LOOKING AHEAD

Thursday (Feb 4)- Experiment 1 Metals
   Due: Standard Addition
   Due: Prelab 2, Experiment 1

Monday (Feb 8)- Molecular Spectroscopy (Ch 13-15), Writing Procedures
   Due: Annotated Figures 1, Experiment 1

Tuesday/Thursday (Feb 9, 11)- Experiment 1 Metals

Monday (Feb 15)- Vibrational Spectroscopy
   Due: Project Overview

BUILDING A SPECTROSCOPIC INSTRUMENT

Components
1. Stable radiation source
2. Wavelength isolation
3. Transparent sample holder/ optics
4. Detector
5. Signal processing
DIAGRAM A MONOCHROMATOR

MONOCHROMATORS

1. Entrance slit- provides rectangular optical image
2. Collimating lens or mirror- makes light beams parallel
3. Dispersive element- disperses light into component wavelengths
4. Focusing element- reforms rectangular optical image focused on focal plane
5. Exit slit- on focal plane, selects desired bandwidth
**BUILDING A SPECTROSCOPIC INSTRUMENT**

**Components**
1. Stable radiation source
2. Wavelength isolation
3. Transparent sample holder/ optics
4. **Detector**
5. Signal processing

**IDEAL DETECTORS**
1. High sensitivity
2. High signal to noise
3. Constant detector response as a function of $\lambda$
4. Fast response time
5. No dark current
6. Signal proportional to radiant power
7. Rugged, cheap, simple

$$S = kP + k_d$$
DETECTORS

![Diagram of different types of detectors and their spectral regions.]

Figure 7-27

PMT
CdS
GaS
PbS
Se/SeO
CdSe
Si photodiode
Thermocouple
Golay cell
1. Photon hits cathode
2. Cathode emits e- that travels through vacuum to the anode
3. Generates a current
4. Converted to a measureable voltage
PN JUNCTIONS

SILICON PHOTodiode

[Diagram of pn junction and silicon photodiode]
MULTICHLANEL SI-BASED DETECTORS

Photodiode array (PDA)
Charge Injection Device (CID)
Charge Coupled Device (CCD)

![Diagram of Si-based detectors](image)

MULTICHLANEL SI-BASED DETECTORS

Photodiode array (PDA)
Charge Injection Device (CID)
Charge Coupled Device (CCD)

![Diagram of Si-based detectors](image)
MULTICHANNEL SI-BASED DETECTORS

Photodiode array
Charge Injection Device (CID)
Charge Coupled Device (CCD)

COMPARING DETECTOR SENSITIVITY

Minimum detectable signal (photons per second per detector element)

<table>
<thead>
<tr>
<th>detector</th>
<th>λ</th>
<th>1 s</th>
<th>10 s</th>
<th>100 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMT</td>
<td>UV</td>
<td>30</td>
<td>6.3</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Vis</td>
<td>122</td>
<td>26</td>
<td>7.3</td>
</tr>
<tr>
<td>PDA</td>
<td>UV</td>
<td>6000</td>
<td>671</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>Vis</td>
<td>3300</td>
<td>363</td>
<td>62</td>
</tr>
<tr>
<td>CCD</td>
<td>UV</td>
<td>31</td>
<td>3.1</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Vis</td>
<td>17</td>
<td>1.7</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Harris, Table 19-2
OBJECTIVES

- Differentiate between atomic and molecular spec.
- Label, diagram, describe each of the following instruments:
  Flame Atomic Absorption
  Atomic Emission
  Atomic Fluorescence
  ICP-OES
- Identify, diagram, and describe how the following instrument components function. Also know why these components are used.
  Sources: HCL, EDL
  Atomizers: Flame, ETV, hydride generation, ICP
ATOMIC ORBITALS

Lighting and Astronomy
Physics Today, December 2009, pg 32

Figure 5. Spectra of representative outdoor lighting sources. Low-pressure sodium (LPS) and high-pressure sodium (HPS) lamps leave large parts of the spectrum relatively unpolluted, whereas the broadband metal halide (MH), white LED, and incandescent (Inc) sources do not.

Diagram showing energy levels and transitions between singlet and triplet states.
ATOMIC SPECTROSCOPY HAS VERY NARROW ABSORPTION LINES ~0.005 NM

In contrast, to molecular spectroscopy absorption bands 10-100 nm.

This requires different instruments than molecular spectroscopies.

