**CHEM 502 - Instrumental Analysis**

**Section 001, Course# 11641, 3.0 Credit Hrs – Fall 2009**

**Time/Location**: 12:30 - 1:45 TR / Sims 302

**Professor:** Dr. Cliff Calloway, [callowayc@winthrop.edu](mailto:callowayc@winthrop.edu)

**Office/Phone:** 312-B Sims Hall / 323-4945

**Office Hours:** MWF 10:00 - 12:00 {And other times by appointment….please don’t hesitate to contact me.}

**Textbook:** Skoog, D.A., Holler, F.J., Crouch, S.R. *Principles of Instrumental Analysis,* 6thedition, 2007.

**Pre-requisites:** Grade of C or better in Chem 313, 314 and Chem 301

**Introduction:**

Chemical analysis methods are frequently used in biotechnology, pharmaceutical, environmental, geological, materials development, forensic, medical, nutritional, and industrial labs. The scientists and engineers conducting research and development for these industries often seek answers to chemical identity, structure, or amounts. As such, chemical analysis plays a critical role in scientific development. Qualitative and quantitative methods of chemical analysis for organic, biochemical, and inorganic compounds fall into two categories….**classical (or wet)** methods and **instrumental** methods. In Chemistry 313/314, we surveyed some classical methods of analysis, including titration, gravimetric and volumetric analysis, as well as some instrumental methods of analysis (gas & liquid chromatography, atomic & molecular spectrometry, and electrochemistry). Although there is not always a clear barrier between the two, the primary difference arises from the type of physical property used to provide information. Classical methods often rely on reactivity or physical properties such as solubility, color, melting and/or boiling points, odors, or refractive indices for qualitative information, while gravimetric, volumetric, and titrimetric measurements provide quantitative information. Classical methods for the separation of mixtures are mainly solvent extractions, precipitation, and distillation. Instrumental methods of analysis typically utilize other physical properties such as absorption or emission of light, mass-to-charge ratio, electrode potential, current, or charge measured with modern sophisticated electronic devices. Separations are carried out by more efficient chromatography and electrophoresis methods.

Instrumental methods of analysis certainly extend well beyond the chemistry lab. Unfortunately, some scientists view and utilize these instruments as "black boxes". The term implies a device in which the scientist places a sample and somehow a number is generated that influences the scientist’s decision-making process. It should be apparent that this approach could be dangerous, as the old saying "Garbage In/Garbage Out" is often true. As such any scientist using sophisticated instrumental equipment needs at least a basic understanding of how these devices are designed to work.

**Course Goals:**

Instrumental Analysis is a broad and continually expanding subject as new technologies emerge, but these methods can generally be categorized as spectroscopic, electrochemical, or chromatographic. In this course, we will essentially take the cover off these "black boxes" to see how these instruments are constructed and how measurements are made from the underlying chemical and physical properties of the substance. In fact, you are likely to see instrumentation represented from other courses you’ve taken, demonstrating the broad impact instrumentation has in science. Quantitative problem solving will be utilized as a means to demonstrate the chemical and physical principles applied to the design and performance of instruments.

The goal of this course is NOT to make you an "expert" on every type of instrumentation to be encountered in a science lab, but rather to introduce and educate you to the common principles as well as the variety of instrumentation available for chemical analysis and the type(s) of information these instruments provide. It is my hope that you will then expand your knowledge of the instruments you come into contact with during your scientific career, thereby avoiding the "black box" problem.

