Chem 502 - Instrumental Analysis **Section 001, Course# 12238, 3.0 Credit Hrs, Fall Semester, 2013**

Time/Location: 12:30 - 1:45 TR / Sims 111
Professor: Dr. Cliff Calloway, callowayc@winthrop.edu
Office/Phone: 312-B Sims Science Building / 323-4945
Office Hours: MTWF 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,* 6th edition, 2007.
Pre-requisites: Grade of C or better in Chem 313, 314 and Chem 301
Co-requisite: Chem 503, Instrumental Analysis Lab
Registration Calendar (link to important dates for registration, S/U, graduation, etc)

Introduction:
Chemical analysis methods are used in biotechnology, pharmaceutical, environmental, geological, materials development, forensic, medical, nutritional, energy and industrial labs daily that have a profound impact on decisions made locally, regionally, nationally and globally. Scientists and engineers conducting research and development for these industries often seek answers to chemical identity, structure, or amounts questions. As such, chemical analysis plays a critical role in scientific development and the quality of our lives. 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.

Winthrop University's faculty adopted a set of four University Level Competencies (ULCs) that describe the qualities our students develop during their Winthrop career. It is easy to see that this course involves solving problems and developing written communication skills. However, you will also learn the responsibilities of chemists to the greater good of our planet and society, as well as the global nature of the chemistry enterprise. Within the discussions of chemical analysis instrument design and applications to the environment, health and materials we use every day, I think you will find this course fits well with all four competencies.

Competency 1:Winthrop graduates think critically and solve problems.

Winthrop University graduates reason logically, evaluate and use evidence, and solve problems. They seek out and assess relevant information from multiple viewpoints to form well-reasoned conclusions. Winthrop graduates consider the full context and consequences of their decisions and continually reexamine their own critical thinking process, including the strengths and weaknesses of their arguments.

Competency 2:Winthrop graduates are personally and socially responsible.

Winthrop University graduates value integrity, perceive moral dimensions, and achieve excellence. They take seriously the perspectives of others, practice ethical reasoning, and reflect on experiences. Winthrop graduates have a sense of responsibility to the broader community and contribute to the greater good.

Competency 3:Winthrop graduates understand the interconnected nature of the world and the time in which they live.

Winthrop University graduates comprehend the historical, social, and global contexts of their disciplines and their lives. They also recognize how their chosen area of study is inextricably linked to other fields. Winthrop graduates collaborate with members of diverse academic, professional, and cultural communities as informed and engaged citizens.

Competency 4:Winthrop graduates communicate effectively.

Winthrop University graduates communicate in a manner appropriate to the subject, occasion, and audience. They create texts - including but not limited to written, oral, and visual presentations - that convey content effectively. Mindful of their voice and the impact of their communication, Winthrop graduates successfully express and exchange ideas.

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.

Student Learning Outcomes:

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, applications
- 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

Course Requirements for 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 requirements, 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 5
- Exam 2: October 1
- Exam 3: October 29
- Exam 4: November 21

- Final Examination (20%): Thursday, December 5, 3:00 p.m. - 5:30 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:

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 <u>each</u> 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 the Office of Disability Services at 323-3290 (Crawford Building, 110A), http://www.winthrop.edu/hcs/default.aspx?id=23186. Once you have your official notice of accommodations, please let me know 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 15^{th} issue of even & odd years, respectively). The paper must cite a minimum of 10 primary literature sources and must be submitted by December 5, 2013. 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 via class meeting time and/or email.

Course Calendar: ***Revised** August 16, 2013

Tentative Schedule*:			
Date		**Lecture Sections**	**Topic**
T, 20-August		Introduction, Ch.1	Figures of Merit
R, 22-August		Ch. 2A	Electronics Basics I
T, 27-August		Ch. 2B-C	Electronics Basics II
R, 29-August		Ch. 3A-C	Operational Amplifiers
T, 3-September		Ch. 5A-B	Signals and Noise, Review
R, 5-September		**Exam 1 (Ch. 1-3C, 5)**	
T, 10-September		Ch. 6A-B	Spectroscopy I
R, 12-September		Ch. 6C-D	Spectroscopy II
T, 17-September		Ch. 7A-B	Optical Components I
R, 19-September		Ch. 7C-D	Optical Components II
T, 24-September		Ch. 7E-7H	Optical Components III
R, 26-September		Ch. 13A	Electronic Spectroscopy I, Review
T, 1-October		**Exam 2 (Ch. 6-7H)**	
R, 3-October		Ch. 13B-D	Electronic Spectroscopy II
T, 8-October		Ch. 15A	Luminescence I
R, 10-October		Ch. 15B-C	Luminescence II
T, 15-October		**Fall Break**	
R, 17-October		Ch. 16A	Infrared Spectroscopy I
T, 22-October		Ch. 16B-C	Infrared Spectroscopy II
R, 24-October		Ch. 18A-C	Raman Spectroscopy, Review
T, 29-October		**Exam 3 (Ch. 13, 15, 16,18)**	
R, 31-October		Ch. 19A-C	Nuclear Magnetic Resonance I
T, 5-November		Ch. 19D-H	Nuclear Magnetic Resonance II
R, 7-November		Ch. 20A-B	Mass Spectrometry I
T, 12-November		Ch. 20C-E	Mass Spectrometry II
R, 14-November		Ch. 30A-B	Capillary Electrophoresis I
T, 19-November		Ch. 30C-D	Capillary Electrophoresis II, Review
R, 21-Novemberl		**Exam 4 (Ch. 19, 20, 30)**	
T, 26-November			Final Exam Review
R, 28-November		**Thanksgiving Break**	
T, 3-December		**Study Day**	
F, 5-December		**Final Exam - 3:00 pm**	

