Analytical Topics to Consider in preparation for the MFAT/GRE

1. Solutions and Measurement: (CHEM 222)

   - Describe the steps in a chemical analysis
   - Know the meaning and use of the following solution concentrations.
     - Molarity
     - Formality
     - Normality
     - Percent (w/w; w/v; v/v)
     - Part-per-million; Part-per-billion
   - Know the approaches needed to make a dilute solution from a more concentrated one.

2. Laboratory Tools: (CHEM 222)

   - Know how an analytical mass measurement is made and the errors associated with the analytical balance.
   - Know the use and precautions associated with volumetric glassware.
   - What considerations must be made in the calibration of glassware.
   - Know the terms associated with various types of chemicals (i.e. primary standard grade, etc..) and the rules for safe and proper handling of these chemicals.

3. Experimental Error: (CHEM 222)

   - Remember your rules of significant digits.
   - Understand the difference between determinate and indeterminate errors.
   - What is uncertainty?
   - How does one/Why is it necessary to propogate errors?
   - What is the difference between tolerance and precision?

4. Statistics: (CHEM 222)

   - What is the purpose for the use of statistics?
   - What assumptions are made when using statistics in a chemical analysis?
   - Know how to calculate the mean and standard deviation for repeated measurements.
   - What is the confidence limit? How is it calculated. How does one use it to determine the number of measurements needed to achieve a desired confidence limit?
   - Know how to perform the Q-test.
   - Know the purpose of performing the tests of comparison (t-tests)
     - comparing mean to the true value
     - comparing 2 means
     - comparing differences between two techniques or operators.
   - Know how to compare the variability between two sets of measurements or two operators. (F-test)
   - What is the meaning/purpose of linear least squares?

5. Chemical Equilibrium: (CHEM 222)

   - What is the meaning of an equilibrium constant?
   - K and ΔG are related in what way?
   - Know how to estimate the solubility of a slightly soluble salt using K_{sp}.
   - Determine the impact of common ions upon the solubility of a slightly soluble salt.
   - Predict the ability to separate two ions by precipitation by the use of K_{sp}.

- Know the difference between stepwise and cumulative formation constants as applied to the formation of complexes.
- Understand the rudiments of acid/base theory including:
  - acid dissociation reaction/K_a
  - base hydrolysis /K_b
  - autoprotolysis of water/K_w
  - relationship of K_w to K_a and K_b
  - relationship of K_a and K_b to each other (i.e. conjugate relationships)
- Know how pH and $[H^+]$ relate
- Understand the dissociation/hydrolysis of polyprotic species and K_a/K_b values

6. Gravimetric Analysis: (CHEM 222)

- Know how combustion analysis is performed.
- Understand the calculations needed to return an empirical formula from combustion analysis data.
- Understand the basis for quantitative determinations via precipitation.
- Know the stoichiometric calculations used in precipitation determinations.
- Understand what a gravimetric factor is/does.
- What are the basic steps in a precipitation gravimetric analysis.

7. Volumetric Analysis: (CHEM 222)

- What are the principles behind a volumetric analysis?
- Understand the basic stoichiometric/solution chemistry manipulations used.
- Know the difference between a direct and back titration.
- Understand the approach used in a precipitation titration including a prediction of the titration curve (using pM, pX), and methods of endpoint detection.
- Know what a Mohr, Volhard and Fajans titration involve.

8. Activity: (CHEM 222)

- Understand the effect of diverse ions upon a chemical equilibrium/In what concentrations ranges are diverse ions generally considered to impact a system?
- What is the meaning of activity?
- What factors control the activity of a substance in solution.
- How is the concept of activity applied to an equilibrium problem for better predictions in "real" solutions.
- What is the difference between concentration equilibrium constant and a thermodynamic equilibrium constant?

9. Systematic Treatment of Equilibria: (CHEM 222)

- What is mass balance? Charge balance?
- What impact does pH have on the solubility of slightly soluble salts (with anions having acidic or basic character)?

