Chemistry 4631

Instrumental Analysis
Lecture 1
Syllabus
Chemistry 4631     Spring 2020

Lecture: MWF 9:00 – 9:50 a.m. Chem 352
Attendance is required.

Instructor: Dr. Teresa D. Golden
Chem 279, 565-2888, tgolden@unt.edu.

Office hours: F 1:00 - 3:00 p.m. Chem 207B.

Prereq: Chem 3451/3452 Quant. Analysis

This course covers electronics, spectroscopy, electrochemistry, chromatography, and selected topics.
Homework:

1) Problem sets will be assigned at the end of each chapter.
2) Also spectral interpretations will periodically be assigned.

Exams: There will be 4-5 in class exams and a comprehensive ACS final exam. Dates for exams will be announced one week ahead of time. The final is scheduled for Wed, 5/6/2020 from 8:00-10:00 a.m. in Room 352.

*Absolutely no make-up exams will be given without a signed physician’s note.

Grading: Exams, quizzes, and assignments will each be given a total point value. The student’s final grade will be: (the total number of points received/total number of points possible) x 100.
<table>
<thead>
<tr>
<th>WEEK</th>
<th>CLASS ASSIGNMENT</th>
<th>TOPICS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ch. 1 &amp; 6 &amp; Appendix</td>
<td>Intro, Stats, Data Analysis, Electromagnetic Spectrum, Quantum Theory</td>
</tr>
<tr>
<td>2</td>
<td>Ch. 6 &amp; 7&lt;br&gt;Lab: Check-in, Practicum</td>
<td>General Components of Optical Instrument and Lasers</td>
</tr>
<tr>
<td>3</td>
<td>Ch. 7&lt;br&gt;Lab: UV-vis</td>
<td>Optical Instruments and Semiconductors</td>
</tr>
<tr>
<td>4</td>
<td>Ch. 13 &amp; 14&lt;br&gt;Lab: UV-vis</td>
<td>UV Theory and Instrumentation</td>
</tr>
<tr>
<td>5</td>
<td>Ch. 16 &amp; 17&lt;br&gt;Lab: FTIR/Fluorescence</td>
<td>IR Spectroscopy Theory and Instrumentation, FTIR</td>
</tr>
<tr>
<td>6</td>
<td>Ch 15 &amp; 18&lt;br&gt;Lab: FTIR/Fluorescence</td>
<td>Fluorescence Spectroscopy</td>
</tr>
<tr>
<td>7</td>
<td>Ch. 8 &amp; 9&lt;br&gt;Lab: AAS/Raman</td>
<td>Atomic Emmision/Absorption Spectroscopy and Raman</td>
</tr>
<tr>
<td>8</td>
<td>Ch. 22&lt;br&gt;Lab: AAS/Raman</td>
<td>Intro to Electrochemistry</td>
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<tr>
<td>9</td>
<td>Spring Break</td>
<td></td>
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<tr>
<td>10</td>
<td>Ch. 23 &amp; 24&lt;br&gt;Lab: Potentiometry/Coulometry/Voltammetry</td>
<td>Potentiometry, Conductivity Techniques</td>
</tr>
<tr>
<td>11</td>
<td>Ch. 24 &amp; 25&lt;br&gt;Lab: Potentiometry/Coulometry/Voltammetry</td>
<td>Voltammetry Techniques</td>
</tr>
<tr>
<td>12</td>
<td>Ch. 26&lt;br&gt;Lab: GC-FID/ GC-MS/HPLC</td>
<td>Intro to Chromatography, Chromatography Theory</td>
</tr>
<tr>
<td>13</td>
<td>Ch. 27&lt;br&gt;Lab: GC-FID/ GC-MS/HPLC</td>
<td>Gas Chromatography Instrumentation</td>
</tr>
<tr>
<td>14</td>
<td>Ch. 28&lt;br&gt;Lab: GC-FID/ GC-MS/HPLC</td>
<td>High Performance Liquid Chromatography Instrumentation</td>
</tr>
<tr>
<td>15</td>
<td>Ch. 11 &amp; 20&lt;br&gt;Lab: XRD</td>
<td>Mass Spectroscopy Instrumentation and Spectra interpretation</td>
</tr>
<tr>
<td>16</td>
<td>QA/QC &amp; Review&lt;br&gt;Lab: Practicum, Check-out</td>
<td>Mass Spectrocopy, QA/QC</td>
</tr>
<tr>
<td>17</td>
<td>Final Exam (ACS)</td>
<td>8:00 -10:00 a.m.</td>
</tr>
</tbody>
</table>
Syllabus