**Specific Course Objectives:**

By the end of this course, you should be able to demonstrate:

* an understanding of how chemical and physical properties of substances are used in the design and construction of modern sophisticated instrumentation used for chemical analysis
* a broad knowledge of the types of instrumentation generally available and the information provided by each
* a knowledge of appropriate instrumental methods for addressing a chemical analysis problem
* the advantages, disadvantages, and limitations of different instruments used for similar types of analyses
* rigorous mathematical methods to evaluate instrument performance

#### Grading/Evaluation:

#### Student Conduct Code: “Responsibility for good conduct rests with students as adult individuals.” Since all graded work (including homework to be collected, quizzes, papers, mid-term examinations, final examination, research proposals, laboratory results and reports, etc.) are used in the determination of academic progress, no collaboration on such work is permitted unless the instructor explicitly indicates that some specific degree of collaboration is allowed. This statement is not intended to discourage students from studying together, seeking help from the instructor, or working together on assignments that are not to be collected. Refer to the “Academic Misconduct Policy” in the online *Student Handbook*: <http://www2.winthrop.edu/studentaffairs/handbook/StudentHandbook.pdf>

#### Grades in this course will be determined from three sources, as follows:

* Homework (20%): Periodically, homework problems will be assigned from the textbook or as handouts, and collected. Due dates for each assignment are the final date each assignment will be accepted. Your lowest homework assignment will be dropped before averaging.
* Mid-term Exams (60%): There will be 4 exams given during the term covering the topics listed below. Make sure to bring pencil and scientific calculator to the exam. Make-up exams will not be given except under extreme circumstances. If you plan to miss an exam with valid excuse, let me know as soon as possible. The exams are scheduled as follows:
  + Exam 1: September 17
  + Exam 2: October 15
  + Exam 3: November 12
  + Exam 4: December 1
* Final Examination (20%): Friday, December 11, 11:30 a.m. – 2:00 p.m. This will be a cumulative final examination given during exam week. If you score higher on the final exam than your lowest mid-term exam, the final exam grade will replace the lowest exam grade, before averaging.

 Letter grades will be assigned as follows:

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 94 - 100%: | A | 90-93%: | A- | 86-89%: | B+ | 82-85%: | B | 78-81%: | B- |
| 74-77%: | C+ | 70-73%: | C | 66-69%: | C- | 62-65%: | D+ | 58-61%: | D |
| 55-57%: | D- |  |  |  |  |  |  |  |  |

**Attendance:**

You are expected to attend each class meeting for the full scheduled time. Instrumental Analysis is a difficult upper-level course and this will help you to concentrate on the appropriate material and reinforce the assigned readings and problems. You are required to bring pencil, paper, textbook, and a scientific calculator to each class. Cell phone calculators are not acceptable.

**Students with Disabilities:**

Winthrop University is dedicated to providing access to education.  If you have a disability and require specific accommodations to complete this course, contact Services for Students with Disabilities, at 323-3290.  Once you have your official notice of accommodations from Services for Students with Disabilities, please inform me as early as possible in the semester.

# **Additional Requirements for Graduate Level Credit:**

# Students wishing to receive graduate level credit for this course are required to complete a 5-7 page review paper on a cutting edge analytical technique. Resources can be found by reviewing either the “Fundamentals Review” or “Applications Review” issues of the journal, *Analytical Chemistry* (June 15th issue of even & odd years, respectively). The paper must cite a minimum of 10 primary literature sources and must be submitted by December 8, 2009. Graduate students should be aware that Winthrop’s +/- grading system is not applicable to courses taken for graduate credit. Letter grades will be assigned as follows: 92%-100% A; 83%-91% B; 74%-82% C, 55%-73% D.

# **Syllabus Changes:**

# While unlikely, the Professor reserves the right to change the course syllabus if circumstances dictate. You will be notified of any change through class meetings and/or email.