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

CHEM 502 -Exam I Name:________________________
September 8, 2013

This exam covers material from Chapters 1, 2, 3 and 5. You will have the entire period to complete the exam. Calculators may be used as appropriate, but may not be shared. SHOW ALL WORK. Full credit will not be given without showing your work or appropriate units. You do NOT have to show a calculation of mean, standard deviation or linear regression slope/intercept, if your calculator does this for you. By signing your name above, you pledge that no help was given or received.

Potentially useful info:

1ppm = 1 µg/mL (aqueous) 1ppm = 1000 ppb $N_a = 6.022 \times 10^{23}\ mol^{-1}$

$\gamma = m/s_x$ $LOD = 3s_{bl}/m$ $\bar{x} \pm \frac{ts}{\sqrt{n}}$ V = IR P = IV

$\tau = RC$ $I = I_o e^{-t/RC}$

A. Multiple Choice (4 pt each)

1. If the signal-to-noise ratio for a signal is 4 after 100 data points have been averaged, how many points should be collected to ensure a S/N of 8?
   a. 200
   b. 300
   c. 400
   d. 600

2. Which of the following is NOT used to report **precision**?
   a. Standard Deviation
   b. Variance
   c. Relative Standard Deviation
   d. Bias

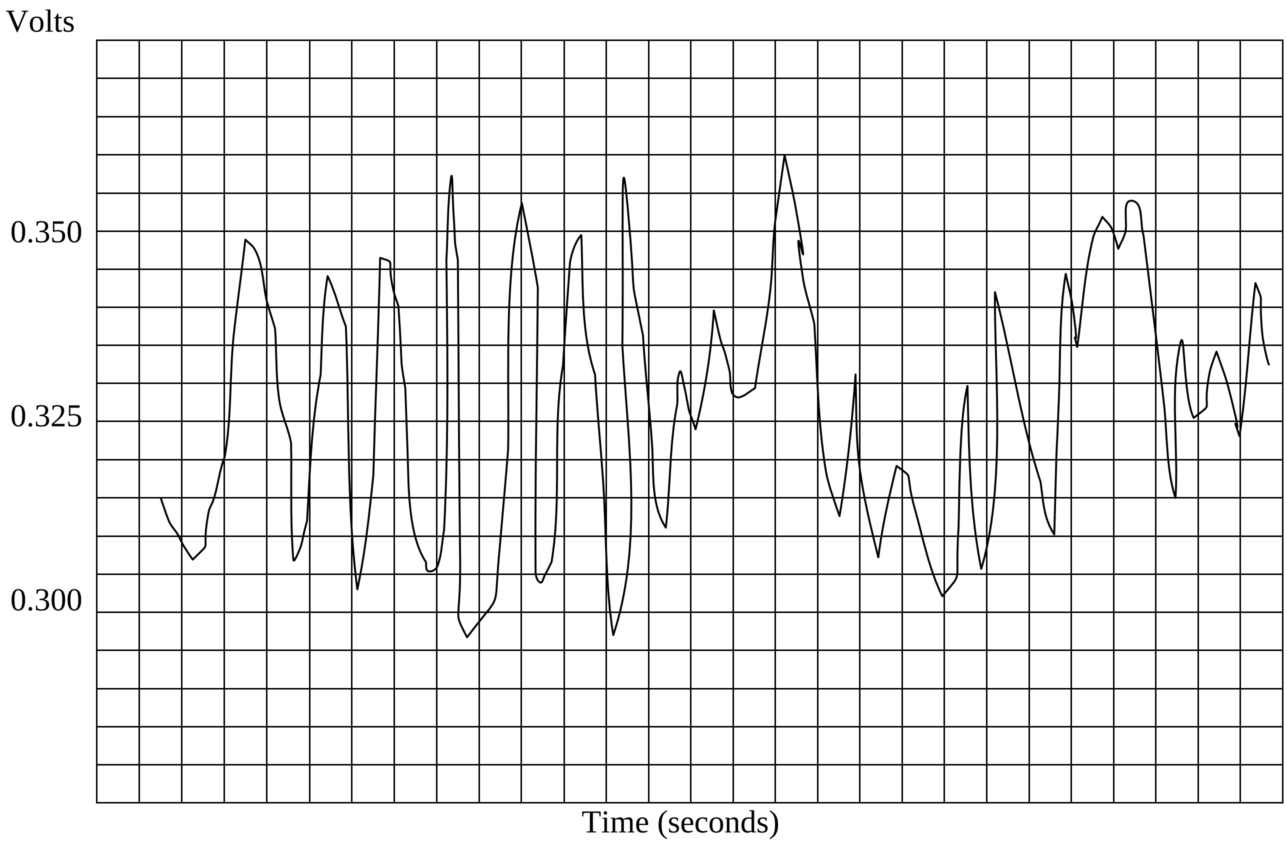
3. The physical property that smoke detectors transduce into an audible signal is the smoke’s
   a. Carbon monoxide
   b. Particulate Matter (soot)
   c. Oxygen depletion
   d. Color

