

Experiment 9

Determination of Zinc in Aqueous Solution by Atomic Absorption Spectrophotometer

Instrument

Atomic absorption spectrophotometer and accessories

Hollow cathode lamps, Zn

Compressed air, and acetylene with regulator valves

Introduction

To analyze a sample by atomic absorption, it is heated to a high temperature most commonly in a flame. After evaporation of the solvent, the flame dissociates chemical bonds and release free metal atoms which absorb light that is characteristic of the individual elements. The band of wavelength at which each element absorb is narrow and almost unique. The unexcited atoms absorb light which raises the valence electron(s) to an excited state. For example, for calcium in a 2000 K flame, there are 1.2×10^7 atoms in the ground state for every atom in the excited atom. Some 65 elements can be determined with good precision and sensitivity by atomic absorption spectroscopy, in contrast to about 10 by the conventional flame photometric method.

The source of light for the atomic absorption spectrophotometer must produce a narrow band of adequate intensity and stability for prolonged periods of time. An ordinary monochromator is incapable of yielding a band of radiation as narrow as the peak width of an atomic absorption line (approximately $0.02 \sim 0.05 \text{ \AA}$). In order for Beer's law to be followed, a source of radiation which emits a line of the same wavelength as that used for an absorption analysis is essential. The radiation emitted must also be for excited state atomic lines of the element. To obtain these characteristics, hollow cathode lamps are employed which have cathodes that are constructed from the element of interest. The lamps are filled with argon or neon at low pressure, which ionizes when voltage is impressed across electrodes. The inert gas bombards the cathode, heating it and causing it to sputter; a metal vapor fills the area. Collision of metal atoms with gas atoms causes them to become excited and to emit light. Figure 1 illustrates geometric features of a hollow cathode lamp. lamps that contain several metals are available, which permit the determination of these elements simultaneously without changing lamps.

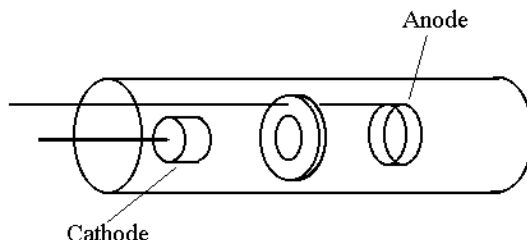


Fig. 1 Schematic of a hollow cathode lamp

A critical part of atomic absorption spectroscopy is the introduction of the sample into the flame and its vaporization and atomization to ground state atoms. Any method which results in a reproducible cloud of ground state atoms in the light path can be used in atomic absorption. In a typical flame

atomizer all or part of a solution is sprayed as a fine mist and spread throughout the flame. Fuel and oxidant are needed to produce a flame in which to burn a sample, the choice being dependent upon the type of burner used.

The optics of an atomic absorption spectrophotometer are similar to those in any type of spectrophotometer. The monochromator is adjusted to focus the wavelength of an atomic line for the element onto a photomultiplier tube in *the single-beam dc system*. A *double-beam ac system* has a chopper (rotating sector mirror) with a dual function : It divides the light into pulses which pass alternately through the flame and through a reference path. The sample and reference beams are recombined and the ratio of the intensity of two types of pulses is measured electronically. See Fig. 2 and 3 for single- and double-beam systems, respectively.

Quantitative determinations in atomic absorption spectrophotometry, like any other spectrophotometric method, rely on the applicability of Beer's law. Absorbance is directly proportional to concentration.

