air oxygen. The graphite furnace only comes into contact with air for a short time during reading. The limit of detection in the graphite cuvette method is almost 1000 times lower than FAAS, since there are no flame negativity in the environment.

The limit of detection in ETAAS is at ppb level. Solid and liquid samples can be studied. The power supply is controlled and homogeneous.
(advantage)

However, it is a time consuming method. Since inert gas is constantly consumed, it is expensive. (disadvantage)

Atomization with Electric Arc

In this method, an electric arc is created between two parallel graphite cuvettes. It makes it possible to increase the temperature up to 4000 °C for materials that are difficult to atomize such as Mo, W, Ti, V.

However, the reproducibility of the electric arc generated in this method is not good and the reproducibility of the results is not good either. The limit of detection is at ppb level.

Hydride Generation Atomization (HGAAS)

This method is used in the analysis of Se, Te, As, Sb, Bi, Pb, Sn, Ge which can form volatile compounds with boron hydrides. It is a modified form of FAAS.

The analyte solution is treated with NaBH_4 and the resulting volatile hydride is introduced into the T-shaped quartz tube placed in the flame by means of an entraining gas such as Ar.

Since the treatment of the analyte with boron hydrides prevents interference from the matrix environment, the limit of observability is reduced to 0.1 ppb. (advantage)

However, the method can only be used for the determination of 8 elements. (disadvantage)

Cold Vapor Atomization (CVAAS)

It is an atomization technique used only for Hg determination. Mercury is the only metallic element with sufficient vapor pressure even at room temperature.

The atomization apparatus is the same as in the hydride. But there is no flame. Mercury is first converted to Hg^{2+} with the aid of an oxidizing acid such as HNO_3 or H_2SO_4 . It is then reduced to the elemental state with SnCl_2 . This mixture is drained into the T pipe by means of an inert gas. The limit of observability is in the order of ppb.