4. Which of the following might be considered an input transducer?
   a. Sample Solution
   b. Light Source
   c. Photodetector
   d. Monochromator

5. The time constant for an RC circuit using a 0.20 μF capacitor and 500 kΩ is:
    a. 1 second
    b. 0.1 seconds
    c. 0.1 milliseconds
    d. 100 seconds

B. Problems. Show all work.

6. Estimate the signal, the noise, and calculate the signal-to-noise ratio for the following analog signal: (9 pt)



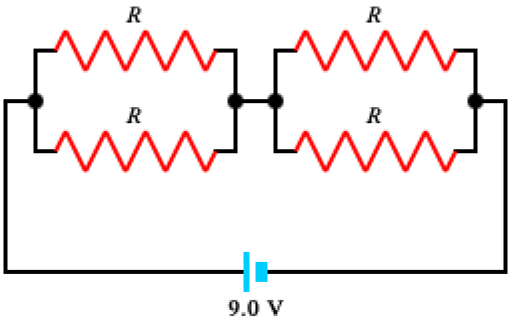
Signal____________________ Noise___________________ S/N_______________

7. The following digital data were obtained when a signal was measured, in μA, on a new instrument:

12.45, 12.89, 12.67, 12.39, 12.50, 12.42, 12.66, 12.64, 12.88, 12.74

Express the 90% confidence interval for these measurements. (6 pt)

8. Consider the following circuit. Each resistor has a value of 470Ω. What is the total resistance for the circuit? (10 pt)



9. The Instrumental Analysis students got together one weekend and built a new spectrofluorometer designed for the analysis of chlorophylls in plant extracts using Radio Shack parts. While characterizing the device, the instrument was found to follow the following linear calibration function:

$$RFI = 2.24\ C_{ch} + 0.2$$

where RFI is the relative fluorescent intensity at the maximum fluorescence wavelength and C_{ch} is the concentration of chlorophyll in parts per billion. During the instrument calibration phase, a standard chlorophyll solution with a concentration of 20.0 ppb was found to produce a mean RFI signal of 44.6 from 10 replicate measurements with a standard deviation of 0.2. A blank solution was found to produce a mean RFI signal of 0.18 from 10 replicate measurements with a standard deviation of 0.02.

a. What is the calibration sensitivity of the spectrofluorometer? (5 pt)

b. Calculate the analytical sensitivity of the spectrofluorometer at 20.0 ppb. (5 pt)

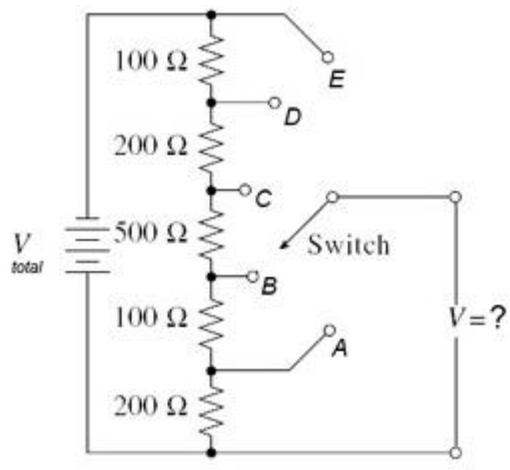
c. Calculate the limit of detection for chlorophyll. (5 pt)

10. The following values were found for the palladium standards when an instrumental assay was performed:

Concentration of Pd Standard (ppm)	Instrument Reading (relative units)	Standard Deviation (relative units)
0.00	42.3	0.2_0
20.00	83.1	0.2_8
50.00	145.2	0.3_7
80.00	206.8	0.4_4

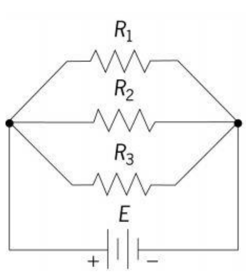
a. Does the above concentration range produce a linear response over the 2 orders of magnitude? Support your answer by reporting the linearity. (10 pt)

11. Consider the voltage divider circuit shown below. If V_{total} is 4.45 volts, what voltage will be measured if the switch is connected to connector "C"? (10 pt)



12. Digital data collected with a computer is probably the most common output used these days. Describe two software methods that can be used to enhance signal-to-noise ratios of digital data. (10 pt)

13. Consider the following circuit where $R_1 = R_3 = 100\ \Omega$ and $R_2 = 200\ \Omega$ and a 9.0 V battery. Calculate the potential drop across each resistor, V_1, V_2, V_3, and the current following through each resistor, I_1, I_2, I_3. (10 pt)



CHEM 502 -Exam II Name:________________________

October, 1, 2013

This exam covers material from Chapters 6-7D. You will have the entire period to complete the exam. Calculators may be used as appropriate, but may not be shared. SHOW ALL YOUR WORK. Calculators can be used to determine mean, standard deviation, and least squares slopes/intercepts when appropriate. Full credit will not be given without showing your other work. Full credit will not be given to an answer expressed without the appropriate units.