10. Monoprotic Acid/Base Equilibria: (CHEM 222)

- Know the treatment and assumptions necessary to determine the pH of a solution of a strong/intermediate or weak acid or base. (i.e. recognition of appropriate approach/calculations).
- Recognize a buffer when you see it. Know how K_a or K_b can be converted to the Henderson-Hasselbach relation and applied easily to buffer systems.

- Know approaches to the preparation of a buffer solution including the appropriate choice of materials for a buffer of a given pH.

11. Polyprotic Acid-Base Equilibria: (CHEM 222)

- Diprotic Acids/Dibasic Bases
  - acidic form
  - -intermediate form
  - basic form
- Know how buffers can be made with diprotic acids or bases
- Extend the concepts of diprotic species to polyprotic systems.
- Know how to determine the principal species of an acid or base as a function of the pH of a solution.
- Understand a fractional composition plot, including how to interpret K_a values from such a plot.
- What is the isoelectric and isoionic pH. What is a zwitterion?

12. Acid/Base Titrations: (CHEM 222)

- prediction of a titration curve of a strong acid titrated with a strong base or vice versa.
- prediction of a titration curve of a weak acid titrated with a strong base or vice versa.
- Titration of diprotic acids or bases with a strong base or acid. Prediction of titration curves.
- Methods for the detection of endpoints
  - indicators: proper choice of, transition ranges, appropriate endpoint to choose in
  - diprotic situations.
  - pH electrode (including derivative plots)

13. EDTA Titrations: (CHEM 222)

- Metal-Chelate complex theory
- EDTA as a chelating ligand and the control of this chelating behavior with manipulation of its Bronsted Acid/Base behavior (pH control of solution to manipulate the correct chelating form of EDTA).
- Formation constants and conditional formation constants in chelation applications.

14. Basic Electrochemistry: (CHEM 222)

- Basis for a galvanic cell
- Electrical potential and its relationship to free energy (ΔG).
- Balancing redox equations
- Notation for electrochemical cells (i.e. potentiometric or galvanic cells)
- Purpose of a salt bridge
- Difference between E and E°
- How does one use ½ reaction potentials and reactions to determine E° for an electrochemical cell?
- How to use cell potential to predict spontaneity of a chemical reaction and free energy.
- Electrochemical cell calculations including
  - Net cell reaction
  - E° and E for a cell
  - ΔG of the cell
  - K_{eq} of the cell
- Understand the basis for the use of an electrochemical cell to extract chemical information. (E-chem cells as chemical probes).

15. Electrodes/Potentiometry: (CHEM 222)

- How is a cell set-up to make chemical measurements (i.e. use of indicator and reference electrodes)?
- Purpose and types of reference electrodes
- Purpose and categorization of indicator electrodes
- Effect of liquid junction/junction potential
- Use of potentiometry to extract chemical information. (i.e. approaches to calibration/manipulation of solution conditions.)
- What is an ionic strength buffer and how is it used in potentiometry?
- How does an ion selective electrode function? (Basic types of ISE)
- How does one convert the potential of an indicator electrode versus a specific reference electrode to its equivalent potential versus a different reference electrode?

16. Redox Titrations: (CHEM 222)

- How does one use potentiometry to predict a titration curve for determining the feasibility of a titration?

17. Spectrophotometry: (CHEM 222)

- Spectrometry vs spectrophotometry
- Properties of light
- What happens when a molecule or atom absorb light? (absorption vs emission in atoms/molecules)
- Understand the importance and application of Beer's Law in Quantitative Analysis
- What limitations are imposed on a Beer's Law calibration at high and low concentrations.
- What is the method of standard additions? How is it implemented?
- What are internal standards? How is calibration by this approach useful?
- What is the basic breakdown of a spectrophotometer? (single and double beam)
- Describe how each of the components of the spectrophotometer function.