Chemistry 4632

Spring 2020

Laboratory: M or W 1:30 – 5:20 p.m. Room 280 and 283 Chemistry

Instructor: Dr. Teresa D. Golden (Room 279 Chemistry, 565-2888 tgolden@unt.edu)

Teaching Assistants: Ali Aminifazl, Jennifer England, and Darshan Karunarathne, Office Hours: MW 10-11 am and TTh 3-4 pm (CHEM 254).

Course Material: Lab Manual (see instructor or TAs). The labs will cover spectroscopy, electrochemistry, chromatography, and selected topics. A pen, calculator, goggles, ruler, and bound lab notebook are required for every lab. All notations, calculations and results are to be included in this lab notebook for each experiment. The TA must sign this book at the end of each lab.
Lab Reports: A formal lab report will be due at the next class period for every lab. This report must include: introduction and theory, experimental section, results, discussion, calculations, graphs, answers to questions, etc. The student will not only be graded on content but also neatness and readability. No late reports will be accepted.

Exams: Lab practicums given during lab time.

Grading: The final lab grade will be calculated using the following: 10% lab book, 10% lab technique and 80% lab reports.
Syllabus
Chemistry 4632   Spring 2020

Week   Lab Assignment*
1 & 2  No Labs
3      Laboratory Practicum: Proper Lab Techniques, Assign Drawers and Glassware
4 & 5  UV Spectroscopy: Mole-ratio and Slope-ratio Method
4 & 5  UV Spectroscopy: Electronic Transitions in Organic Molecules
6 & 7  Infrared Spectroscopy: Spectra of Aldehydes and Ketones
6 & 7  Fluorescence Spectroscopy: Determination of Fluorescein in Antifreeze
8      Atomic Absorption Spectroscopy: Determination of Fe in Food
9      Spring Break
10 & 11 Voltammetry: CV of Vitamin C w/ Graphite Electrodes and Conductivity
10 & 11 Potentiometry: Ion selective electrode, Fluoride in Water and Toothpaste and Voltammetry
12 & 13 GC/FID: Hydrocarbons & Gasoline
12 & 13 GC/MS: Volatile Organics
14 & 15 HPLC: Caffeine
14 & 15 HPLC: Drug Analysis
16     QA/QC and Final Exam

Chem 4631
Syllabus

Chemistry 4631          Spring 2020

California State University Study – Multitasking
  take notes
Purdue University Study - Spacing Effect
  restudy previous material
Washington University – Self-testing (Active testing)
  study groups
Harvard Study – Memory and fine motor skill
  take notes

Study Tips:
  1. Attend Class
  2. Reread/Rewrite Notes Each Week
  3. Write and Draw to Study (Practice Test)
Introduction

Instrumentation - used by chemist to solve analytical problems.

- Measurement of physical properties
- Identification of unknowns
- Preparation of components
<table>
<thead>
<tr>
<th>Characteristic Properties</th>
<th>Instrumental Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission of radiation</td>
<td>Emission spectroscopy (X-ray, UV, visible, electron, Auger); fluorescence, phosphorescence, and luminescence (X-ray, UV, and visible)</td>
</tr>
<tr>
<td>Absorption of radiation</td>
<td>Spectrophotometry and photometry (X-ray, UV, visible, IR); photoacoustic spectroscopy; nuclear magnetic resonance and electron spin resonance spectroscopy</td>
</tr>
<tr>
<td>Scattering of radiation</td>
<td>Turbidimetry; nephelometry; Raman spectroscopy</td>
</tr>
<tr>
<td>Refraction of radiation</td>
<td>Refractometry; interferometry</td>
</tr>
<tr>
<td>Diffraction of radiation</td>
<td>X-Ray and electron diffraction methods</td>
</tr>
<tr>
<td>Rotation of radiation</td>
<td>Polarimetry; optical rotary dispersion; circular dichroism</td>
</tr>
<tr>
<td>Electrical potential</td>
<td>Potentiometry; chronopotentiometry</td>
</tr>
<tr>
<td>Electrical charge</td>
<td>Coulometry</td>
</tr>
<tr>
<td>Electrical current</td>
<td>Amperometry; polarography</td>
</tr>
<tr>
<td>Electrical resistance</td>
<td>Conductometry</td>
</tr>
<tr>
<td>Mass</td>
<td>Gravimetry (quartz crystal microbalance)</td>
</tr>
<tr>
<td>Mass-to-charge ratio</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>Rate of reaction</td>
<td>Kinetic methods</td>
</tr>
<tr>
<td>Thermal characteristics</td>
<td>Thermal gravimetry and titrimetry; differential scanning colorimetry; differential thermal analyses; thermal conductometric methods</td>
</tr>
<tr>
<td>Radioactivity</td>
<td>Activation and isotope dilution methods</td>
</tr>
</tbody>
</table>
Instruments