Potentially useful info:

$h = 6.626 \times 10^{-34}$ J s $c = 2.998 \times 10^{8}$ m s^{-1} $N_a = 6.022 \times 10^{23}$ mol^{-1}

$1eV = 1.6022 \times 10^{-19}$J $k = 1.381 \times 10^{-23}$ J/K $LOD = 3s_{bl}/m$ $\bar{x} \pm \frac{ts}{\sqrt{n}}$

$c = \lambda\nu$ $c = v\eta$ $\Delta E = h\nu$ $A = -\log T$ $A = \varepsilon bc$ $y = A\sin(2\pi\nu t + \phi)$

$P_b = 1/\Delta\nu$ $n\lambda = d(\sin\theta_i + \sin\theta_r)$ $\lambda = 2t\eta/n$ $d\theta_r/d\lambda = n/(d\cos\theta_r)$

$D = F(d\theta_r/d\lambda)$ $D^{-1} = d/nF$ $R = \lambda/\Delta\lambda = nN$ $f/\# = F/d$

A. Multiple Choice (4 pt each)

1. Which of the following is NOT a requirement for coherent radiation?
   a. Same frequency
   b. Same wavelength
   c. Same phase
   d. Same amplitude

2. Which of the following refers to the amount of light emitted from a light source?
   a. Radiant Power
   b. Intensity
   c. Refractive Index
   d. Steradians

3. Which instrument combination would be appropriate for a spectrometer to measure absorbance in the 200-360 nm range?

	Source	Sample Holder
a.	Tungsten bulb	Quartz cuvette
b.	Deuterium lamp	Plastic cuvette
c.	Nernst glower	NaCl salt plates
d.	Deuterium lamp	Quartz cuvette

4. Which combination of grating groove density and spectrometer focal length would yield the highest resolution?
   a. 120 grooves/mm and 0.12m
   b. 120 grooves/mm and 1.2m
   c. 1200 grooves/mm and 0.12m
   d. 1200 grooves/mm and 1.2 m

5. An IR transmittance spectrum is measured using a sample cell with a path length of 50 μm. For a sample measured at 1700 cm^{-1} the %T = 10%. If the %T at 1700 cm^{-1} needs to be increased to 32%, what path length should be used?
   a. 16 μm
   b. 25 μm
   c. 100 μm
   d. 160 μm

B. Problems. Be sure to show ALL work for full credit.

6. Ambient air temperature is around 300K (23 °C). The thermal energy for air can be calculated by $E = k \cdot T$, where k is Boltzman's constant. What wavelength (μm) <u>and</u> wavenumber (cm^{-1}) of electromagnetic radiation has an equivalent energy? (10 pt)

7. The oscillating electric or magnetic field of light can be described using a sinusoidal function similar to AC electric current: $y = A\sin(2\pi\nu t + \phi)$. Define each variable: y, A, ν,t, ϕ. (10 pt)

8. Light with a wavelength of 350nm passes from air, into glass with an index of refraction of 1.43. Calculate the velocity, frequency, and wavelength of the light in the glass medium. (10 pt)

9. A solution of a substance with a molar absorptivity of 2.15×10^3 L mol^{-1} cm^{-1} produces a percent transmittance of 60.96% in a 1.00 cm cell. A second solution of the same compound produces a percent transmittance one-half of the first solution. Assuming linear response (hint: for absorbance), what is the concentration ratio of the two solutions ([solution2]/[solution1]) (10 pt)

10. Compare spontaneous versus stimulated emission. What light sources use stimulated emission? (10 pt)

11. A Czerny-Turner monochromator contains a grating blazed with 1250 grooves/mm and irradiates polychromatic radiation at an incident angle of 45 degrees. Calculate the wavelength of radiation (in nanometers) that will appear at a reflection angle of 20 degrees in the second order. (10 pt)

12. The sodium D lines from a sodium lamp consist primarily of a doublet at 589.5 and589.0 nm. Suppose we can obtain a grating with 500 lines/cm of any size we choose. How large of a grating would be required to separate the two sodium lines in the first order? (10 pt)

13. Describe the “photoelectric effect”. Be sure to include descriptions including “frequency” and “amplitude”. (10 pt)

14. A sample solution has a true absorbance of 1.500. The solution is measured in a spectrometer where 0.50% stray (unwanted) light reaches the detector. What will be the measured transmittance and absorbance of the sample solution in this spectrometer? (10 pt)

CHEM 502 -Exam 3 Name:________________________

October 31, 2013

This exam covers material from Chapters 13, 15, 7I, 16 and 18 (Electronic & Vibrational Spectroscopy). You will have the entire period to complete the exam. Calculators may be used as appropriate, but may not be shared. SHOW ALL WORK. Full credit will not be given without showing your work. You do not need to show standard statistical calculations including mean, standard deviation, and least squares. Full credit will not be given to an answer expressed without the appropriate units. By signing your name above, you pledge that no help was given or received.