ATOMIC SPECTROSCOPY INSTRUMENTS

Source- line sources
  Hollow Cathode Lamp (HCL)
  Electrodeless Discharge Lamp (EDL)
Nebulizers
Sample Atomizers
  Flame, ETV, hydride, ICP
Wavelength selection
  monochromator
Detector
  PMT, CID
SOURCES

NARROW BANDWIDTH SOURCES ARE REQUIRED FOR ATOMIC SPECTROSCOPY

Effective source bandwidth:
0.001 nm

Effective absorption bandwidth:
0.002-0.005 nm

The linewidth of the source must be narrower than the linewidth of the atomic vapor for Beer’s law to be obeyed.
NARROW BANDWIDTH SOURCES ARE REQUIRED FOR ATOMIC SPECTROSCOPY

Source spectrum
Effective bandwidth: 
~0.001 nm

Sample Absorption
Effective bandwidth: 
0.002-0.005 nm

Signal at detector
Smaller due to absorption in flame and mono throughput

SPECTRAL LINE BROADENING EFFECTS

HCLs produce lines of fundamentally $10^{-4}$ nm

Broadened by:
- Uncertainty Effect
- Doppler broadening
- Pressure broadening

Effective width 0.002-0.005 nm
ELECTRODELESS DISCHARGE LAMP (EDL)

The second type of line source is an electrodeless discharge lamp (EDL). An EDL contains a small quantity of the analyte as either the element or often as the iodide salt in a quartz bulb (Figure 17.6). The bulb is filled with an inert gas, typically Ar, at low pressure. The bulb is surrounded by a radio frequency coil.

When the coil is powered to generate an intense electromagnetic field, an inductively coupled discharge occurs in the low-pressure lamp with characteristic line emission of the element. The EDL is a more intense source than an HCL and often has a narrower line width. EDLs require a different type of power supply. It is particularly for the more volatile elements that the EDL can be attractive: lamps are available for As, Bi, Cd, Cs, Ge, Hg, P, Pb, Rh, Sb, Se, Sn, Te, TI, and Zn.

ATOMIC SPECTROSCOPY INSTRUMENTS

Source- line sources
- Hollow Cathode Lamp (HCL)
- Electrodeless Discharge Lamp (EDL)

Nebulizers
Sample Atomizers
- Flame, ETV, hydride, ICP

Wavelength selection
- monochromator
Detector
- PMT, CID
SAMPLE NEBULIZATION AND ATOMIZATION

Sample must be converted to gaseous atoms or ions

Sample introduction often limiting factor in:
  - accuracy,
  - precision, and
  - detection limits

METHODS OF SAMPLE INTRODUCTION

<table>
<thead>
<tr>
<th>Method</th>
<th>Type of Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pneumatic nebulization</td>
<td>Solution or slurry</td>
</tr>
<tr>
<td>Ultrasonic nebulization</td>
<td>Solution</td>
</tr>
<tr>
<td>Electrothermal vaporization</td>
<td>Solid, liquid, or solution</td>
</tr>
<tr>
<td>Hydride generation</td>
<td>Solution of certain elements</td>
</tr>
</tbody>
</table>

Concentric tube

Fritted disk

Cross-flow

Babington
PNEUMATIC NEBULIZERS

Concentric tube

High-pressure gas flow

Sample solution

Cross-flow

High-pressure gas flow

Sample solution

Fritted disk

High-pressure gas flow

Sample solution

Drain

Babington

Sample

Solution film

Orifice

High-pressure gas flow

Burner head generates flame

Flame

Burner head

Fuel

Spray chamber

Oxidant

Nebulizer

Glass bead

To drain

Interconal layer

Preheating region

Burner head

Volume percent

Diameter (μm)

Harris, Quantitative Chemical Analysis, 8e
© 2011 W. H. Freeman
LAMINAR FLOW BURNER

Burner head
Burner head locking ring
Pressure relief vents
Flow spoiler (Panton plastic)
Flow spoiler retaining screw
Auxiliary oxidant
Flow
Nebulizer adjusting knob
Sample capillary
Nebulizer
To waste
Nebulizer oxidant

STRUCTURE OF THE FLAME

Interzonal region
Secondary combustion zone
Primary combustion zone
Fuel-oxidant mixture

Different portions of the flame may be used based on analyte of interest
**STRUCTURE OF THE FLAME**

Different portions of the flame may be used based on analyte of interest.