All instruments have the same basic components:

- **Stimulus**
  - Energy Source

- System under study (sample)

- **Response**
  - Analytical Information
The response is almost always represented by peaks,
but can also be color or a number (i.e. temperature, pH, etc...)
Chemist choose the correct analytical method or instrument to solve a problem.

In order to do this, the chemist must understand a wide variety of instruments and the limitations of each one.
To correctly select the instrument, the problem must be clearly defined.

1. What accuracy is required?
2. How much sample is available?
3. What is the concentration range of the analyte?
4. What components of the sample will cause interference?
5. What are the physical and chemical properties of the sample matrix?
6. How many samples are to be analyzed?
### TABLE 1-3 Numerical Criteria for Selecting Analytical Methods

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Figure of Merit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Precision</td>
<td>Absolute standard deviation, relative standard deviation, coefficient of variation, variance</td>
</tr>
<tr>
<td>2. Bias</td>
<td>Absolute systematic error, relative systematic error</td>
</tr>
<tr>
<td>3. Sensitivity</td>
<td>Calibration sensitivity, analytical sensitivity</td>
</tr>
<tr>
<td>4. Detection limit</td>
<td>Blank plus three times standard deviation of a blank</td>
</tr>
<tr>
<td>5. Concentration range</td>
<td>Concentration limit of quantitation (LOQ) to concentration limit of linearity (LOL)</td>
</tr>
<tr>
<td>6. Selectivity</td>
<td>Coefficient of selectivity</td>
</tr>
</tbody>
</table>
# Precision

## TABLE 1-5  Figures of Merit for Precision of Analytical Methods

<table>
<thead>
<tr>
<th>Terms</th>
<th>Definition*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute standard deviation, $s$</td>
<td>$s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}}$</td>
</tr>
<tr>
<td>Relative standard deviation (RSD)</td>
<td>$RSD = \frac{s}{\bar{x}}$</td>
</tr>
<tr>
<td>Standard deviation of the mean, $s_m$</td>
<td>$s_m = \frac{s}{\sqrt{N}}$</td>
</tr>
<tr>
<td>Coefficient of variation, CV</td>
<td>$CV = \frac{s}{\bar{x}} \times 100%$</td>
</tr>
<tr>
<td>Variance</td>
<td>$s^2$</td>
</tr>
</tbody>
</table>

*x_i = numerical value of the ith measurement.  

$\bar{x} = \text{mean of } N \text{ measurements} = \frac{\sum_{i=1}^{N} x_i}{N}$
Bias

$$\text{Bias} = \mu - x_t$$

$\mu$ – population mean

$x_t$ – true concentration
Bias

Sample – finite number of experimental observations (all the replicate).

The sample is a fraction of the infinite number of observations possible. (i.e. 50 measurements).

This infinite number of observations (measurements) is called the population or universe of data.
Sensitivity

Instruments or methods ability to discriminate between small differences in analyte concentration.
Selectivity

Degree to which the method is free from interference by other species contained in the sample matrix.
Detection Limit

Minimum concentration or mass of analyte that can be detected at a known confidence level.
Dynamic Range

**Figure 1-7** Useful range of an analytical method. LOQ = limit of quantitative measurement; LOL = limit of linear response.
Applications of UV/vis Spectrometry

Calibration curve

Calibration standards need to approximate the composition of sample to be analyzed

If cannot match the matrix – best to use the standard addition method (Chapter 1).
Calibration

- Standard Addition Method
- Internal Standard
Data Analysis

Standard addition method
Add one or more increments of a standard solution to sample aliquots of the same size.
Each solution is diluted to a fixed volume and absorbance is measured.
Plot Absorbance versus Volume Standard Solution, mL.
Data Analysis

Determination of Stoichiometry of Complex Ions

– Mole-ratio method
– Method of continuous variation
Data Analysis

Mole-ratio Procedure

– A known concentration of central atom is prepared
– A known concentration of ligand is prepared at the same concentration
– Add complexing ligand in increments and measure absorbance after each addition
– Plot absorbance versus mole ratio (ligand:metal)
Data Analysis

Determination of Stoichiometry of Complex Ions

Mole-ratio procedure

Example: What is the number of CN- ions attached to Cd$^{3+}$ in basic solution?

