Chapter 9
Atomic Absorption (AAS) and Atomic Fluorescence Spectrometry (AFS)

AAS: the most widely used method for the determination of single elements in analytical samples.

9A Sample Atomization Techniques (mainly flame and electrothermal atomization)

9A-1 Flame Atomization

A solution of the sample is nebulized by a flow of gaseous oxidant, mixed with a gaseous fuel, and carried into a flame where atomization occurs.

Atomization (原子化) is the critical step in flame spectrometry and limits its precision.
Types of Flames

Air: 1700°C ~ 2400°C
O₂, Nitrous oxide: 2500°C ~ 3100°C

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxidant</th>
<th>Temperature, °C</th>
<th>Maximum Burning Velocity, cm s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>Air</td>
<td>1700–1900</td>
<td>39–43</td>
</tr>
<tr>
<td>Natural gas</td>
<td>Oxygen</td>
<td>2700–2800</td>
<td>370–390</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Air</td>
<td>2000–2100</td>
<td>300–440</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Oxygen</td>
<td>2550–2700</td>
<td>900–1400</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Air</td>
<td>2100–2400</td>
<td>158–266</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Oxygen</td>
<td>3050–3150</td>
<td>1100–2480</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Nitrous oxide</td>
<td>2600–2800</td>
<td>285</td>
</tr>
</tbody>
</table>

Flashback (火舌回閃): burning velocity > gas flow rate
Gas flow rate >> burning velocity will blow off the burner.

Flame structure varies with fuel-to-oxidant ratio as well as with the type of fuel and oxidant.

FIGURE 9-2 Regions in a flame.
FIGURE 9-3 Temperature profiles in °C for a natural gas-air flame.

Flame absorption profiles

Mg: No. of Mg atom increases and then decreases at secondary combustion zone due to formation of oxides (long exposure time).

Ag: not easily oxidized. The absorption increases with exposure time.

Cr: forms very stable oxides.
**Flame Atomizer:**
The most reproducible of all liquid-sample-introduction method. However, the sampling efficiency (sensitivity) is lower than other methods (large sample drain and short residence time \(\sim 10^{-4}\) sec in the optical path).

![A laminar-flow burner.](image)

**Electrothermal Atomizer:** (AAS & AFS)
Entire sample is atomized in a short period (enhanced sensitivity):
\(\mu\)l sample \(\rightarrow\) evaporation \(\rightarrow\) ashing \(\rightarrow\) atomization (2000-3000°C).
Residence time > 1 sec.

![Cross-sectional view of a graphite furnace with integrated L'vov platform.](image)
FIGURE 9-6(b)(c) (b) Longitudinal configuration of the graphite furnace. Note the temperature profile shown in blue along the path of the furnace. In the longitudinal configuration, the temperature varies continuously along the path, reaching a maximum at the center. (c) Transverse configuration of the furnace. The temperature profile is relatively constant along the path.

Electrothermal atomizer:
Sample volume: 0.5 ~ 10 µL
Detection limit: $10^{-10}$~$10^{-13}$ g
Relative precision: 5~10%

Direct analysis of solid samples is also possible.

FIGURE 9-7 Typical output for the determination of lead from a spectrophotometer equipped with an electrothermal atomizer. The sample was 2 µL of canned orange juice. The times for drying and ashing are 20 and 60 s, respectively.
9A-3 Specialized Atomization Techniques

* Glow-discharge atomization
  (sample must be conductor)

* Hydride generation

\[ 3 \text{BH}_4^{-}(aq) + 3 \text{H}^+ (aq) + 4 \text{H}_3\text{AsO}_3 (aq) \rightarrow \]
\[ 3 \text{H}_3\text{BO}_3(aq) + 4 \text{AsH}_3(g) + 3 \text{H}_2\text{O}(l) \]

* Cold vapor atomization (Hg)

FIGURE 9-8
(a) Cross section of a cell for glow-discharge atomization of solid samples.
(b) Craters formed on sample surface by six jets of ionized argon.