Some potentially useful info:

1ppm = 1 μg/mL (aqueous) 1 ppm = 1000 ppb $N_a = 6.022 \times 10^{23}\ mol^{-1}$

$h = 6.626 \times 10^{-34}$ J s $c = 2.998 \times 10^{8}\ m\ s^{-1}$ $1eV = 1.6022 \times 10^{-19} J$

$k = 1.381 \times 10^{-23}$ J/K $\frac{S}{N} = \frac{\bar{x}}{s_x}$ $LOD = 3s_{bl}/m$ $c = \lambda\nu$ $\Delta E = h\nu$

$A = -\log T$ $A = \varepsilon bc$ $\frac{N_j}{N_0} = \frac{P_j}{P_0}\exp\left(\frac{-E_j}{kT}\right)$ $n\lambda = d(\sin\theta_I + \sin\theta_r)$ $\lambda = 2t\eta/n$

$d\theta_r/d\lambda = n/(d\cos\theta_r)$ $D = F(d\theta_r/d\lambda)$ $D^{-1} = d/nF$ $R = \lambda/\Delta\lambda = nN$

f/# = F/d $\frac{s_c}{c} = \frac{0.434 s_T}{T\log T}$ $f = \frac{2\nu_M}{c}\nu$ $\nu_m = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ $\mu = \frac{m_1 m_2}{m_1 + m_2}$

A. Multiple Choice (4 pt each)

1. Which of the following would NOT cause non-linear absorption data, i.e. – deviations from Beer's Law?
   a. high concentration
   b. large slit widths
   c. stray light hitting the detector
   d. high ionic strength in all solutions

2. To minimize the uncertainty in the measured concentration of an unknown using a visible spectrophotometer, the analyst should
   a. Use a wavelength exhibiting high absorptivity.
   b. Select a wavelength where only the analyte responds.
   c. Adjust the absorbance of the unknown so that it is close to the mean absorbances of the standards used to develop the calibration curve.
   d. All of the above.

3. The wavelength of light fluoresced by molecules is longer than that absorbed because
    a. The molecules move faster, which produces a “red shift” in the fluorescence.
    b. Some of the absorbed energy causes bonds in the molecule to break, releasing energy, which results in the longer wavelength.
    c. Some of the energy absorbed by the molecules is lost to molecular vibrations before the fluorescence is produced, which results in a longer wavelength.
    d. The molecules are excited by the absorption and react with solvent molecules, which changes the electronic transition energy and therefore the wavelength.

4. If a source of stray light in an absorption spectrophotometer is eliminated, what would expect to happen to the measurement of the absorbance of a solution with A ≈ 1.0?

$$A = -log\left[\frac{P + P_{stray}}{P_o + P_{stray}}\right]$$

    a. The measured absorbance would increase because more light would be absorbed in the cell resulting in a higher absorbance.
    b. The measured absorbance would decrease because the measured power of light with the blank in the cell would be increased.
    c. The measured absorbance would increase because removing the stray light would decrease the ratio of the measured power of light with the sample in the cell to the measured power of light with the blank in the cell.
    d. The measured absorbance would decrease because removing the stray light would decrease the ratio of the measured power of light with the sample in the cell to the measured power of light with the blank in the cell.

5. Hydrogen cyanide (HCN) is a linear molecule. There should be _________ vibrational modes possible.
    a. 3
    b. 4
    c. 6
    d. 9

B. Problems. Be sure to show ALL work for full credit.

6. A portable photometer with good linearity gave a photocurrent reading of 298 μA for a solvent solution and 159 μA when replaced with an absorbing solution. Calculate the percent transmittance and absorbance of the solution. The photometer was set to zero with no light hitting the detector. (10 pt)

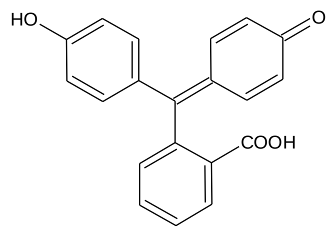
7. In acid, chromate (CrO_4^{-2}) is in equilibrium with dichromate ($Cr_2O_7^{-2}$):

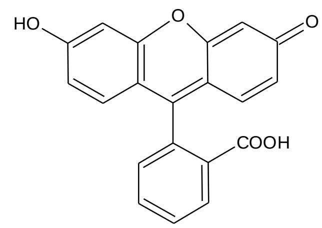
$$2CrO_4^{-2} + 2H^+ \rightleftharpoons Cr_2O_7^{-2} + H_2O$$

The equilibrium constant for this reaction is 4.2×10^{14}. A 4.00×10^{-4} mol/L $K_2Cr_2O_7$ solution is prepared using pH 5.60 buffer as solvent. Calculate the equilibrium concentrations of CrO_4^{-2} and $Cr_2O_7^{-2}$. At 400 nm, the molar absorptivities for chromate and dichromate are 1.88×10^3 L cm^{-1} mol^{-1} and 1.89×10^2 L cm^{-1} mol^{-1}. What will be the theoretical absorbance of the solution in a 1.00 cm cell? (10 pt)

8. Sketch a double-beam UV/Vis spectrometer (in-space or in-time) and label the major components. (10 pt)

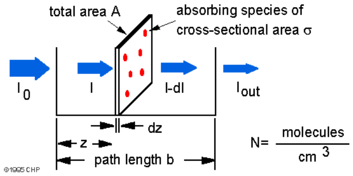
9. Which of the following compounds would you expect to exhibit the greater fluorescence? Explain your answer. (10 pt)





10. A Michaelson interferometer with mirror velocity of 7.50 mm/s is used to modulate the fundamental emission wavelength of a Nd:Yag laser, 1064 nm. What will be the frequency of the recorded interferogram? (10 pt)

11. Derive Beer's Law: A = εbc (10 pt)



12. Nitrogen monoxide has a vibrational absorption frequency at 6.2 μm. What is the bond force constant for nitrogen monoxide, in N/m? (10 pt)

13. A Raman spectrometer is built using a helium-neon laser (632.8 nm). What is the absolute wavelength, in nanometers, for an anti-Stokes Raman frequency shift of 350 cm^{-1}? (10 pt)

Bonus (5 pt): What is PittCon? (If you've emailed me the answer, no need to duplicate here.)