18. Spectrometry: (CHEM 222)

- What process occurs in a basic spectrometric measurement?
- Describe the experimental measurement by flame atomic emission. The process, the instrument, calibration.
- How does atomic absorption differ from flame emission?

19. Separations: (CHEM 222)

- How does a solvent extraction work?
- What is the basis behind chromatography?
- Understand the terms: retention time, partition coefficient, resolution, plate height, theoretical plate.
- Know the basis of band broadening in chromatography. (Van Deemter equation and its terms)
- Understand the basic layout of a gas chromatograph and several detectors used.
- Know the basic layout of high performance liquid chromatography and detectors.
- How does one calculate a theoretical plate? HETP?

20. Electronics/Signals Section: (CHEM 322)

- The meaning of signal, background, signal-to-noise ratio, signal - to background ratio. How might integration time affect improvements in the S/N (greater integration time improves S/N by the $(t)^{1/2}$.
- What is meant by the terms sensitivity and limit of detection. How might one quantify each?
- The normal approaches to calibration (linear vs 2nd order polynomial) Why might a 2nd order polynomial need more calibration stds than that of a linear curve.
- What is the method of standard additions. Why is it used? How is it accomplished? `also consider the idea of internal standards.
- Consider remembering voltage, current, Ohms/Kirchoff law problems and simple circuits.
- Remember how to derive operational amplifier circuits and their purposes.
- Don't forget power supplies and the ideas of voltage filters.

21. Mass Spectrometry: (CHEM 322)

- Understand the basic layout of the mass spectrometer.
- Remember the differences between single and double focusing, quadrupole and time-of-flight mass analyzers.
- Resolution is an important concept in mass spectrometry; What sort of resolution does each mass analyzer give..
- What important ionization sources might be used. How does each impact the overall mass spectrum?
- What information can be obtained from the parent peak? (i.e. # of C, H, N, O)
- Impact of elements on M+1, M+2 peaks.
- General ideas on fragmentation that can occur with various sources. What molecules might fragment more readily that others.

22. Basic Spectroscopy (Physical Chem) (CHEM 322)

- Remember your emr theory and how to convert between wavelength, energy, wavenumber.
- Understand the regions of the electromagnetic spectrum and the types of chemical information that may be obtained from each region. For example the infrared region provides information on molecular vibrations, etc.
- Understand the processes by which atoms and molecules may absorb or emit light. I.e energy diagrams etc..
- Remember the processes of Raman scattering and the meaning of Stokes and Anti-stokes lines. What is contained within the shifts in energy?

23. UV-Vis Spectroscopy Instrumentation Concepts: (CHEM 322)

- The basic components in a typical spectrometer or spectrophotometer. Of particular know the sources, the monochromators, detectors and the ideas related to instrument optics such as dispersion, resolution.

24. UV-Vis Spectrophotometry: (CHEM 322)

- Understand Beer-Lambert law and how to apply it.
- Know what limits the working range of calibration (i.e. stray light limits) and other causes of non-linear behavior.
- Remember applications of UV-Vis as applied to photometric titrations and other types of applications.
- How does one correlate the absorption with structure. Conjugation and functional groups.
- What concentration detection limits might be typical.

25. Fluorescence and Phosphorescence. (CHEM 322)

- What processes occur in molecules which create phosphorescence and fluorescence.
- What structural considerations would you expect from a molecule which fluoresces?
- How is quantitative information derived, relationship of P_f to that of incident power.
- What causes non-linear behavior in calibration. What might be an expected LOD?
- What sorts of qualitative information might be derived from spectra?

