Ch 313 FINAL EXAM OUTLINE
Spring 2009

NOTE: Use this outline at your own risk – sometimes a topic is omitted that you are still responsible for. It is meant to be a study aid and is <u>not meant to be a replacement</u> for actually reviewing the lecture notes and homework assignments.

<u>Ch 1 - Introduction</u>

- Goal and Method
- Stimuli for various Instrumental Methods
- Basic components of instruments
- Basic statistics review
- Calibration Curves - sensitivity, detection limits (LOD)

<u>Ch 6 – An Introduction to Spectrometric Methods</u>

- EM radiation – wavelength, frequency, photons
- EM spectrum (know qualitatively) - calculations of □ and □
- Superposition of waves – constructive and destructive interference
- Fraunhofer Diffraction – order, intensity, widths of color bands, blue diffracted <u>smaller</u> angle than red
- Refraction of Light - refractive index, dispersion, unequal widths of color bands, blue refracted <u>larger</u> angle than red
- Interactions of Radiation and Matter – absorption, emission, luminescence, scattering
- Atomic vs. Molecular transitions

<u>Ch 7 – Components of Optical Instruments</u>

- Spectroscopy, Optical Instruments, Optical Spectroscopic Methods
- % basic elements of optical instruments
- Sources of Radiation
- Optical materials – visible, UV, IR
- Filters – FWHM, bandwidth
- Grating monochromator design and components
- Echellette grating and the grating equation, holographic gratins
- Reciprocal Linear Dispersion
- Resolving Power of Monochromators
- Light Gathering Power of Monochromators
- Effect of slit width on resolution
- Resolution
- Radiation Transducers - vacuum phototube, photomultiplier tube, photodiodes, photodiode arrays, CCD's, spectral response

<u>Ch 13 – An Introduction to Ultraviolet-Visible Molecular Absorption Spectrometry</u>

- Transmittance and absorbance
- Beer's Law – wavelength dependence of molar absorptivity
- Absorbance spectrum – molar absorptivity is wavelength dependent
- Limitations to Beer's Law - concentration effect, chemical deviations (equilibrium), polychromatic radiation, stray light
- Light sources – UV and Vis, blackbody radiation and continuum sources
- Single vs. Double Beam Instruments – how double beam instruments remove the background
- Double Dispersing Instruments - How stray light controls the LOD
- Multichannel Instruments

Ch 14 – Applications of Ultraviolet-Visible Molecular Absorption Spectrometry

- Absorption by Organic Molecules - types of electronic transitions, e.g. □ → □*, allowed vs. forbidden transitions
- General Absorbance Spectrum
- Spectral details are lost in the liquid phase - fine structure from vibrational sublevels
- Qualitative Analysis - Solvent shifts, effect of ring substituents on aromatic rings, effect of pH (indicators)
- Quantitative Analysis - mixtures, sample matrix and standard addition methods, derivative spectroscopy, enzyme kinetics

Ch 15 - Molecular Luminescence Spectrometry

- Fluorescence, Phosphorescence and Nonradiative Decay - Singlet vs. triplet states, Jablonski Diagrams
- Quantum Yields
- Vibrational relaxation, internal conversion, intersystem crossing
- Luminescence lifetimes
- Fluorescence and structure
- Illustration of the Heavy Atom Effect
- Emission and excitation spectra
- Instruments for Measuring Fluorescence and Phosphorescence
- Xe-arc lamps
- Spectrofluorometers - corrected spectra
- Phosphorimeters
- Selectivity
- Effect of Concentration on Fluorescence Intensity
- Absorbance vs. Fluorescence Signals
- Comparing UV-Vis to Fluorescence LOD's
- Applications – Inorganic, Organic, Forensics, Imaging

Equations to know

$R = \langle\lambda\rangle/\Delta\lambda\rangle$, R(max) = **n**N for a grating monochromator
LOD = $3\sigma_{bl}/m$
calibration and analytical sensitivities
$c = \lambda\nu$, $E = h\nu$
$m\lambda = d(\sin i$ " $\sin r)$
$1/2|\lambda_1 - \lambda_2| = \omega D^{-1}$
$T = P/P_o$, $A = -\log(T)$
Beer's Law $A = \varepsilon bc$

Ch 8, 9, & 10 - An Introduction to Optical Atomic Spectrometry, Atomic Absorption and Atomic Fluorescence Spectrometry, and Atomic Emission Spectrometry

- atomic spectra - emission, absorption, fluorescence
- line broadening
- flame atomization - common fuel mixtures
- flame populations
- flame structure and T profile
- sample positioning and flow rates
- atomization and nebulization
- burners
- electrothermal atomization - graphite furnace
- Atomic Absorption Spectroscopy - hollow cathode lamps
- interferences - releasing & protecting agents, ionization in flames
- LOD's as a function of atomization method
- Inductively Coupled Plasma (ICP) Spectroscopy
    - source
    - sample injection
    - instrumentation (echelle gratings, etc)
    - applications (multiple elements simultaneously)
    - LOD's and interferences