CHEM 502 - Exam 4 Name:________________________

November 21, 2013

This exam covers material from Chapter 19 (NMR). You will have the entire period to complete the exam. Calculators may be used as appropriate, but may not be shared. SHOW ALL WORK. Full credit will not be given without showing your work. You do not need to show standard statistical calculations including mean, standard deviation, and least squares slope & intercepts. Full credit will not be given to an answer expressed without the appropriate units. By signing your name above, you pledge that no help was given or received.

Some potentially useful info:

$h = 6.626 \times 10^{-34}$ J s $c = 2.998 \times 10^{8}$ m s^{-1} $N_a = 6.022 \times 10^{23}$ mol^{-1}

1eV = 1.6022×10^{-19}J $k = 1.381 \times 10^{-23}$ J/K   LOD = $3s_{bl}/m$ $\bar{x} \pm \frac{ts}{\sqrt{n}}$

$c = \lambda\nu$ $\Delta E = h\nu$ $A = -\log T$ $A = \varepsilon bc$ $\frac{N_j}{N_0} = \frac{P_j}{P_0}\exp\left(\frac{-E_j}{kT}\right)$

$n\lambda = d(\sin\theta_i + \sin\theta_r)$ $\lambda = 2t\eta/n$ $d\theta_r/d\lambda = n/(d\cos\theta_r)$ $D = F(d\theta_r/d\lambda)$

$D^{-1} = d/nF$ $R = \lambda/\Delta\lambda = nN$ f/# = F/d $f = \frac{2\nu_M}{c}\nu$ $\frac{s_c}{c} = \frac{0.434 s_T}{T\log T}$

$\nu_m = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ $\mu = \frac{m_1 m_2}{m_1 + m_2}$ $\mu = \gamma p$ $\nu = \frac{\gamma B_0}{2\pi}$

$E = -m\frac{\gamma h}{2\pi}B_0$ $\delta(ppm) = \frac{\nu(sample) - \nu(reference)}{\nu(reference)} x10^6$

C. Multiple Choice (4 pt each)

1. Which of the following ONLY contain spin active nuclei?
   a. ^{2}H, ^{12}C, ^{19}F
   b. ^{1}H, ^{12}C, ^{19}F
   c. ^{1}H, ^{13}C, ^{19}F
   d. ^{1}H, ^{2}H, ^{12}C

2. What signals do you expect to see from a ^{1}H NMR of 1,1 dichloroethane, CH_3CHCl_2?
   a. A doublet and a quartet.
   b. A doublet and a triplet.
   c. A singlet and a quartet.
   d. A singlet and a doublet.

3. The energy difference between the allowed spin states for an ^{1}H nucleus is ________ the strength of the external magnetic field in which it is placed.
    a. exponentially related to
    b. directly proportional to
    c. inversely proportional to
    d. logarithmically related to

4. Electromagnetic radiation in the __________ region is used in 1H NMR spectroscopy.
    a. X-Ray
    b. Ultraviolet
    c. Microwave
    d. Radio wave

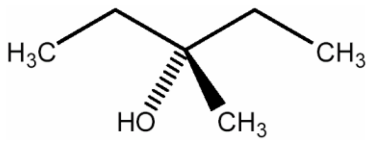
5. ^{27}Al has a spin quantum number of 5/2. How many nuclear spin states are allowed?
    a. 10
    b. 6
    c. 5
    d. 2

D. Problems. Be sure to show ALL work for full credit. (10 pt each)

6. The chair form of cyclohexane has protons in two distinctive environments, axial and equatorial. When the proton NMR of cyclohexane is run on a 100-MHz instrument at 23^{o}C, only one signal for the compound is observed. At low temperatures, two distinct signals are observed. Explain this observation.

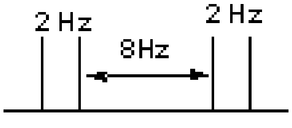
7. Why is carbon-carbon splitting not typically seen in ^{13}C NMR spectra?

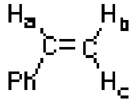
8. Predict the number of signals expected (disregarding splitting) in the ^{1}H and ^{13}C NMR spectrum of the compound shown below.



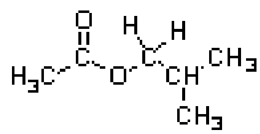
9. An NMR spectrometer that operates at a frequency of 60 MHz for ^{13}C operates at what frequency for ^{1}H NMR spectra?

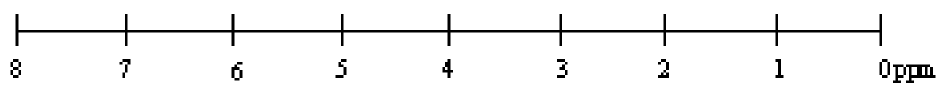
10. The following splitting pattern represents one of the vinyl protons of styrene, shown below. Identify which proton is represented (H_a, H_b or H_c) and list the coupling constants (J values) for the splitting pattern. (Ph = aromatic ring).





11. Using the scale below, draw the ^{1}H NMR spectrum for isobutyl acetate, shown below. Present the peaks with correct splitting patterns and approximate chemical shift. Just above each peak, indicate the relative integration value of each type of hydrogen.