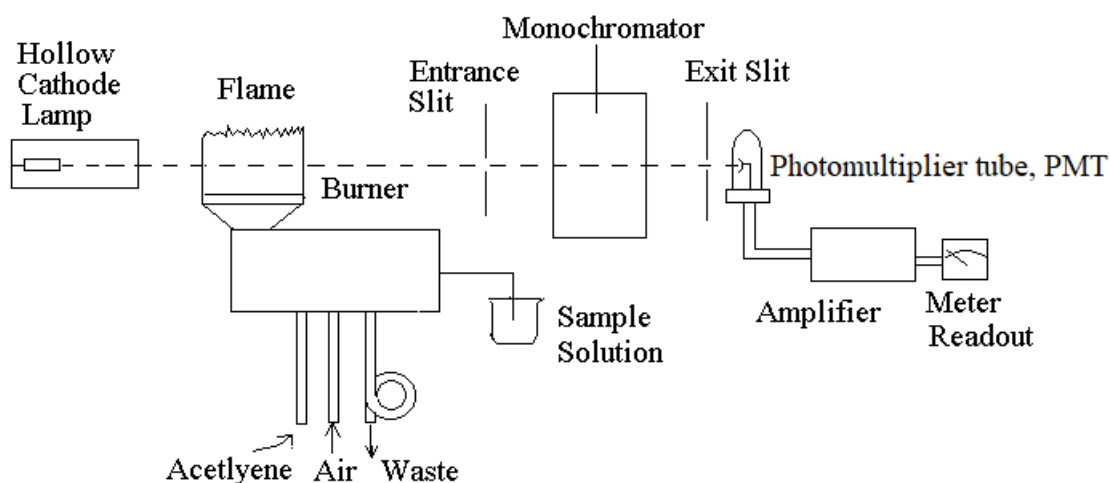


Fig. 2 Single-beam system

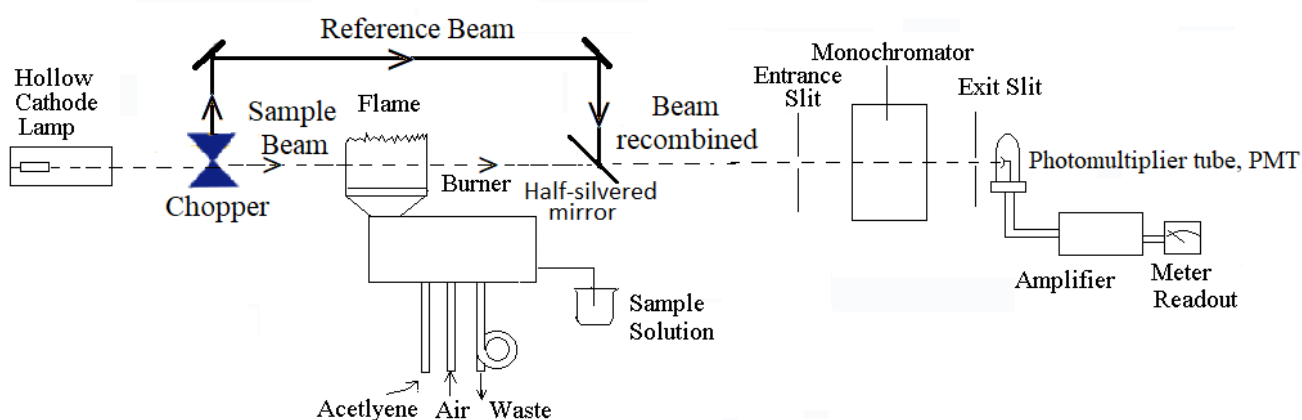


Fig. 3 Double-beam system

Quantitative Performance of the Instrument

Sensitivity and detection limit are terms used to describe the quantitative performance of an instrument. **Sensitivity** (for atomic absorption **only**) is defined as the concentration of the test element in aqueous solution which will produce a percent adsorption of 1 %, or an absorbance of 0.0044. It is expressed in terms of $\mu\text{g/ml}$ per 1 % absorption or $\mu\text{g/g}$ per 1 % absorption most frequently. The detection limit is the concentration which gives a signal twice the noise level of the background. Fig. 6 and 7 illustrate sensitivity and detection limit, which are determined at the primary resonance lines of elements for optimum operating conditions. If a signal of twice the background is less than the amount required for a 1 % absorption of an element at its primary resonance line, the presence of the element at the concentration for a given sensitivity can easily be measured. However, if the detection limit and the sensitivity are almost the same, a large percentage of the signal will be due to noise and the error in measuring that particular element at that concentration will be great.

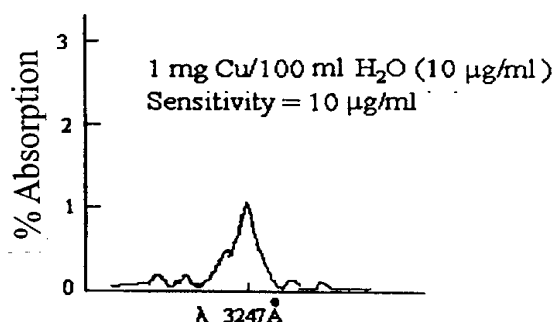


Fig. 6 The sensitivity of an atomic absorption spectrophotometer.

