CHEM 503 - Instrumental Analysis Lab
Section 001, Course# 11642, 1.0 Credit Hrs – Fall 2009

Introduction

The purpose of this course is to expose students to the various types of equipment that are likely to be encountered in an industrial or government chemical analysis laboratory. While the industrial or government lab **may** be better equipped than our academic one, the basic types of instrumentation will be the same. The instruments are located in various places within Sims, but most are located in Sims 310, along with sample and standard preparation workspace.

You will work in small groups (2 or 3 students) for data collection, but further collaboration on processing data or reporting is prohibited. Background references are required reading, and can assist in processing data, introductory, and discussion concepts.

Each group will have an unknown sample(s) for most projects. Directions for the operation of each instrument (student manuals) are located near each device. You are expected to familiarize yourselves with this manual before you begin the instrumental work. Usually, the instructor will demonstrate operating procedures prior to your measurements, but this is not a substitute for reading. Feel free to ask questions when they arise. Each group member is expected to contribute to making solutions as well as getting hands-on experience with each device.

Each instrument you encounter contains delicate components, even those instruments that appear to be out-dated. Handle them with care. If you believe that a malfunction has occurred, inform the instructor before continuing. You should always consult the instructor before making changes in instrumental parameters other than those described in the student manual and **never** perform an operation you have not been "checked-out" on by the instructor. These instruments are typically quite expensive ($5,000 - $200,000).

Course Objectives:

- Gain hands-on experience with sophisticated laboratory instrumentation
- Develop an understanding of the components of laboratory instrumentation and how different parameters can influence data output
- Perform rigorous data collection and data analysis with the aid of desktop computers
- Improve technical writing skills through written reports

Course Co-requisite:

- Chem 502, Instrumental Analysis. If you drop the course, you must also drop the lab.

Time/Location:

- Monday, 2:00 – 4:50 pm
- Sims 310

Instructor:

- Dr. Cliff Calloway, callowayc@winthrop.edu
- 312-B Sims Hall, x4945 (323-4945, if calling off campus)

- Office Hours: 10:00-12:00 MWF and by appointment…please don't hesitate to contact me

Required Materials (please bring each week):

- Experiment handouts and course textbook (i.e. – "Skoog book")
- Laboratory notebook, one per student pair is adequate...the type with duplicate pages is handy, since each student can have a copy of the raw data
- Safety glasses
- A calculator that performs least squares analysis, mean and standard deviation
- Lab Coat (optional)

Required Laboratory Work:

There will be a total of **thirteen lab assignments** valued at **50 pt each** and a **comprehensive lab final exam** valued at **50 pt**. Each group will complete one assignment per week. An assignment generally consists of: (1) a lab **notebook**, 10 pt, (2) a lab **report**, 30 pt and (3) a lab **quiz**, 10 pt.

- **Notebook:** At the beginning of each lab period, each group must submit, for approval, a written experimental plan, including a detailed scheme for the preparation of solutions and for carrying out the task of the lab assignment. (See Laboratory Notebook below for further details.)
- **Report:** The lab report will consist of: Title Page, Introduction, Procedure, Sample Calculations, Results, Conclusion, Discussion, and Reference sections. (See Laboratory Report below for further details.)
- **Quiz:** A written 10-15 minute quiz will be given at the beginning of the laboratory period covering the previous week's lab. (See Laboratory Quiz below for further details.)

Laboratory Notebook Format (10):

This section is a group effort and each group member will receive the same number of points. Checking each other's work could be helpful. As is usual in scientific notebooks, write clear and concise statements, in black ballpoint ink.

- Each notebook experiment should include: (1) a title and brief purpose, and (2) a step-by-step plan for executing the lab. Then, as work progresses, the exact results (masses, volumes, concentrations, etc.) are recorded and/or calculated. The plan should be written in imperative voice.
- Glassware, such as volumetric pipets and/or volumetric flasks, as well as approximate amounts to be weighed, should be clearly specified. Available equipment for each project is specified in the project handout.
- We rarely obtain the "exact" mass planned. However, obtaining a slightly different mass from what has been "pre-calculated" will rarely change subsequent procedures to follow, only the "actual" concentrations.