12. Compare the three commercially available types of magnets available for NMR spectroscopy, including field strength, resolution, sensitivity and cost.

13. What is the purpose of the deuterated solvents used in NMR? Why might D_2O be chosen over $CDCl_3$ for a compound?

Bonus (5 pt): What does the acronym NMR actually stand for? Must be complete…no partial.

CHEM 502 - Final Exam   Name:______________________________
December 5, 2013

Directions:

The final exam covers material from all chapters covered this semester. You will have 150 minutes to complete the exam. Calculators may be used as appropriate, but may not be shared. You are expected to know how to do standard statistical calculations with your calculator, including mean, standard deviation, and linear least squares calculation of slope & intercept. Be sure to attempt all problems and SHOW ALL WORK; partial credit will be given for incomplete solutions that are somewhat correct and logically presented. Be neat and orderly in your solutions; I cannot give full credit for work that I cannot read or understand.

Potentially useful info:

$h = 6.626 \times 10^{-34}$ J s $c = 2.998 \times 10^{8}$ m s^{-1} $N_a = 6.022 \times 10^{23}$ mol^{-1}

$e = 1.6022 \times 10^{-19}$C   1 eV = 1.6022×10^{-19} J $k = 1.3807 \times 10^{-23}$ J K^{-1}

R = 8.314 J mol^{-1} K^{-1} = 0.0821 L atm mol^{-1} K^{-1} 10Å = 1 nm = 1000 pm = 1×10^{-9}m

$c = \lambda\nu n$ $\Delta E = h\nu$ $A = -\log T$ $A = \varepsilon bc$ $T = P/P_o$ $\gamma = m/s_x$

$n\lambda = d (\sin \theta_i + \sin \theta_r)$ $\lambda = 2t\eta/n$ $d\theta_r/d\lambda = n/(d \cos \theta_r)$ $D = F(d\theta_r/d\lambda)$

$D^{-1} = d/nF$ $R = \lambda/\Delta\lambda = nN$ f/# = F/d   LOD = $3s_{bl}/m$ $\bar{x} \pm \frac{ts}{\sqrt{n}}$ $\mu = \frac{m_1 m_2}{m_1 + m_2}$

$\frac{N_j}{N_0} = \frac{P_j}{P_0}\exp\left(\frac{-E_j}{kT}\right)$ $\frac{\Delta\lambda}{\lambda_o} = \frac{\nu}{c}$ $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ $\mu = \gamma p$ $\nu = \frac{\gamma B_0}{2\pi}$

$E = -m\frac{\gamma h}{2\pi}B_0$ $\delta(ppm) = \frac{\nu(sample) - \nu(reference)}{\nu(reference)} x10^6$

A. Multiple Choice: Circle the correct answer. Each question has one best answer. (3 pt each)

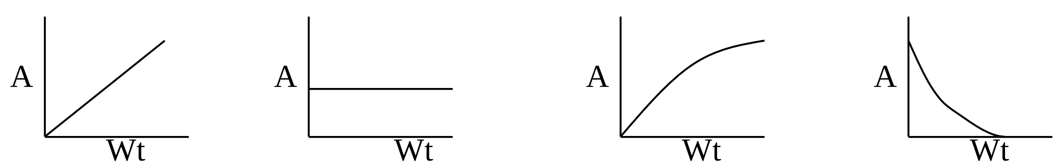
1. Which of the following is not used to describe the precision of a data set?
   a. signal-to-noise ratio
   b. relative standard deviation
   c. variance
   d. limit of detection

2. The following statement best describes what type of detector: "A very sensitive device in which electrons emitted from the photosensitive surface strike a second surface called a dynode, which is positive with respect to the photosensitive detector, resulting in gain."
   a. phototube
   b. charge coupled device
   c. photodiode
   d. photomultiplier

3. A tungsten lamp is a commonly used light source for which region of the electromagnetic spectrum?
   a. Ultraviolet
   b. Infrared
   c. Microwave
   d. Visible

4. The difference in path length traveled by two rays from a diffraction grating is 600 nm. Other wavelength(s) also observable include:
   a. 250 nm
   b. 300 nm
   c. 450 nm
   d. All of the above would be observed

5. A molecule BA has an absorption peak at 550 nm in aqueous solution. Consider a plot of absorbance at 550 nm vs. the weight (Wt) of BA added to a solution. If the volume change is negligible as BA is added, which of the curves below best represent the shape of the plot over a <u>large</u> mass range?



1 2 3 4

   a. Curve 1
   b. Curve 2
   c. Curve 3
   d. Curve 4

6. Resolution of two closely spaced wavelengths in a spectrophotometer will depend on:
   a. The intensity of the light source.
   b. The sensitivity of the detector.
   c. The concentration of the sample
   d. The dispersion of the monochromator.

7. Which of the following is NOT used as a detector for UV/Vis light?
   a. photomultiplier tube
   b. charged coupled device
   c. linear diode array
   d. Michaelson interferometer

8. Oscillating electric or magnetic fields can be described using a sinusoidal function: $y = A\sin(2\pi\nu + \phi)$. The frequency of the wave is represented by:
   a. y
   b. ν
   c. A
   d. ϕ

9. Which of the following is NOT an advantage of Fourier transform spectroscopy?
   a. Offers improved signal-to-noise ratio.
   b. Allows acquisition of spectra in a very short time.
   c. Can be used in all the important regions of the electromagnetic spectrum.
   d. Allows signal averaging for spectra.