FIGURE 9-9
A hydride generation and atomization system for AAS.
Review:

1) What is "resonance line"; give an example.
2) Explain the functions of atomization and nebulization.
3) Define absorption spectrum: The spectrum formed by electromagnetic radiation that has passed through a medium in which radiation of certain frequencies is absorbed.

9B Atomic Absorption Instrumentation

AAS Instruments consist of

1) Radiation source (光源)
2) Sample holder (atomizer cell containing the gaseous atomized sample) (樣品容器)
3) Wavelength selector (波長選擇器)
4) Detector (transducer) (偵測器，檢測器)
5) Signal processor & readout (訊號處理器)
Components of Optical Instruments

FIGURE 7-1
Components of various types of instruments for optical spectroscopy.

Absorption measurement

Fluorescence & phosphorescence measurement

Emission & chemiluminescence measurement

FIGURE 7-2
(a) Construction materials and (b) wavelength selectors for spectroscopic instruments.
Wavelength Selector (波長選擇器)

Filters (濾光片)
* Interference filters (干涉濾光片)
* Absorption filters (吸收濾光片)
  (visible region)

Monochromators (單色器)
* Prism monochromators
* Grating (光柵) monochromators
  Czerny-Turner monochromator

FIGURE 7-11
Output of a typical wavelength selector.

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FIGURE 7-12
(a) Schematic cross section of an interference filter. Note that the drawing is not to scale and that the three central bands are much narrower than shown. (b) Schematic to show the conditions for constructive interference.

\[ n \lambda' = \frac{2d}{\cos \theta} \]
\[ n \lambda'' = 2d (\theta \to 0) \]
\[ \lambda = \lambda' n \]
\[ \lambda = 2dn/n \]

\( n \): integer, the order of interference
\( n \): refractive index

FIGURE 7-13
Transmission characteristics of typical interference filters.

Effective bandwidth = 45 Å
Effective bandwidth = 45 Å
Effective bandwidth = 15 Å

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Ch7 Components of Optical Instruments
Absorption filters: colored glass or a dye suspended in gelatin and sandwiched between glass plates.

FIGURE 7-16 Effective bandwidths for three types of filters.

Monochromators

Monochromators are designed for spectral scanning. They use slits, lenses, mirrors, windows, and gratings or prisms.

FIGURE 7-18 Two types of monochromators: (a) Czerney-Turner grating monochromator and (b) Bunsen prism monochromator. (In both instances, $\lambda_1 > \lambda_2$)
FIGURE 7-19  Dispersion for three types of monochromators. The points A and B on the scale in (c) correspond to the points shown in Figure 7-18.

\[ n\lambda = CB + BD = dsini + dsinr = d(sini + sinr) \]

- \( n = 1 \): first-order line
- \( n = 2 \): second-order line
- \( n = 3 \): third-order line
- ... (example 7-1)

Different wavelengths reflect at different angles (angular dispersion).

FIGURE 7-21  Mechanisms of diffraction from an Echellette-type grating.
Review:

1) Describe components of various instruments for optical spectroscopy.

2) Why wavelength selector is required in spectroscopic analyses?

3) Describe the difference between filters and monochromators.

![Diagram](image)

**FIGURE 7.1(a)** In (a), the arrangement for absorption measurements is shown. Note that source radiation of the selected wavelength is sent through the sample, and the transmitted radiation is measured by the detector-signal processing-readout unit. With some instruments, the position of the sample and wavelength selector is reversed.

**Beer’s Law:** \[ A = \varepsilon bc \]

AAS requires a **narrow** source bandwidth relative to the width of an absorption line or band. (atomic absorption line width: 0.002~0.005 nm)
Problems:
1) Absorption lines: 0.002~0.005 nm. Effective bandwidths of monochromators are significantly greater than widths of AA.
2) Poor sensitivity: only small fraction of radiation is absorbed.