---

**SELECT FUEL AND OXIDANT BASED ON ANALYTE**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxidant</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>Air</td>
<td>1700–1900</td>
</tr>
<tr>
<td>Natural gas</td>
<td>Oxygen</td>
<td>2700–2800</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Air</td>
<td>2000–2100</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Oxygen</td>
<td>2550–2700</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Air</td>
<td>2100–2400</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Oxygen</td>
<td>3050–3150</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Nitrous oxide</td>
<td>2600–2800</td>
</tr>
</tbody>
</table>

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Note: The table information is sourced from www.wikipedia.com.
**SELECT FUEL AND OXIDANT BASED ON ANALYTE**

![Chemical structure](https://www.wikipedia.com/)

<table>
<thead>
<tr>
<th>Fuel</th>
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<th>Temperature °C</th>
</tr>
</thead>
<tbody>
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<td>Natural gas</td>
<td>Air</td>
<td>1700–1900</td>
</tr>
<tr>
<td>Natural gas</td>
<td>Oxygen</td>
<td>2700–2800</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Air</td>
<td>2000–2100</td>
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<tr>
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<td>2550–2700</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Air</td>
<td>2100–2400</td>
</tr>
<tr>
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<td>Oxygen</td>
<td>3050–3150</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Nitrous oxide</td>
<td>2600–2800</td>
</tr>
</tbody>
</table>

**ELECTROTHERMAL ATOMIZER-GRAPHITE FURNACE**

![Graphite furnace](https://www.ems.psu.edu/~pisupati/)

Graphite furnace

Sample port

Sample weighed onto graphite platform

Light in

Curved L'vov platform

Furnace wall

End view
**ELECTROTHERMAL ATOMIZER- GRAPHITE FURNACE**

**GRAPHITE FURNACE**

**FIGURE 20-10** Reduction of interference by using a matrix modifier. (a) Graphite furnace temperature profile for analysis of Mn in seawater. (b) Absorbance profile from 10 µL of 0.5 M reagent-grade NaCl subjected to temperature profile in panel a. Absorbance is monitored at the Mn wavelength of 279.5 nm with a bandwidth of 0.5 nm. (c) Reduced absorbance from 10 µL of 0.5 M NaCl plus 10 µL of 50 wt% NH₄NO₃ matrix modifier. [From M. N. Quigley and F. Vernon, "Matrix Modification Experiment for Electrothermal Atomic Absorption Spectrophotometry," *J. Chem. Ed.* 1996, 73, 980.]
### Comparing Flame and Furnace Sample Delivery

<table>
<thead>
<tr>
<th></th>
<th>Flame absorption</th>
<th>Furnace absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limits (ng/g)</td>
<td>10–1 000</td>
<td>0.01–1</td>
</tr>
<tr>
<td>Linear range</td>
<td>$10^2$</td>
<td>$10^2$</td>
</tr>
<tr>
<td>Precision</td>
<td></td>
<td></td>
</tr>
<tr>
<td>short term (5–10 min)</td>
<td>0.1–1%</td>
<td>0.5–5%</td>
</tr>
<tr>
<td>long term (hours)</td>
<td>1–10%</td>
<td>1–10%</td>
</tr>
<tr>
<td>Interferences</td>
<td></td>
<td></td>
</tr>
<tr>
<td>spectral</td>
<td>very few</td>
<td>very few</td>
</tr>
<tr>
<td>chemical mass</td>
<td>many</td>
<td>very many</td>
</tr>
<tr>
<td>Sample throughput</td>
<td>10–15</td>
<td>3–4</td>
</tr>
<tr>
<td>Dissolved solid</td>
<td>s/element</td>
<td>min/element</td>
</tr>
<tr>
<td></td>
<td>0.5–5%</td>
<td>&gt;20% slurries and solids</td>
</tr>
<tr>
<td>Sample volume</td>
<td>large</td>
<td>very small</td>
</tr>
<tr>
<td>Purchase cost</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

### Hydride Generation

![Hydride Generation Diagram](Image)
## METHODS OF SAMPLE INTRODUCTION

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<td>Solid, liquid, or solution</td>
</tr>
<tr>
<td>Hydride generation</td>
<td>Solution of certain elements</td>
</tr>
<tr>
<td>Direct insertion</td>
<td>Solid, powder</td>
</tr>
<tr>
<td>Laser ablation</td>
<td>Solid, metal</td>
</tr>
<tr>
<td>Spark or arc ablation</td>
<td>Conducting solid</td>
</tr>
<tr>
<td>Glow-discharge sputtering</td>
<td>Conducting solid</td>
</tr>
</tbody>
</table>