10. Compared to a dispersive spectrometer, a diode array spectrometer
   a. Is faster
   b. Has higher resolution
   c. Depends less on drift of the light source
   d. Can measure higher absorbances

11. Having the appropriate wavelength and bandwidth for a spectrophotometric analysis is very important. Which is the best statement regarding bandwidth?
   a. The bandwidth should be as large as possible.
   b. The bandwidth should be as small as possible.
   c. The bandwidth should be as large as possible, but small compared with the band being measured.
   d. The bandwidth only needs to be larger than the band being measured.

12. We discussed several phenomena when light strikes a sample. Which statement best describes what can happen when light strikes a sample?
   a. Light can be absorbed.
   b. Light can be transmitted or absorbed.
   c. Light can be transmitted, absorbed, or reflected.
   d. Light can be transmitted, absorbed, reflected, or scattered.

13. Which is the correct order for the parts in a general “scanning” absorption spectrophotometer?
   a. Light source, sample compartment, wavelength selector, detector, readout
   b. Light source, wavelength selector, sample compartment, detector, readout
   c. Sample compartment, wavelength selector, detector, readout
   d. Light source, sample compartment, detector, wavelength selector, readout

14. Which statement is correct about lasers?
   a. Lasers provide isolated lines of multiple wavelengths for many applications.
   b. Lasers provide continuum wavelengths for many applications.
   c. Lasers provide non-isolated lines of variable wavelengths for many applications.
   d. Lasers provide isolated lines of a single wavelength for many applications.

15. Which statement is correct?
   a. Monochromatic light is a single wavelength; polychromatic light is many wavelengths.
   b. Monochromatic gratings pass single wavelengths of light, polychromatic gratings pass may wavelengths of light.
   c. Monochromatic light is black light; polychromatic light is white light.
   d. Monochromatic light has many wavelengths; polychromatic light is a single wavelength.

16. Which figure of merit best describes the minimum detectable amount of an analyte?
   a. LDR
   b. γ_c
   c. LOD
   d. S/N

17. Which of the following is NOT true about high pass RC filters?
   a. Contain a resistor and a capacitor
   b. Block low frequency electrical signals
   c. Will decrease the signal-to-noise ratio
   d. Common component of modern electronic instruments

18. Which of the following is NOT an advantage of 300 MHz NMRs over 60 MHz NMRs?
   a. Higher resolution for closely spaced peaks.
   b. Better sensitivity from higher population differences.
   c. Easier interpretation of spectra.
   d. Faster analysis time.

19. A resonance signal on a 60 MHz NMR shows at 5.30 ppm. On a 300 MHz, the same resonance will appear at
   a. 5.30 ppm.
   b. 26.6 ppm.
   c. 10.6 ppm.
   d. 1.06 ppm.

20. Which nucleus is NOT observable by NMR?
   a. Hydrogen-2 (Deuterium)
   b. Carbon-13
   c. Boron-11
   d. Oxygen-16

B. Problems: Be sure to show all work to receive full credit, and attempt all problems.

21. Stray light hitting the detector in a spectrometer will produce erroneous results when the absorbance of a solution is measured. A given spectrometer is reported to have 2% stray light. Calculate the apparent absorbance if the measured absorbance is 0.750. (5 pt)

22. Express 450 nm (10 pt):

a. in Angstroms (Å)

b. as a frequency, in Hz

c. as a wavenumber

d. as an energy in kilojoules per mole

e. In what region of the electromagnetic spectrum, does 450 nm fall?

22. A 0.0200 gram blood sample was decomposed by a microwave digestion technique followed by dilution to 100.0 mL in a volumetric flask. Aliquots of the sample solution were treated with a lead complexing reagent and water as shown below. The resulting solutions were analyzed by UV/Vis at 375 nm. Calculate the percentage of lead in the original sample. (10 pt)

Volume of sample taken (mL)	Reagent volumes used (mL)			Absorbance at 375 nm (1.00 cm cell)
	86.9 ppb Pb^{+2} std	Ligand	H_2O	
10.0	0.00	20.0	30.0	0.155
10.0	4.00	20.0	26.0	0.216

23. A new absorbance instrument was found to follow the following calibration function for an analyte X:

$$A = 3.61\ C_X + 0.2$$

where A is the absorbance and C_X is the concentration of X in parts per billion. During the instrument calibration phase, a standard X solution with a concentration of 20.0 ppb was found to produce a mean signal of 4.6 from 10 replicate measurements with a standard deviation of 0.2. A blank solution was found to produce a mean A signal of 0.02 from 20 replicate measurements with a standard deviation of 0.01. (5 pt)

d. What is the calibration sensitivity of the instrument (No graph required.)

e. Calculate the analytical sensitivity at 20.0 ppb.

f. Calculate the limit of detection.

24. Consider the following circuit where $R_1 = 100\ \Omega$ and $R_2 = 200\ \Omega$ and $R_3 = 300\ \Omega$ and a 9.0 V battery. Calculate the total resistance for the circuit, the potential drop across each resistor, V_1, V_2, V_3, and the current following through each resistor, I_1, I_2, I_3. (10 pt)