26. Atomic Spectroscopy - Flames (CHEM 322)

- Know the basic breakdown on an AES instrument and AAS instrument.
- Understand the basics of sample introduction via nebulization.
- Know what happens to a sample once it enters a flame (see your lab and text for this). What sort of interferences might you expect? How would one correct for them?
- What effects do flame temperatures have on the interferences or for that matter on the actual emission of a sample. What would happen to analyte ionization with increasing flame temperature?
- What approximate concentrations can be detected? What limits the upper end of the calibration curve? (self-absorption)
- What do Boltzmann, Einstein-Boltzmann equations do for us?
- Why is flame aa involve a wider scope of elements that flame emission?   How does it differ from flame emission in terms of the hollow cathode source and the use of modulation.
- How does a graphite furnace afford better LODs compared to flame aa. Also how does it work?

27. Atomic Spectroscopy - Plasmas (CHEM 322)

- What is an ICP? How does it function and in what ways can it prove to provide a more interference-free analysis compared to that of flames?

28. Infrared Spectrophotometry/Raman Spectroscopy. (CHEM 322)

- What is the basic breakdown of a dispersive IR instrument
- What is attenuated total reflectance?
- What criteria must be met for a sample to be ir active? Raman active?
- What chemical information can be derived from the IR absorbance spectra? (functional group and fingerprint region).
- Remember what you learned from organic chemistry about interpretation of IR, preparation of samples, and why IR is not commonly used for quantitative determinations.

29. Potentiometry: (CHEM 322)

- Understand the basics of electrochemistry, including redox reactions, galvanic cells and electrolytic cells.
- Be able to construct and electrochemical cell from a picture, describe a cell reaction from a shorthand notation for an electrochemical cell.
- Understand the effects on an electrochemical cell if electrolysis is allowed to occur.
- Know how to derive information of chemical nature from potentiometric data using the Nernst equation.
- Understand the difference between the various types of reference electrodes, indicator electrodes.
- How is cell potential used to derive the voltage of an individual electrode and how is this converted to its potential versus a different reference electrode.
- What is an ISE and how is it actually similar and different to electrodes which are described via the Nernst equation rather than the ISE relationship.
- How does a pH electrode function and how calibrated?

- How are electrodes used to monitor a titration? What do first and second derivatives do in improving the ability to accurately located the endpoint.
- How does one calculate the potential of a titration reaction at the equivalence point?

30. Electrolytic Methods: (CHEM 322)

- Understand the ideas of electrolytic cells.
- What sort of faradaic and non-faradaic processes occur at the surface of an electrode?
- What transport processes govern current response in an electrochemical cell?
- Know the basic processes of linear sweep voltammetry, cyclic voltammetry, and anodic stripping voltammetry. What calibration relationships can be used to derive quantitative information. How can they be used to derive qualitative information?
- What is the Randles-Sevcik equation. How do n, D and scan rate relate as well as the concentration of a sample?
- Why is a three -electrode system used instead of just two.
- Hydrodynamic voltammetry might be of interest too.

31. Basic chromatography. (CHEM 322)

- Know your ideas about the partition coefficient, partition ratio and their importance.
- Remember the ideas of HETP, N and those parameters which are used to describe column efficiency.
- Remember how to define resolution.
- Of what purpose is the van Deemter equation.
- What is a van Deemter plot?

32. GC. (CHEM 322)

- Describe the basic layout of a GC instrument.
- Know the difference between a packed and capillar y column.
- Be able to describe the major types of detectors used and the types of compounds to which they are best suited.
- What gains can be made using temperature programming.
- How are quantitative and qualitative data derived? (Conc = K(peak area) for same volume samples)

33. HPLC (CHEM 322)

- Describe the basic HPLC Instrument.
- Understand detectors commonly used (i.e UV-Vis that we previously described) and others.
- What types of samples are commonly used.
- What is normal phase versus reversed phase HPLC.

These basics will provide a pretty solid preparation. There are obviously a lot of other things that could also be covered. If you choose, may want to think a little about the NMR you have learned in organic chemistry. (used for elemental analysis particularly in solid materials and powders). **In addition, the efforts you made in interpreting IR, NMR, and MS in organic chemistry may prove to benefit you.**