

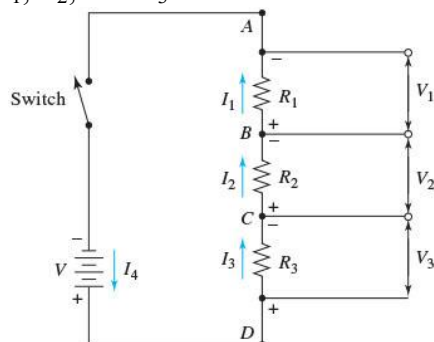
## Analytical Chemistry II – FINAL EXAM

- It is not allowed to put any additional items (*e.g.* cell phone, calculator) on the bench.
- Sign the exam paper, and sign the attendance list at the beginning of the exam.
- You have to hand in the exam paper before leaving the classroom.
- The exam consists of two parts (I and II).
- You can answer in English or Chinese language.
- Do not use pencil; use pen.
- If you cheat (*e.g.* use cell phone), you will be punished.

### I. Choose the most accurate answer:

Circle the letter corresponding to your choice, or write the answer letter next to the question.  
(maximum:  $20 \times 4 = 80$  points)

1. Which formula relates  $V_1$  with  $V$ ,  $R_1$ ,  $R_2$ , and  $R_3$  in the circuit below?



- a)  $V_1 = V \left( \frac{R_1}{R_1 + R_2 + R_3} \right)$   
 b)  $V_1 = V \left( \frac{R_1 + R_2 + R_3}{R_2 + R_3} \right)$   
 c)  $V_1 = V \left( \frac{R_2 + R_3}{R_1 + R_2 + R_3} \right)$   
 d)  $V_1 = V(R_1 + R_2 + R_3)$   
 e)  $V_1 = V \left( \frac{R_1 + R_2 + R_3}{R_1} \right)$

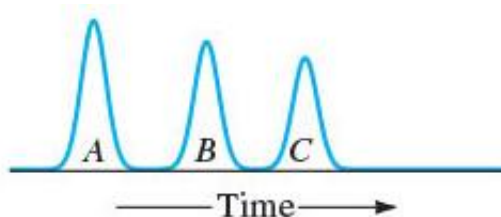
2. What is the definition of absorbance ( $A$ )? ( $P_0$  – power of incident light,  $P$  – power of transmitted light)

- a)  $A = \frac{P_0}{P}$   
 b)  $A = \log \frac{P_0}{P}$   
 c)  $A = \frac{P}{P_0}$   
 d)  $A = \log \frac{P}{P_0}$   
 e)  $A = P - P_0$

3. Which of the following light sources provides line spectrum?
- a) deuterium lamp
  - b) the Sun
  - c) tungsten lamp
  - d) EDL lamp
  - e) xenon arc lamp
4. Which element can readily be analyzed by cold-vapor atomization atomic absorption spectrometry?
- a) uranium
  - b) sodium
  - c) mercury
  - d) silicon
  - e) cadmium
5. In flame atomization atomic absorption spectrometry, how do we call a cation that preferentially reacts with a species that would otherwise react with the analyte to cause a chemical interference?
- a) releasing agent
  - b) radiation buffer
  - c) ionization suppressor
  - d) ionization promotor
  - e) protective agent
6. Which light source is suitable for molecular absorption spectroscopy at 200-300 nm?
- a) deuterium lamp
  - b) Globar
  - c) HCL lamp
  - d) nichrome wire
  - e) tungsten lamp
7. The zone in inductively coupled plasma source used for atomic emission spectroscopic measurements has a temperature of:
- a) ~ 100 K
  - b) ~ 600 K
  - c) ~ 1000 K
  - d) ~ 6000 K
  - e) ~ 150000 K
8. Intersystem crossing
- a) occurs when radiation promotes a molecule directly to a state with sufficient kinetic energy for a bond to break.
  - b) is the process in which a molecule in one spin state changes to another spin state with nearly the same total energy.
  - c) is a radiationless process in which a molecule loses electronic energy while transferring that energy to the solvent or another solute.
  - d) is observed when an excited species emits radiation of the same frequency as that used to cause the excitation.
  - e) is required for fluorescence to occur.
9. Which wavelength region is called middle infrared?
- a) < 0.78  $\mu\text{m}$
  - b) 0.78-2.5  $\mu\text{m}$
  - c) 2.5-50  $\mu\text{m}$
  - d) 50-1000  $\mu\text{m}$
  - e) > 1000  $\mu\text{m}$