Laboratory Report Format (30):

We will be following the general guidelines for the text of manuscripts submitted to the journal; ***Analytical Chemistry***, except no Abstract section is required. Lab reports must be typed. The general format of each section is outlined below. Each student must write his/her own report in his/her own words; Plagiarism will not be tolerated. Reports are due one week after completing data collection. Late reports will be penalized 3 points per weekday late, and the weekend counts as 1 day.

Title Page: Give your experiment an appropriate title. Be creative and specific, that is, use a different title than the one listed in the manual. Example: "Determination of Arsenic in Human Hair by Atomic Fluorescence Spectrometry." Include your name, date of experimental work, and lab partner name(s) on the title page. **(1)**

Introduction: Each experiment handout gives specific instructions as to what should be discussed in the Introduction section. Even though the items are numbered on the project handouts, the Introduction section itself should be in paragraph form with division of the topics into paragraphs. Presentation of topics should follow the same order as that given in the handout. Remember, it is customary to write reports in the passive voice: i.e., "The concentration of the unknown is to be determined by the standard addition method." **not** "I (or We) will use the standard addition method to determine the concentration of the unknown."

Schematic (block) diagrams: Instrument block diagrams are required for most lab introductions. Draw a **full-page** block diagram of the instrument used in the experiment. Give the drawing a figure number, title, and label all of the major components clearly. (Example: "Figure 1: Block diagram of a Spectrofluorometer") Word processors, such as Microsoft Word or WordPerfect will adequately draw block diagrams. Do not simply copy one from the textbook, as these usually present more detail than is typically required. **(5)**
*The Introduction Section of the laboratory report is due **before** experimental work begins. Instrumental Analysis is a difficult upper-level course, and it is essential that students be properly prepared. By writing the Introduction section of the report ahead of time, students will, hopefully, be adequately prepared and perform well in the laboratory.*
Report Procedure: Do not recopy the information from your lab notebook. If the notebook plan was used without alteration, simply state this fact in a sentence or two; otherwise state what deviations in the procedure had to be made. In addition, all instrument parameters should be tabulated (ex. Table1. Instrument Parameters). **(3)**
Sample Calculations: This section should contain a sample of each type of calculation used in solution preparation and data analysis. **Units** should be clearly expressed. Each sample calculation must be preceded by one or two sentences to explain the operation being performed. Example: "The residual current is subtracted from the limiting current to obtain the diffusion current." Sample calculations of a statistical nature (mean, standard deviation, and least squares slopes/intercepts) do not have to be shown. *Since equation writing can be tedious and time-consuming with a word processor, the calculation may be handwritten into the report, but type the description*. **(5)**
Data and Results: This section is essentially composed of tables and/or graphs, usually starting with your raw data (weights, volumes, instrument readings, etc.). Introduce this section with one or two paragraphs explaining what is presented in each table and/or graph. Each lab experiment handout lists what results are to be included. Number and specifically title each table and figure. Beginning students are typically too general in titling graphs and tables. Numbering each will allow you to reference a table or figure in the section's introductory paragraph and subsequent discussion and conclusion sections. All numbers should have correct units and significant figures. Report any unknown letter. (See below for proper table and graph construction.) **(8)**
Conclusions: In this section, the overall results of the analysis will generally be restated and, whenever instructed, compared to literature values. Pertinent comments and observations about the results are also made and sources of error (not personal errors) should be discussed. **(3)**
Discussion: At the end of each experiment handout there are one or more discussion question(s). These should be answered in paragraph form, showing good understanding of the material and principles involved. **(3)**
Literature Cited: You are responsible for reading the references cited in each experiment. These will help you answer questions. List those references in the correct format at the end of your report. Be sure to indicate (with superscripts) in the report where references are being used. **(2)**

Note: You will be writing reports frequently for the remainder of your career. For example, progress reports to supervisors, reports to customers, annual reports, grant applications, and government regulatory reports are common in the workplace. You will find you are often evaluated on how well you write such reports, in addition to doing the science correctly. The only

way to improve your writing skill is to practice often. All students have found the writing to be much easier as the course progresses.