## GLOW-DISCHARGE ATOMIZER

![Diagram of Glow-Discharge Atomizer](image)
**ATOMIC SPECTROSCOPY INSTRUMENTS**

Source- line sources
- Hollow Cathode Lamp (HCL)
- Electrodeless Discharge Lamp (EDL)

Nebulizers

Sample Atomizers
- Flame, ETV, hydride, ICP

Wavelength selection
- monochromator

Detector
- PMT, CID

---

*Atomic Emission spectroscopy*
EXAMPLE PARMS

Cu (Copper)
A.W. 63.54

Preparation of Standard Solutions
Recommended Standard Materials
Copper metal strip or wire  99.99%

Solution Technique
Dissolve 1.000 g of copper metal in a minimum volume of 1.1 nitric acid and dilute to 1 liter to give 1000 µg/mL Cu.

Recommended Instrument Parameters
Atomic Absorption
Working Conditions (Fixed)
Lamp current  4 mA
Puff  acetylene
Support  air
Flame stoichiometry  oxidizing

Working Conditions (Variable)

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Slit Width (mm)</th>
<th>Optimum Working Range (µg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>324.7</td>
<td>0.8</td>
<td>0.03-10</td>
</tr>
<tr>
<td>327.4</td>
<td>0.2</td>
<td>0.1-24</td>
</tr>
<tr>
<td>327.9</td>
<td>0.2</td>
<td>0.2-48</td>
</tr>
<tr>
<td>334.1</td>
<td>0.2</td>
<td>0.3-40</td>
</tr>
<tr>
<td>341.6</td>
<td>0.2</td>
<td>1-200</td>
</tr>
<tr>
<td>352.2</td>
<td>0.2</td>
<td>4-400</td>
</tr>
<tr>
<td>346.2</td>
<td>1.0</td>
<td>10-2000</td>
</tr>
</tbody>
</table>

Flame Emission
Wavelength  327.4 nm
Slit width  0.5 mm
Puff  acetylene
Support  nitrous oxide

FLAME ATOMIC ABSORPTION SCHEMATIC

Ebert monochromator
SPECTRAL INTERFERENCES

Spectral overlap - rare as lines are so narrow
Absorption and scattering from
1. Flame - take blank measurement
2. Matrix - ratio two nearby lines

Solutions:
1. Measure two nearby lines
2. Use broadband source

CHEMICAL INTERFERENCES

Processes in flame roughly at equilibrium
- Regard flame as solvent medium

Chemical interferences
Formation of low volatility compounds - reduces fraction of atomized sample
Dissociation equilibria -

\[
\begin{align*}
\text{MO} & \leftrightarrow \text{M} + \text{O} \\
\text{M(OH)}_2 & \leftrightarrow \text{M} + 2\text{OH} \\
\text{NaCl} & \leftrightarrow \text{Na} + \text{Cl}
\end{align*}
\]

Ionization equilibria -

\[
\begin{align*}
\text{M} & \leftrightarrow \text{M}^+ + \text{e}^- \\
\text{M(g)} & \leftrightarrow \text{M}^+(g) + \text{e}^-(g)
\end{align*}
\]

\[
K = \frac{[\text{M}^+][\text{e}^-]}{[\text{M}]}
\]
SOURCE SELF REVERSAL

Operating HCL at high current results in:
1. Minimum at $\lambda_{\text{max}}$
2. Broader bandwidth

ZEEMAN INTERFERENCES

Something about magnetic field causing splitting in absorption bands

Read more about this pg 242
MAKING ATOMIC SPECTROSCOPIC INSTRUMENTS

Atomic Absorption Spectroscopy
- flame
- graphite furnace
Atomic Emission Spectroscopy
Atomic Fluorescence Spectroscopy
Inductively Coupled Plasma- Optical Emission Spectroscopy

ATOMIC ABSORPTION SPECTROSCOPY

Diagram of atomic absorption spectroscopy process.
ATOMIC ABSORPTION SPECTROSCOPY

Signal at Detector

Flame only
Flame + lamp
Flame + lamp + sample
ATOMIC ABSORPTION SPECTROSCOPY
DOUBLE BEAM DESIGN

ATOMIC EMISSION SPECTROSCOPY

(1) Source
(2) Wavelength selector
(3) Sample
(4) Detector
(5) Signal processor and readout

Excited state population

\[ \frac{N^*}{N_0} = \frac{g^*}{g_0} e^{-\Delta E/kT} \]
TABLE 8-1 Types of Atomizers Used for Atomic Spectroscopy