**Course Calendar: \*Revised – August 25, 2009**

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| **Tentative Schedule\*:** |  |  |  |
| **Date** |  | **Lecture Sections** |  |
| T, 25-August |  | Introduction, Ch.1 |  |
| R, 27-August |  | Ch. 2A |  |
| T, 1-September |  | Ch. 2B-C |  |
| R, 3-September |  | Ch. 3A-C |  |
| T, 8-September |  | Ch. 5A-B |  |
| R, 10-September |  | Ch. 5C |  |
| T, 15-September |  | Ch. 6A-B; Review |  |
| R, 17-September |  | **Exam 1 (Ch. 1-3C, 5)** |  |
| T, 22-September |  | Ch. 6C-D |  |
| R, 24-September |  | Ch. 7A-B |  |
| T, 29-September |  | Ch. 7C-E |  |
| R, 1-October |  | Ch 7F-7I |  |
| T, 6-October |  | Ch. 13 |  |
| R, 8-October |  | Ch. 15 |  |
| T, 13-October |  | Ch. 16A; Review |  |
| R, 15-October |  | **Exam 2 (Ch. 6-7, 13, 15)** |  |
| T, 20-October |  | **Fall Break** |  |
| R, 22-October |  | Ch. 16B-C |  |
| T, 27-October |  | Ch. 18A |  |
| R, 29-October |  | Ch. 18B-C |  |
| T, 3-November |  | Ch. 19A-C |  |
| R, 5-November |  | Ch. 19D-H |  |
| T, 10-November |  | Ch. 26A-F; Review |  |
| R, 12-November |  | **Exam 3 (Ch. 16, 18, 19)** |  |
| T, 17-November |  | Ch. 29A-C |  |
| R, 19-November |  | Ch. 30A-B |  |
| T, 24-November |  | Ch. 30C-E; Review |  |
| R, 26-Novemberl |  | **Thanksgiving Break** |  |
| T, 1-December |  | **Exam 4 (Ch. 26, 29, 30)** |  |
| R, 3-December |  | Review & Course Evaluation |  |
| T, 8-December |  | **Study Day** |  |
| F, 11-December |  | **Final Exam – 11:30 am** |  |

\*Subject to change, if weather or events make it necessary.

### Instrumental Analysis Student Competencies

#### *Principles of Instrumental Analysis, 6th. ed.*, Douglas A. Skoog, F. James Holler, Stanley R. Crouch, 2007.

#### Chapter 1 Student competencies

***Upon completion of this chapter, students should be able to:***

* Differentiate between Classical Methods of Analysis and Instrumental Methods of Analysis.
* Describe the different domains through which data is passed within a sophisticated instrument.
* Understand the terms detector, transducer, and sensor.
* Have a general knowledge of how to select an analytical method for chemical analysis.
* Calculate and interpret analytical figures of merit, including accuracy, precision, signal-to-noise ratio, sensitivity (calibration and analytical), limit of detection (LOD), linearity via log-log plots, and linear dynamic range (LDR)
* Utilize calibration, standard addition, and internal standard methods of analysis, as introduced in Quantitative Analysis.

#### Chapter 2 Student competencies

***Upon completion of this chapter, students should be able to:***

* Utilize the basic laws of electricity, including Ohm’s Law, Kirchoff’s current and voltage laws, and the power law to find voltage, current, resistance or wattage.
* Determine the total resistance in a series circuit or calculate voltage at various points in a voltage divider.
* Determine the total resistance in a parallel circuit or calculate the current at various points in a current divider.
* Differentiate between dc and ac circuits.
* Work with expressions for sinusoidal currents, including terms related to amplitude, period, frequency, angular velocity, and phase angle.

#### Chapter 3 Student competencies

#### *Upon completion of this chapter, students* *should be able to:*

#### Understand purpose of an operational amplifier in instrument measurement including general structure of these integrated circuits

#### Understand difference between inverting and non-inverting inputs

#### Understand the operational modes used including comparator, voltage follower, and current follower

#### Know how operational amplifiers are used for current & voltage amplification

#### Chapter 5 Student competencies

***Upon completion of this chapter, students should be able to:***

* Determine and interpret the meaning of the signal-to-noise ratio.
* Explain sources of instrumental noise, including shot, flicker, and environmental noise, and factors that influence the magnitude of each.
* Classify an instrument as shot or flicker noise limited.
* Understand the various hardware techniques used to reduce environmental and external electronic noise sources.
* Describe the purpose of differential and instrumental amplifiers in instrumental design as well as contrast the advantages and disadvantages of each type of amplifier
* Describe the purpose of high pass; low pass; and narrow band pass analog filters in instrument design.
* Discuss the technique of modulation/demodulation in noise reduction of dc signals.
* Describe how a lock-in amplifier works.
* Understand the various software techniques used to reduce noise including ensemble averaging, boxcar averaging, digital filtering, and Fourier transform.