Laboratory quizzes:

The project quizzes are typically 3-4 questions and cover the essential skills and concepts demonstrated in each lab project. You will need blank paper, calculator, and pencil. Students often comment that writing a good lab report is adequate preparation for quizzes. **(10)**

Laboratory Final:

The laboratory final is cumulative and will be given during the regular exam period, Monday, December 14, 11:30 – 2:00. **(50)**

Letter Grades:

As you have probably calculated, a total of 700 points are possible in CHEM 503. Your lowest project will be dropped, if all projects are completed. Letter grades will be assigned based on the percentage of 650 points 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-	

Important Notes:

1. Again, lab reports are to be your own work, *no group effort*, and are covered by the university honor code. Copies of old lab reports from previous years are off limits. 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 examinations, 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
2. All laboratory work (including reports) must be completed to receive a passing grade. The absolute deadline for submission of written work is Study Day, 5:00 pm.
3. Handwritten (rather than typed) reports will not be accepted. These will be returned and late points assessed. The late report policy is strictly enforced.
4. Remember that the lab experiment is a learning experience. Do not get overly upset if your results do not seem to come out as planned. Try to determine the source of error and comment in your conclusion section. If your results are way off from an expected value, with **no** valid explanation, penalty point(s) will be assessed to the conclusion section.
5. Some of the procedures are lengthy, so you may begin to prepare solutions or clean glassware early, if you wish. In any event, all group members must be present when the lab period officially begins, when reports and notebooks are collected, and quizzes given.
6. You should expect to attend each lab for the full period. If you must miss a lab period, see the instructor as soon as possible. Excused absences for illness will be verified through the student health service or doctor. If you have other reasons for absence, see Student Affairs. Make up labs will be scheduled only in special circumstances.

7. 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.
8. Syllabus Change: While unlikely, the Professor reserves the right to change the course syllabus if circumstances (weather or other events) dictate. You will be notified of any change through lab meetings and/or email.

Tables and Graphs:

A Properly Constructed Table will have the following features:

1. Contain all the data necessary to verify a calculation.
2. Common data is presented only once, as a header. You know you have common data if a column contains the same value.
3. Each column is labeled with the name of the variable and the units in parentheses.
4. The average or other statistical data are presented at the bottom.
5. The table is numbered (if more than one table is to be used) and titled.

Ex.

Table 2. Determination of Iron by Titration with $K_2Cr_2O_7$

Standard $K_2Cr_2O_7$ (1.3987 g in 250.00 mL): 0.019016 M

Weight Ore Sample (g)	Volume $K_2Cr_2O_7$ (mL)	% Fe in ore (wt%)
0.5362	35.63	42.34
0.6788	45.22	42.45
0.6211	41.08	42.14

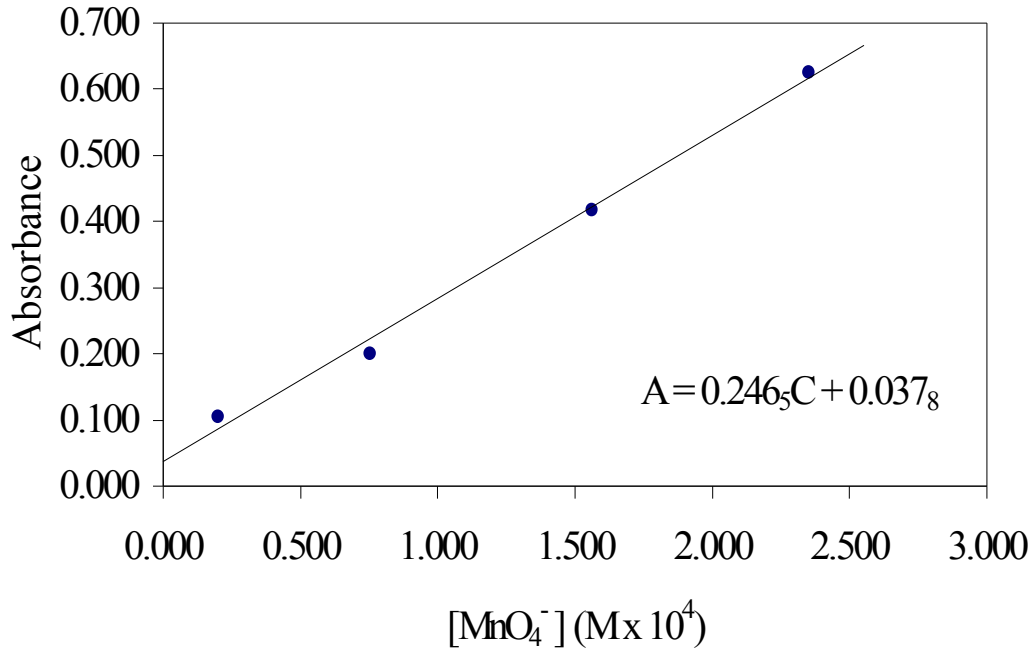
Average = 42.31% Fe
Standard Deviation = 0.16% Fe