<table>
<thead>
<tr>
<th>Type of Atomizer</th>
<th>Typical Atomization Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame</td>
<td>1700–3150</td>
</tr>
<tr>
<td>Electrothermal vaporization (ETV)</td>
<td>1200–3000</td>
</tr>
<tr>
<td>Inductively coupled argon plasma (ICP)</td>
<td>4000–6000</td>
</tr>
<tr>
<td>Direct current argon plasma (DCP)</td>
<td>4000–6000</td>
</tr>
<tr>
<td>Microwave-induced argon plasma (MIP)</td>
<td>2000–3000</td>
</tr>
<tr>
<td>Glow-discharge plasma (GD)</td>
<td>Nonthermal</td>
</tr>
<tr>
<td>Electric arc</td>
<td>4000–5000</td>
</tr>
<tr>
<td>Electric spark</td>
<td>40,000 (?)</td>
</tr>
</tbody>
</table>

BOLTZMANN DISTRIBUTION

\[
\frac{N^*}{N_0} = \frac{g^*}{g_0} e^{-\Delta E/kT}
\]

TABLE 20-3 Effect of energy difference and temperature on population of excited states

<table>
<thead>
<tr>
<th>Wavelength difference of states (nm)</th>
<th>Energy difference of states (J/atom)</th>
<th>Excited-state fraction (N^*/N_0) @ 2500 K</th>
<th>Excited-state fraction (N^*/N_0) @ 6000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>(7.95 \times 10^{-19})</td>
<td>(1.0 \times 10^{-10})</td>
<td>(6.8 \times 10^{-5})</td>
</tr>
<tr>
<td>500</td>
<td>(3.97 \times 10^{-19})</td>
<td>(1.0 \times 10^{-5})</td>
<td>(8.3 \times 10^{-3})</td>
</tr>
<tr>
<td>750</td>
<td>(2.65 \times 10^{-19})</td>
<td>(4.6 \times 10^{-4})</td>
<td>(4.1 \times 10^{-2})</td>
</tr>
</tbody>
</table>
ATOMIC FLUORESCENCE SPECTROSCOPY

1. Source
2. Wavelength selector
3. Sample
4. Detector
5. Signal processor and readout

Nonradiative transition
Absorption
Atomic fluorescence transitions

INDUCTIVELY COUPLED PLASMA

Atomic Emission Spectroscopy (AES)
Optical Emission Spectroscopy (OES)
INDUCTIVELY COUPLED PLASMA (ICP) ATOMIZER
INDUCTIVELY COUPLED PLASMA (ICP)

Nebulizer - Ultrasonic
Atomization - Inductively Coupled Plasma
Wavelength selection - Echelle Monochromator
Detector - Charge Injection Device (CID)
INTERFERENCES

Types of interference:
- spectral: unwanted signals overlapping analyte signal
- chemical: chemical reactions decreasing the concentration of analyte atoms
- ionization: ionization of analyte atoms decreasing the concentration of neutral atoms

\[ M(g) \rightleftharpoons M^+(g) + e^- (g) \]

\[ K = \frac{[M^+][e^-]}{[M]} \]

DETECTION LIMITS

<table>
<thead>
<tr>
<th>Element</th>
<th>AAS Flame</th>
<th>AAS Electrothermal</th>
<th>AES Flame</th>
<th>AES ICP</th>
<th>AES Flame</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>30</td>
<td>0.1</td>
<td>5</td>
<td>0.2</td>
<td>5</td>
</tr>
<tr>
<td>As</td>
<td>200</td>
<td>0.5</td>
<td>2</td>
<td>0.08</td>
<td>15</td>
</tr>
<tr>
<td>Ca</td>
<td>1</td>
<td>0.25</td>
<td>0.1</td>
<td>0.0001</td>
<td>0.4</td>
</tr>
<tr>
<td>Cd</td>
<td>1</td>
<td>0.01</td>
<td>2000</td>
<td>0.07</td>
<td>0.1</td>
</tr>
<tr>
<td>Cr</td>
<td>1</td>
<td>0.25</td>
<td>5</td>
<td>0.04</td>
<td>0.6</td>
</tr>
<tr>
<td>Cu</td>
<td>2</td>
<td>0.05</td>
<td>10</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe</td>
<td>1</td>
<td>0.25</td>
<td>50</td>
<td>0.09</td>
<td>0.3</td>
</tr>
<tr>
<td>Hg</td>
<td>500</td>
<td>5</td>
<td>1</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Mg</td>
<td>0.2</td>
<td>0.002</td>
<td>5</td>
<td>0.003</td>
<td>0.3</td>
</tr>
<tr>
<td>Mn</td>
<td>2</td>
<td>0.01</td>
<td>0.1</td>
<td>0.3</td>
<td>1</td>
</tr>
<tr>
<td>Mo</td>
<td>5</td>
<td>0.5</td>
<td>100</td>
<td>0.2</td>
<td>8</td>
</tr>
<tr>
<td>Ni</td>
<td>0.2</td>
<td>0.02</td>
<td>0.1</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Pb</td>
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<td>0.2</td>
<td>600</td>
<td>0.4</td>
<td>0</td>
</tr>
<tr>
<td>Sn</td>
<td>5</td>
<td>5</td>
<td>300</td>
<td>0.1</td>
<td>0.1</td>
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<tr>
<td>V</td>
<td>25</td>
<td>1</td>
<td>200</td>
<td>0.06</td>
<td>25</td>
</tr>
<tr>
<td>Zn</td>
<td>1</td>
<td>0.005</td>
<td>50000</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>
DETECTION LIMITS