The source temperature and pressure are kept below that of the atomizer: narrow the emission width.

FIGURE 9-10 Absorption of a resonance line by atoms.

Hollow-cathode lamp (中空陰極管)

- tungsten
- 300 V: sputtering (5~15 mA)
- Ionization of Ar

FIGURE 9-11 Schematic cross section of a hollow-cathode lamp (中空陰極管).

The efficiency of hollow-cathode lamp depends on its geometry and the operating voltages. High voltages lead to greater intensities, but with Doppler broadening and self-absorption disadvantages.
Electrodeless Discharge Lamps (EDL)

FIGURE 9-12  Cutaway of an Electrodeless Discharge Lamps (EDL). About 10–100 times higher in radiant intensity than that of hollow-cathode lamps. Available > 15 elements.

Contain metals of interest and a few torr of inert gas (Ar).

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9B-2 Spectrophotometers (光譜儀)

FIGURE 9-13  Typical flame spectrophotometers.
FIGURE 9-13(a) Single-beam design (單光束設計).

FIGURE 9-13(b) Double-beam design (雙光束設計).

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7E Radiation Transducers

7E-1 Introduction: Responds to photon or to heat

7E-2 Photon Transducers (變換器, 轉換器) (photoelectric or quantum detectors (p. 191)
  * Barrier-layer photovoltaic cells (visible region: maximum sensitivity at 550 nm)
  * Phototubes (vacuum phototube)
  * Photomultiplier tubes (光倍增管)
  * Silicone photodiodes
  * Charge-transfer transducers
  * Photoconductivity transducers (PbS)

7E-5 Thermal Transducers
  * Thermocouples
  * Bolometers (輻射熱測定計)
  * Pyroelectric (焦電) Transducers

FIGURE 7-28 Schematic of a typical barrier-layer cell.

FIGURE 7-29 A phototube and op amp readout. The photocurrent induced by the radiation causes a voltage drop across $R$, which appears as $v_o$ at the output of the current-to-voltage converter. This voltage may be displayed on a meter or acquired by data-acquisition system.
Photomultiplier tube (PMT: 光倍增管):
PMTs, members of the class of vacuum tubes (phototubes), are extremely sensitive detectors of light in the ultraviolet, visible and infrared ranges of the light. These detectors multiply the current produced by incident light by as much as 100 million times, in multiple dynode stages.
Dynode 1 is maintained at a voltage approximately 90 V more positive than the cathode.

**FIGURE 7-31(b)** Cross-sectional view.

**FIGURE 7-31(c)** Electrical diagram illustrating dynode polarization and photocurrent measurement.
FIGURE 7-32 (a) Schematic of a silicon photodiode. (b) Formation of depletion layer, which prevents flow of electricity under reverse bias.

7E-3 Multichannel Photon Transducers

Photodiode array (PDA): 1D
Charge-injection devise (CID): 2D
Charge-coupled device (CCD): 2D

FIGURE 7-33
A reverse-biased linear diode-array detector:
(a) cross section and (b) top view.
9C Interferences in AA Spectroscopy

9C-1 Spectral Interferences

The absorption or emission of an interfering species either overlaps or lies so close to the analyte absorption or emission that resolution by the monochromator becomes impossible.

1) Overlapping line (separation < 0.1 Å)
2) Broadband absorption of combustion products
3) Absorption or scattering of sample matrix
4) Scattering by products of atomization (oxides of Ti, Zr, W)

In flame atomization, spectral interferences by matrix products are not widely encountered and often can be avoided by variations in the analytical variables, such as flame temperature and fuel-to-oxidant ratio.

Band and Continuous Spectra Associated with Atomic Spectra

Use N₂O instead of air. High temp. decomposes CaOH.