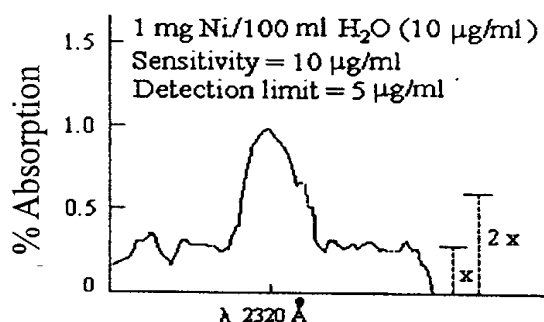


Fig. 7 The detection limit of an atomic absorption spectrophotometer.

Factors Affecting the quantity of the Material Reaching the Flame

Several factors affect the quantity of material that reaches the flame.

1. The rate of aspiration of the material to the flame: This is usually is affected by gas pressure and, sometime, by viscosity.
2. Viscosity of the material to be analyzed: A high concentration of dissolved solids will affect the rate of flow and cause it to move slowly through the aspirator.
3. Choice of solvent: Some organic solvents will increase the absorbance by a factor of two or four. Organic solvents also improve the efficiency of the aspirator because their surface tensions are also lower than that of water.
4. Surface tension of solvent: A lower surface tension allows smaller droplets to be formed. Smaller droplets permit more of the sample to reach the flame in the premix burner.

Temperature of the Flame

The percentage of atoms in the ground state is controlled by the temperature of the flame. Occasionally interfering element prevent the formation of ground state atoms. Sometimes, the element

to be determined forms compounds of stable complexes which do not dissociate into atoms at the same temperature as the calibration standard. For example, Phosphorus causes fewer calcium ions to be converted to free atoms than would be formed in its absence.

Calibration of Standards

Ideally, the calibration standard is in a similar matrix to that of the sample solution. If samples of area are to be analyzed for Zn^{2+} , then the standard solutions should be made to simulate spectrum.

Most elements produce a signal corresponding to 1 % absorption at a concentration of less than 1 $\mu\text{g/ml}$. Therefore, a solution of about 1 $\mu\text{g/ml}$ of any of these elements can readily be measured by atomic absorption. At concentration above 50 $\mu\text{g/ml}$, the linearity between absorbance and concentration decreases. Thus, the calibration standards should be kept within an optimum range for each element.

In the event standards cannot be prepared identical to the unknowns, the technique of standard additions should be used. For example, in an analysis for zinc in urine, a known amount of zinc is added to the sample so that it contains 0.2 $\mu\text{g/ml}$ of additional zinc. To another portion of sample, zinc is added to give an additional 0.4 $\mu\text{g/ml}$, etc. . After reading the absorbances of these solutions, a plot similar to Fig. 8 is made. The line is extrapolated to the value for the zinc concentration in the original urine sample.