10. Which device is the key component in modern infrared spectrometers that enable recording infrared absorption spectra?
- a) prism
  - b) ion source
  - c) Michelson interferometer
  - d) diffraction wedge
  - e) diffraction grating
11. What is the main function of reflectron in time-of-flight mass analyzer?
- a) to improve vacuum
  - b) to compensate for kinetic energy dispersion
  - c) to compensate for mass dispersion
  - d) to reflect laser light
  - e) to create ions
12. Which technique would you apply to study distribution of iron on the surface of silicon?
- a) HPLC
  - b) LA-ICP-MS
  - c) FIA-ICP-MS
  - d) UV-Vis absorption spectrometry
  - e) ESI-MS
13. What is the characteristic feature of nanoelectrospray ionization?
- a) compatibility with inductively coupled plasma source
  - b) use of very high pressures (several atmospheres)
  - c) very high limits of detection (in terms of total analyte mass)
  - d) very high ionization efficiencies
  - e) very long desolvation times
14. Which element can normally be found in atmospheric pressure chemical ionization source?
- a) Taylor cone
  - b) laser
  - c) ion trap
  - d) heated filament
  - e) corona electrode
15. Which factor does not have strong influence on resistance to mass transfer in mobile phase?
- a) diffusion coefficient in stationary phase
  - b) diffusion coefficient in mobile phase
  - c) diameter of packing material
  - d) retention factor
  - e) linear velocity of mobile phase
16. Which technique is particularly useful in analysis of samples that contain low-molecular-weight compounds whose boiling points differ significantly?
- a) UV-Vis absorption spectrometry
  - b) thin-layer chromatography
  - c) ion-exchange liquid chromatography
  - d) reversed-phase liquid chromatography
  - e) GC with temperature programming

17. Which mobile phase, commonly used in gas chromatography, gives the lowest theoretical plate height at high average linear velocities?
- a)  $\text{H}_2$
  - b) He
  - c)  $\text{N}_2$
  - d)  $\text{H}_2\text{O}$
  - e)  $\text{CH}_3\text{OH}$
18. Which statement about HPLC is true?
- a) Gradient elution cannot be used to change polarity of mobile phase during separation.
  - b) To assure optimum separation, sample injection volume should be small (microliter range).
  - c) Large particles of column packing provide high column efficiency.
  - d) It is not necessary to use in-line filter because the reciprocating piston pump automatically removes precipitates.
  - e) Proportioning valve is used to vary total flow rate of the mobile phase entering the column during separation.
19. In gradient elution,
- a) total flow rate of the mobile phase is decreased
  - b) electric field gradient is applied to the column
  - c) temperature of the column is decreased
  - d) the ratio of solvents is varied in a preprogrammed way
  - e) all the compounds have the same retention time
20. The chromatogram shows elution of compounds A, B, and C from a reversed-phase chromatographic column using a high-polarity mobile phase. What is the polarity order of the three compounds (from high to low)?



- a)  $C > B > A$
- b)  $A > C > B$
- c)  $A > B > C$
- d)  $B > A > C$
- e)  $A = B = C$

## II. Answer the following questions: (maximum: $4 \times 5 = 20$ points)

- Indicate the question letter before answering.
- Provide a complete, accurate, clear, high-quality answer to every part of each task.
- Adhere to the answer length limits. Up to 3 points may be deducted per question for exceeding the length limits.
- Handwriting must be clear.
- Schemes and graphs must be labeled.