#### Chapter 6 Student competencies

***Upon completion of this chapter, students should be able to:***

* Describe the wave and particle properties of electromagnetic radiation.
* Inter-convert between wavelength, frequency, period, energy, and wavenumber.
* Describe the relative ordering of the electromagnetic spectral regions and the types of transitions that occur in each region.
* Describe the superposition of wave theory, and how this relates to Fourier transform
* Describe diffraction of radiation.
* Define coherent radiation, blackbody radiation, fluorescence, phosphorescence, resonance fluorescence, Stokes and Anti-Stokes Shifts.
* Contrast line, band, and continuum spectra.
* Inter-convert between transmittance and absorbance data.
* Utilize Beer’s Law to determine concentrations from absorbance data, and vice versa.

#### Chapter 7 Student competencies

***Upon completion of this chapter, students should be able to:***

* Describe and diagram the basic components in absorption, emission, and luminescence optical spectrometers
* List and describe some common light sources used in the infrared, visible, and UV regions of the electromagnetic spectrum
* Describe the differences between line, continuum, and quasi-continuum light sources, and the applications of each.
* Describe the components of a laser.
* Describe the four mechanisms involved in a laser and which processes contribute to or attenuate laser power.
* Describe various wavelength selectors including absorption filters, interference filters, and monochromators (Bunsen, Czerny-Turner, and Echelle.
* Describe how diffraction gratings disperse light.
* Utilize the grating formula to calculate wavelengths at various incident and reflected angles for various orders.
* Understand the terms single channel and multi channel radiation transducer.
* List and describe phototubes, photomultiplier tubes, and silicon photodiodes.
* List and describe linear diode arrays, charge coupled devices, and charge injection devices.

#### Chapter 13 Student competencies

***Upon completion of this chapter, students should be able to:***

* Differentiate between radiant power and intensity.
* Define and calculate transmittance and absorbance.
* Differentiate between absorptivity and molar absorptivity in Beer’s Law
* Derive Beer’s Law.
* Give limitations to Beer’s Law
* Utilize Beer’s Law in solving for concentration of mixtures and equilibrium concentrations.
* Describe what is meant by photometric error.
* Describe the components and arrangements of a single beam and double beam spectrophotometer and the purpose of each design.
* Describe common sources and detection systems used in molecular UV/Vis spectrometry.

#### Chapter 15 Student competencies

***Upon completion of this chapter, students should be able to:***

* Explain the terms resonance fluorescence, Stokes shift, diamagnetic, paramagnetic, singlet state, doublet state, and triplet state.
* Draw energy level diagrams representing fluorescence and phosphorescence indicating absorption, internal conversion, vibrational relaxation, intersystem crossing, fluorescence, and phosphorescence.
* Distinguish between fluorescence and phosphorescence.
* Define quantum yield.
* Discuss variables that affect fluorescent and phosphorescent quantum yield including structure relationships, type of transition, dissolved oxygen, heavy atoms, temperature and pH.
* Explain relationship between fluorescent intensity and concentration leading to quantitative methods of analysis
* Discuss sources of deviation from linearity for fluorescence including self-quenching and self-absorption
* Explain the difference between Excitation and Emission Spectra.
* Describe the typical components and arrangement of a typical spectrofluorometer.
* Describe the components used for phosphorimetry.
* Discuss standardization of fluorescence instruments
* Discuss methods of analysis in molecular luminescence including the use of fluorescent derivatives and measurement of luminescent lifetime.
* Use calibration curve and standard addition methods of analysis for concentration determination from luminescence measurements