Ch 12 - Atomic X-Ray Spectrometry

- Emission of X-Rays – Electron Beam Source
- Continuum and Line Sources
- Line Spectra (K, L, M...)
- Origin of X-Ray Line Spectra
- Radioactive Sources
- X-Ray Fluorescence
- Diffraction and Bragg's Law
- Photon Counting
- Wavelength Dispersive versus Energy Dispersive Instruments

Ch 16 & 17 - An Introduction to Infrared Spectrometry and Applications of Infrared Spectrometry

- Theory - wavenumbers
- vibrational frequency
- absorption process and selection rules
- types of vibrations (normal modes)
- calculating wavenumber of a peak
- frequency-mass and force constant-bond strength correlations
- Definition of the Fourier Transform – know what it does qualitatively
- Instrumentation
    - IR sources
    - optics
    - sample handling
    - detectors - pyroelectric (DTGS), photoconducting (MCT), wavelength ranges
- FTIR
    - Fellget's (Multiplex) Advantage
    - Michelson interferometer
    - interferogram and Fourier Transformation
    - resolution of a Michelson Interferometer
    - single-beam instrumentation
    - performance

- advantages/disadvantages

- Applications of IR
- Qualitative IR - peak identification from a correlation chart
- Quantitative IR - reasons why IR less sensitive and why FTIR has improved sensitivity
- Diffuse Reflectance
- ATR Spectrometry
- IR Microscopy

Ch 18 – Raman Spectroscopy

- Rayleigh scattering (from Ch 6 – section 6B-10)
- Raman Scattering – Stokes and anti-Stokes
- Excitation and Mechanism of Raman Spectra
- Comparison of Raman & IR Spectra
- Instrumentation
  - source
  - sample illumination system
  - fiber optics
  - spectrometers: dispersive and Fourier Transform
- Process Analytical Chemistry

Ch 19 - Nuclear Magnetic Resonance Spectroscopy

- Theory of NMR – nuclear spin states, spin quantum number (I), number of spin states 2I+1, energy levels in an external magnetic field, ΔE and absorption of radiofrequency radiation
- Classical Description of NMR – precession, circularly polarized radiation, Larmor Frequency
- FT-NMR – pulsed excitation, free induction decay (FID)
- Origin of the Chemical Shift, Shielding
- General Correlation Chart
- Theory of the Chemical Shift – electronegativity, hybridization, acidic protons, magnetic anisotropy
- 1^{st} Order Interpretation of NMR Spectra – spin-spin splitting (N+1 rule), simple interpretation of an NMR spectrum, signal integration
- FT-NMR Spectrometers
- Resolution of FT-NMR Spectrometers
- Carbon-13 NMR

Ch 20 - Molecular Mass Spectrometry

- outline of technique (sample → fragments etc), ion sources
- hard vs. soft ionization
- electron impact (EI) ionization
- electron impact ion source
- McLafferty rearrangement
- example electron impact spectra – alkanes and aromatics
- chemical ionization (CI) – methane as reagent gas
- electrospray ionization and spectra
- Instrumentation outline
- Mass analyzers - magnetic sector, quadrupole, time of flight
- electron multiplier detector

Ch 26 - An Introduction to Chromatographic Separations

MAJOR GOAL: Be able to use the Rate Theory of Chromatography to practically explain what controls plate height in separations, e.g. find μ_{opt}, diffusion constants in the mobile and stationary phases, temperature effects, particle size, etc.

- General Description of Chromatography
- Classification of Chromatographic Methods
- Elution in Column Chromatography
- Plate Theory – band broadening, experimental evaluation of H and N from the chromatogram
- Rate Theory - longitudinal diffusion, stationary phase-mass transfer term, eddy diffusion, Van Deemter equation, optimal flow rate
- Practical Control of Separation
- Resolution
- Retention (Capacity) Factor – optimal value
- Selectivity Factor
- Resolution, capacity factor, and selectivity combined expression

Ch 27 - Gas Chromatography

- basic description of process (stationary phase, mobile phase, match sample polarity to stationary phase, separate by boiling points, etc)
- Basic Instrumentation
- injection port – know split vs. splitless
- packed columns, solid support, bonded phases, liquid-coated stationary phases
- capillary columns – we use WCOT
- common stationary phases in capillary GC – be able to draw structure of a polysiloxane, know cross-linking and column bleed (max column temperature)
- Effect of particle size on the Eddy Diffusion term
- temperature programming
- detectors – thermal conductivity, FID, ECD
- Gas Chromatography-Mass Spectrometry – TIC vs. SIC
- example separations

Ch 28 - High Performance Liquid Chromatography

- HPLC, scope of LC, partition chromatography
- LC van Deemter plots – understand effect of particle size and lack of B-term

- Instrumentation
  - mobile phase – isocratic vs. gradient elution, "sparging"
  - reciprocating pumps
  - sample injection
  - columns – bonded vs liquid-coated phases same as GC
  - detectors - UV-Vis, refractive index, LC-MS

- normal vs. reversed phase separations
- mobile phase
- Applications