<table>
<thead>
<tr>
<th>Absorbance</th>
<th>Mole ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.210</td>
<td>0.75</td>
</tr>
<tr>
<td>0.425</td>
<td>1.50</td>
</tr>
<tr>
<td>0.645</td>
<td>2.25</td>
</tr>
<tr>
<td>0.852</td>
<td>3.00</td>
</tr>
<tr>
<td>1.00</td>
<td>3.75</td>
</tr>
<tr>
<td>1.12</td>
<td>4.50</td>
</tr>
<tr>
<td>1.14</td>
<td>5.25</td>
</tr>
<tr>
<td>1.15</td>
<td>6.00</td>
</tr>
</tbody>
</table>
Data Analysis

Determination of Stoichiometry of Complex Ions

Absorbance vs. mole ratio graph showing a linear relationship between the two variables.
Data Analysis

Determination of Stoichiometry of Complex Ions

Mole-ratio procedure

There are four ligands to one metal ion

\[ \text{[Cd(CN)\textsubscript{4}]^{2-}} \]
Data Analysis

Determination of Stoichiometry of Complex Ions

Method of Continuous Variation

Total number of moles of ligands + moles of $M^{n+}$ is constant.
Data Analysis

Determination of Stoichiometry of Complex Ions

Method of continuous variation

Procedure:

– Mix 2.0 mL of one solution (0.01 M) and 8.0 mL of the other (0.01 M) (must use 10 mL for all other measurements)
– Measure absorbance of each mixture
– Plot absorbance versus mole fraction of ligand

(moles of ligand/moles of ligand + moles of metal)
Data Analysis

Determination of Stoichiometry of Complex Ions
Method of Continuous variation

Example:

Determine the ratio of ligand to metal for the Fe\(^{2+}\)-phenanthroline system, if a continuous variation gave the following:

<table>
<thead>
<tr>
<th>Absorbance</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.1</td>
</tr>
<tr>
<td>0.22</td>
<td>0.2</td>
</tr>
<tr>
<td>0.33</td>
<td>0.3</td>
</tr>
<tr>
<td>0.45</td>
<td>0.4</td>
</tr>
<tr>
<td>0.56</td>
<td>0.5</td>
</tr>
<tr>
<td>0.67</td>
<td>0.6</td>
</tr>
<tr>
<td>0.76</td>
<td>0.7</td>
</tr>
<tr>
<td>0.65</td>
<td>0.8</td>
</tr>
<tr>
<td>0.33</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Data Analysis

Determination of Stoichiometry of Complex Ions
Method of continuous variation

Absorbance vs. mole fraction of chelate graph.
Data Analysis

Determination of Stoichiometry of Complex Ions
Method of continuous variation

\[ 0.75 = \frac{0.75}{0.75 + 0.25} \]

0.75 – mole fraction of chelate
0.25 – mole fraction of metal

3 times as much ligand as metal ion
Data Analysis

Determination of Stoichiometry of Complex Ions
Method of continuous variation

Very low ligand concentrations give low absorbance on the first side of the curve. On the second side you have high ligand concentrations but low Fe$^{2+}$. 
Determination of Stoichiometry of Complex Ions

Method of continuous variation

Coordination number = 6
(ligand binds twice to Fe$^{2+}$, bidentate ligand)
Applications of UV/vis Spectrometry

Quantitative Analysis
- Useful for both organic and inorganic systems
- Sensitive ($10^{-4}$ to $10^{-5}$ M)
- Moderately selective
- Good accuracy
- Easy and convenient to use
Assignment

• Read Chapter 1
• Read Appendix 1
• Homework: Ch. 1: 11 and
  Appendix 1: 1, 2, 10, and 12
  (extra credit)