#### Chapter 16 Student competencies

***Upon completion of this chapter, students should be able to:***

* Describe the various types of molecular vibrations and the factors that lead to infrared radiation absorption.
* Describe and utilize mathematical relationships from the classical and quantum mechanical models for molecular vibration to calculate vibrational frequencies.
* Calculate the number of normal modes of vibration for linear and non-linear molecules.
* Describe vibrational coupling and its consequences.
* Discuss various components of infrared spectrometers.
* Explain time and frequency domain spectroscopy
* Describe the frequency problem in time domain IR spectroscopy and a Michelson interferometer.
* Use mathematical relationships to relate interferogram to source frequencies.
* Use mathematical relationships to calculate resolution in Fourier transform instruments.
* Compare dispersive and Fourier transform IR spectrometers.

#### Chapter 18 Student competencies

***Upon completion of this chapter, students should be able to:***

* Describe the mechanism leading to Raman and Rayleigh scattering, including definition of virtual state, leading to Stokes and Anti-Stokes shifts.
* Compare the factors that lead to Raman spectra with infrared spectra.
* Describe the components of a typical Raman spectrometer.
* Convert frequency shifts in Raman spectra to wavelength for a given source.
* Explain how a depolarization ratio is determined in Raman and the information gained.

#### Chapter 19 Student competencies

***Upon completion of this chapter, students should be able to:***

* Describe how a proton NMR spectrum arises quantum and classical descriptions, including calculation of transition frequency and influence of magnetic field strength.
* Use Boltzman calculation for population of excited state.
* Describe saturation and relaxation processes in NMR
* Describe Fourier transform in NMR.
* Describe environmental influences to NMR signals including chemical shift and spin-spin splitting.
* Discuss decoupling techniques in NMR
* Describe the components of a typical FT-NMR.
* Describe the purpose of locking and shimming an NMR spectrometer.
* Describe and show how NMR can be used for qualitative analysis.
* Apply NMR theory to carbon-13 nuclei.
* Discuss application of 2-D NMR to structure elucidation.

#### Chapter 26 Student competencies

#### *This chapter will be covered quickly for review of separation concepts. You should be familiar with these and be able to:*

#### Define chromatographic separation terms including partition coefficient, retention time, retention volume, adjusted retention time and volume, capacity factor, relative retention, number of plates, and plate height

#### Understand the major driving forces that lead to chromatographic band broadening, including multiple path, longitudinal diffusion, and mass transfer.

#### Understand the factors that influence resolution in chromatographic systems.

#### Apply chromatographic systems to problems of qualitative and quantitative analysis.

#### Chapter 29 Student competencies

***Upon completion of this chapter, students should be able to:***

* Describe supercritical fluids including properties relative to gases and liquids, such as density, diffusion, and viscosity.
* Draw a block diagram for SFC instrument.
* Give examples of types of detectors used in SFC
* Compare advantages & disadvantages of SFC relative to HPLC and GC.
* Describe the effect of pressure on chromatograms.
* Describe the advantageous properties of supercritical carbon dioxide
* Compare supercritical fluid and liquid-liquid extractions.

#### Chapter 30 Student competencies

***Upon completion of this chapter, students should be able to:***

* Describe the separation mechanism in electrophoresis.
* Describe common current applications of electrophoresis.
* Draw a block diagram of a CE system.
* Compare CE and slab electrophoresis.
* Relate migration velocity to field strength and electrophoretic mobility.
* Describe how the structural features of substance influence electrophoretic mobility.
* Calculate plate height and number of plates in a capillary.
* Describe the mechanism of electroosmotic flow, and the effect on positive, negative, and neutral analytes
* Use van Deemter’s equation to compare separation efficiency relative to HPLC & GC
* Discuss electrokinetic and hydrodynamic (pressure) injection methods in CE
* Give examples of common detectors used in CE