FIGURE 8-8 Molecular flame emission and flame absorption spectra for CaOH. Atomic emission wavelength of barium is also indicated.
9C-2 Chemical Interferences (more common)(化學干擾)
Result from various processes occurring during atomization that alter the absorption characteristics of the analyte.

a) Formation of compounds of low volatility with anions or cations.
   High temperature, releasing agent, protective agent.

b) Dissociation Equilibria: MO, M(OH)₂, MOₓ, ...

c) Ionization Equilibria
   Ionization suppressor

   EDTA  chelate  8-hydroxyquinoline  APCD

### Table 9.2
Degree of Ionization of Metals at Flame Temperatures

<table>
<thead>
<tr>
<th>Element</th>
<th>Ionization Potential, eV</th>
<th>Fraction Ionized at the Indicated Pressure and Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P = 10⁻⁴ atm</td>
</tr>
<tr>
<td>Cs</td>
<td>3.893</td>
<td>0.01</td>
</tr>
<tr>
<td>Rb</td>
<td>4.176</td>
<td>0.004</td>
</tr>
<tr>
<td>K</td>
<td>4.339</td>
<td>0.003</td>
</tr>
<tr>
<td>Na</td>
<td>5.138</td>
<td>0.0003</td>
</tr>
<tr>
<td>Li</td>
<td>5.390</td>
<td>0.0001</td>
</tr>
<tr>
<td>Ba</td>
<td>5.210</td>
<td>0.0006</td>
</tr>
<tr>
<td>Sr</td>
<td>5.692</td>
<td>0.0001</td>
</tr>
<tr>
<td>Ca</td>
<td>6.111</td>
<td>3 × 10⁻³</td>
</tr>
<tr>
<td>Mg</td>
<td>7.644</td>
<td>4 × 10⁻⁷</td>
</tr>
</tbody>
</table>

Ionization equilibrium: the degree of ionization of a metal is strongly influenced by the presence of other ionizable metals in the flame. When T is increased?
9D Atomic Absorption Analytical Techniques

9D-1 Sample preparation
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- Decomposition: hot mineral acids, oxidation with liquid reagents, combustion in oxygen bomb, ashing at high temperature, high temperature fusion with reagents.
- Electrothermal (ET) atomization: atomized directly.

9D-2 Sample Introduction by Flow Injection (Chapter 33)

9D-3 Organic Solvents

9D-4 Calibration Curves (non-linear)

9D-5 Standard-Addition Method (widely used to reduce matrix interference)

9D-6 Applications of AAS
Sensitive for quantitative determination of more than 60 metals.

Detection limit: 1-20 ng/mL for flame
0.002-0.01 ng/mL for ET

Accuracy: 1-2% for flame
5-10% for ET
1D Calibration of Instrumental Methods

Calibration determines the relationship between the analytical response and the analyte concentration. Usually this is determined by the use of chemical standards.

* **Comparison with Standards** (page 11)
  Direct comparison, Titrations

* **External-Standard Calibration** (page 11)
  Least-Squares Method

* **Standard-Addition Methods** (page 13)

* **The Internal-Standard Method** (page 17)
FIGURE 1-8 Calibration curve for the determination of isooctane in a hydrocarbon mixture. The residual is the difference between an experimental data point $y_i$ and that calculated from the regression model, $m x_i + b$, as shown in the insert.

$\text{FIGURE 1-10 Linear calibration plot for the method of standard additions.}$

The concentration of the unknown solution may be calculated from the slope $m$ and the intercept $b$, or it may be determined by extrapolation, as explained in the text.
FIGURE 1-11 Spreadsheet for standard-addition Example 1-1.

FIGURE 1-12 Spreadsheet to illustrate the internal-standard method for the flame spectrometric determination of sodium.
Review:

1) Describe the types and mechanisms of radiation transducers.

2) What is the essential requirement of sources used in atomic absorption? Give two kinds of source.

3) Mechanisms of photomultipliers and silicone diodes.

4) Explain possible interferences in AA spectroscopy.