TABLE 20-4  Comparison of atomic analysis methods

<table>
<thead>
<tr>
<th></th>
<th>Flame absorption</th>
<th>Furnace absorption</th>
<th>Plasma emission</th>
<th>Plasma–mass spectrometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limits (ng/g)</td>
<td>10–1 000</td>
<td>0.01–1</td>
<td>0.1–10</td>
<td>0.000 01–0.000 1</td>
</tr>
<tr>
<td>Linear range</td>
<td>10^2</td>
<td>10^2</td>
<td>10^3</td>
<td>10^8</td>
</tr>
<tr>
<td>Precision</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>short term (5–10 min)</td>
<td>0.1–1%</td>
<td>0.5–5%</td>
<td>0.1–2%</td>
<td>0.5–2%</td>
</tr>
<tr>
<td>long term (hours)</td>
<td>1–10%</td>
<td>1–10%</td>
<td>1–5%</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>Interferences</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>spectral mass</td>
<td>very few</td>
<td>very few</td>
<td>many</td>
<td>few</td>
</tr>
<tr>
<td>chemical mass</td>
<td>many</td>
<td>very many</td>
<td>very few</td>
<td>some</td>
</tr>
<tr>
<td>Sample throughput</td>
<td>10–15 s/element</td>
<td>3–4 min/element</td>
<td>6–60 elements/min</td>
<td>all elements in 2–5 min</td>
</tr>
<tr>
<td>Dissolved solid</td>
<td>0.5–5%</td>
<td>&gt;20% slurries and solids</td>
<td>1–20%</td>
<td>0.1–0.4%</td>
</tr>
<tr>
<td>Sample volume</td>
<td>large</td>
<td>very small</td>
<td>medium</td>
<td>medium</td>
</tr>
<tr>
<td>Purchase cost</td>
<td>1</td>
<td>2</td>
<td>4–9</td>
<td>10–15</td>
</tr>
</tbody>
</table>

SOURCE: Adapted from TJA Solutions, Franklin, MA.

Harris, Quantitative Chemical Analysis, 8e
EXAMPLE 8-2

Calculate the ratio of sodium atoms in the 3p excited states to the number in the ground state at 2500 and 2580 K.

Solution

We calculate $E$, in Equation 8-1, by using an average wavelength of 589.3 nm (5893 Å) for the two sodium emission lines corresponding to the $3p \to 3s$ transitions. We compute the energy in joules using the constants found inside the front cover:

$$\hat{E} = \frac{\lambda}{589.3 \text{ nm} \times 10^{-7} \text{ cm/nm}} = 1.697 \times 10^4 \text{ cm}^{-1}$$

$$E_i = \frac{1.602 \times 10^{-19} \text{ eV} \times 1.986 \times 10^{-7} \text{ J/eV}}{3.37 \times 10^{-38} \text{ J}}$$

The statistical weights for the 3s and 3p quantum states are 2 and 6, respectively, so:

$$\frac{E_i}{E} = \frac{6}{2} = 3$$

Substituting into Equation 8-1 yields

$$\frac{N_i}{N_e} = 3 \exp \left( \frac{-3.77 \times 10^{-19} \text{ J}}{1.38 \times 10^{-21} \text{ J/K} \times 2500 \text{ K}} \right)$$

$$= 3 \times 5.725 \times 10^{-4} = 1.72 \times 10^{-3}$$

Replacing 2500 with 2580 in the previous equation yields

$$\frac{N_i}{N_e} = 1.79 \times 10^{-4}$$