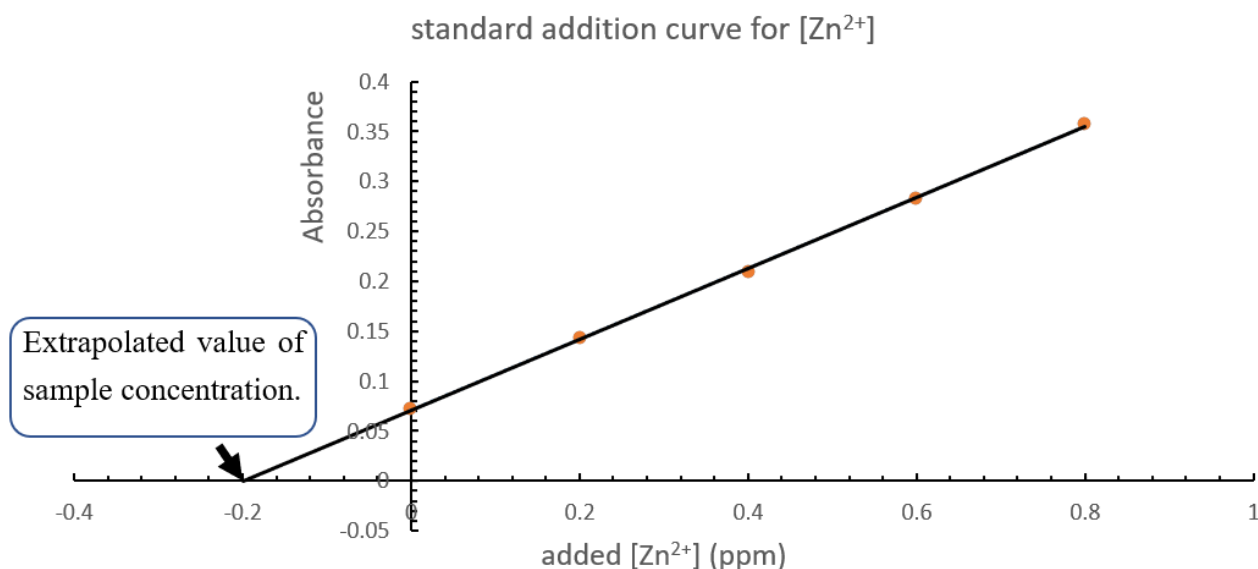


Fig. 8 Results of standard addition technique for the determination of Zn.

Procedure

A. Ordinary Calibration Curve Method

1. From the 1000 ppm Zn^{2+} stock solution, prepare solutions that contain: 0.1, 0.2, 0.4, 0.8, and 5.0 $\mu\text{g/ml}$ Zn^{2+} . This can be done by pipetting 0.25 ml of the stock solution (1000 ppm) into a 50 ml volumetric flask and diluting to the mark; this solution will be 5 ppm Zn^{2+} . From the solution of 5 ppm Zn^{2+} , the remaining solutions can be made by diluting 0.5, 1.00, 2.00, and 4.00 ml of the 5 ppm Zn^{2+} solution in 25 ml volumetric flasks, respectively.
2. Put some deion water into a small and clean beaker. Allow it to be aspirated into the flame.

3. Aspirate the first solution into the flame until stable absorption signal is obtained. Aspirate the remaining solutions into the flame, each followed by water.
4. Aspirate the unknown into the flame last.
5. Record the absorbance for each solution.

B. Calibration by Standard Addition Technique

1. From the 1000 ppm Zn^{2+} stock solution, prepare a 10 ml standard solution containing 25 $\mu\text{g/ml}$ Zn^{2+} .
2. To a **25.00 ml** of unknown, add 0.10 ml of the 25 $\mu\text{g/ml}$ standard solution of Zn ion in a clean 25 ml volumetric flasks. This will increase the Zn ion concentration of the unknown by 0.1 $\mu\text{g/ml}$.
3. Repeat with 25 ml aliquots of the unknown and the addition of 0.20, 0.30, and 0.40 ml of the 25 $\mu\text{g/ml}$ Zn^{2+} standard solution, respectively, to increase the unknown samples by 0.2, 0.3, and 0.4 $\mu\text{g/ml}$.
4. Zero the instrument with distilled deion water and aspirate the unknown solution with added zinc successively, aspiration distilled deion water between each sample.

Calculation

A. Ordinary Calibration Method

Construct a calibration curve by plotting absorbance vs. concentration in micrograms per milliliter. Determine the concentration of the unknown from the calibration curve.

B. Standard Addition Technique

Make volume corrections and **plot the data in a manner similar to Fig. 8.** Extrapolate the line to the value of the unknown sample concentration.

儀器設定:

Zn

λ :

slit:

Hollow cathode lamp (HCL) current :

C₂H₂: air :

blank:

結果:

A: calibration curve

濃度(ppm)	0.1	0.2	0.4	0.8	unknown
吸收值					
線性方程式				線性相關係數	
unknown 濃度(ppm)					

B: standard addition curve

添加濃度(ppm)	unknown (0)				
吸收值					
線性方程式				線性相關係數	
unknown 濃度(ppm)		當 A=0, unknown conc. = 濃度 (濃度的絕對值)			