A Properly Constructed Graph will have the following features:

1. Computer generated. Hand drawn graphs will not be accepted.
2. Titled and numbered. For example: Figure 1: Beer's Law Plot for MnO_4^- at 530 nm
3. Axes are neatly labeled followed by the units in parentheses.
4. Generate a full page (8.5" x 11") plot. (Not shown below.)
5. Make sure data points are clearly visible.
6. For linear data, the best-fit line (all except obviously stray data points) is drawn. The least squares fit equation should be included with the graph.
7. The numerical labels on the axes indicate the number of significant figures in the data.
8. Large and small numbers should be reported in exponential format. In some graphs, the exponents can be removed from the plot and placed in parentheses along with the axis label, but opposite in sign.

Ex. The data point is: 4.955×10^{-4} M → 4.955 is plotted, and axis has [X] (M x 10^4)

Figure 3: Beer's Law Plot for MnO_4^- (λ = 530 nm)



Analytical Figures of Merit

The following analytical figures of merit serve as indicators for the characteristics of an instrumental technique with regards to a specific analyte. You will be asked to calculate several of these for each experiment.

A. Accuracy. Accuracy indicates how close the measured analyte concentration is to the "true" analyte concentration. To find the accuracy of a technique, one must have a standard reference material (SRM) or an official measure of the true concentration of an analyte in a specific sample. In most cases, we will use analyte concentrations reported on the labels of certain products, or the concentrations calculated from the preparation procedure of some of our synthetic unknowns. Although these values will not provide the true accuracy of the technique, they will produce close approximations.

Accuracy is most commonly reported as percent error. If C_m is the measured analyte concentration, and C_t is the true concentration, then the accuracy is reported as:

$$\%\text{error} = \left| \frac{C_t - C_m}{C_t} \right| \times 100\%$$

B. Precision. Precision indicates the reproducibility of repetitive measurements of equivalent analyte solutions. It is usually expressed in one of five forms: standard deviation, variance, relative standard deviation, percent relative standard deviation, or as confidence limits. For our purposes, precision will usually be reported with concentration units as a confidence limit, since we will be measuring the precision associated with the determination of an analyte concentration.

Standard Deviation. The standard deviation (s) for a number of measurements may be calculated using the standard equation as given in Skoog (Appendix 1, a1B-1, pg. A-6). Many hand calculators will automatically determine the standard deviation for a given set, when the number of significant digits is less than five (H.E. Solberg, *Anal. Chem.*, **1983**, 55, 1661). This is certainly acceptable and perhaps preferable for our lab.

Technically, about 16 different measurements are necessary to get an accurate value for s. However, due to time limitations, we will take a short cut and typically use only 3-5 different measurements. Another useful shortcut in the measurement of s involves measuring the amount of noise imposed on one continuous, analog signal. The standard deviation that would be observed in the measurement of 16 different samples is approximately equal to one fifth of the peak-to-peak variations in the signal observed for a single sample monitored over time (at a 99% confidence level).

Relative Standard Deviation. The relative standard deviation (RSD) is defined as the standard deviation (s) of a set of measurements divided by the mean ($\bar{x}$) of all of the measurements. Notice that this is a unitless quantity and is sometimes reported as the percent relative standard deviation (%RSD) or coefficient of variation (CV).

$$\%\text{RSD} = \frac{s}{\bar{x}} \times 100\%$$

Confidence Limits. Confidence limits define **an interval** that encloses the "true" value of a quantity with a given confidence (90%, 95%, etc.) depending on the choice of "t". Values for "t" are available in tabular form in *Skoog* (Appendix 1, p. A-13). For instance, the true value, $\mathbf{C_t}$, will be enclosed within the interval:

$$\mathbf{C_m \pm \frac{t\,s}{\sqrt{n}}}$$

90%, 95%, etc. of the time depending on the value for t chosen from Table a1-4 in Skoog (where n is the total number of measurements acquired). When using this table, be sure to note that the number of degrees of freedom equals n-l!

C. Signal to Noise Ratio. The signal to noise ratio (S/N) is defined as the mean value of a measurement, S (signal units), divided by the measurement of the noise associated with that signal, N (also in signal units). The S/N is therefore a unitless quantity. The noise is usually reported as the standard deviation in the signal (s), so S/N is equal to the inverse of the relative standard deviation in the signal.

$$S/N = 1/RSD$$

D. Sensitivity. We will only be concerned with the measurement of the calibration sensitivity for this lab. This is merely the slope measured for a calibration curve (m), and must have units consistent with signal/concentration. For example, the calibration sensitivity of a Beer's Law technique (with a Beer's Law plot having units of Absorbance (a unitless value) on the y-axis and Molar concentration on the x-axis) result in a slope with units --- M^{-1}, or L mol^{-1}.

E. Limit of Detection. The LOD is that analyte concentration which yields an analytical signal equal to 3 times the standard deviation in the blank signal measurement, s_{bl}. In other words, the LOD is that concentration of analyte that would yield a S/N of 3:

$$LOD = \frac{3\,s_{bl}}{m}$$

As before, s_{bl}, may be found from repetitive blank measurements, or from 1/5 of the peak to peak noise of a continuous blank signal. Note that the LOD must have concentration units. By definition, the LOD includes only ONE significant figure (Ex. A LOD of 3.5 mmol is misleading, a LOD of 4 mmol would be correct.)

F. Linearity of Calibration Curves. The linearity of a set of data is best measured by plotting the logarithm of the measured signals (log S) versus the logarithm of their corresponding concentrations (log C). If the data is linear, a plot of these values should yield a straight line with a slope of 1.00.

$$S = m\,C$$

$$\log S = \log m + (1.00)\log C$$

It is important to remember that any signal due to the blank or background must be subtracted from S to give accurate results. In other words, the y-intercept of a plot of S versus C must be zero. *If this is not the case, temporarily subtract the value of the y-intercept from each data point before calculating the log.* A calibration curve is considered linear if the slope of the log-log plot falls within the range 0.95 to 1.05.

G. Linear Dynamic Range. The LDR is the concentration range over which a calibration curve is linear. It is defined on the lower end by the LOD, and on the upper end by that concentration of analyte that yields a signal that falls no more than 5% below the extrapolated straight portion of the calibration curve. The LDR is usually expressed in units of "orders of magnitude" or "decades". This is easily determined with the log-log plot. As an example, assume the LOD for a particular measurement falls at 5 mg/L, and the upper limit of the range falls at 220 mg/L. The LDR is expressed as:

$$\log(220) - \log(5) = 1.6 \text{ orders of magnitude (decades)}$$

CHEM 503 Lab Rotation Schedule – Fall 2009

NMR Fourier Transform Spectroscopy and Signal Processing

AAS Analysis of Coins by Flame Atomic Absorption Spectrometry

MLS Determination of Quinine in Tonic Water by Molecular Luminescence Spectrometry and Heavy Atom Fluorescence Quenching

IR Determination of Benzoyl Peroxide in Acne Solutions, Quantitative IR

EL Basic Electronics and Logic Circuits

SMF Single-Molecule Fluorescence

ICP Simultaneous Determination of Zinc and Magnesium in Spaghetti by ICP; Signal-to-Noise Optimization

DP Data Processing – Moving Avg./Savitzky Golay/Ensemble/Fourier Analysis

GCMS Optimization of an Ion Trap Mass Spectrometer for Nicotine Derivative Analysis

LCMS Molecular weight Determination of an Unknown Organic Compound with High Resolution Mass Spectrometry

POL Sucrose Kinetics by Polarimetry

SA Surface Analysis

CE Capillary Electrophoresis

Date\Group	A	B	C
8/31	Introduction	Introduction	Introduction
9/7	NMR	AAS	MLS
9/14	MLS	NMR	AAS
9/21	AAS	MLS	NMR
9/28	IR	EL	ICP
10/5	ICP	IR	EL
10/12	EL	ICP	IR
10/19	Spring Break	Spring Break	Spring Break
10/26	ICP	DP	GCMS
11/2	GCMS	ICP	DP
11/9	DP	GCMS	ICP
11/16	LCMS	POL	CE
11/23	CE	LCMS	POL
11/30	POL	CE	LCMS
12/7	SA	SA	SA