A. Explain the operation of matrix-assisted laser desorption/ionization source. Illustrate this explanation with a scheme.

- answer length limit: 1 figure with labels, 150 words

B. Explain the operation of magnetic sector mass analyzer. Illustrate this explanation with a scheme.

- answer length limit: 1 figure with labels, 150 words

C. Define the following terms used in chromatography field:

- answer length limit: 80 words per point

- (1) mobile phase
- (2) distribution constant
- (3) retention time
- (4) linear flow velocity
- (5) column resolution

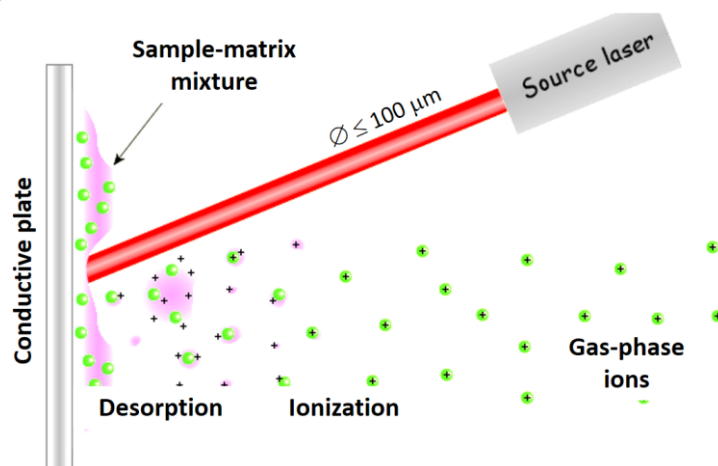
D. Draw detailed block diagram of gas chromatograph. Explain the operational principle of this instrument.

- answer length limit: 1 figure with labels, 150 words

ANSWERS: (You can also use the reverse sides.)

A.

- A sample is co-crystallized with a chemical matrix on conductive support.
- Matrix is in huge excess relative to analytes.
- The sample-matrix deposit is irradiated with laser beam.
- The matrix absorbs the energy; it facilitates desorption and ionization of the analytes.
- It is a soft ionization technique.
- Singly charged ions are dominant (simple spectra).
- It is suitable for analysis of medium-size and large molecules.
- Matrix interference occurs in the low  $m/z$  range.
- There are problems with matrix homogeneity ("sweet spots").
- It is mostly qualitative.



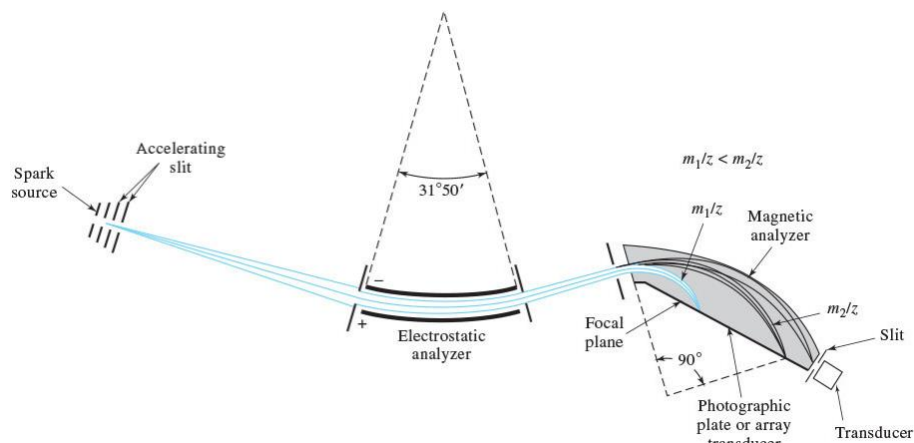
## B.

- Magnetic sector analyzers use a permanent magnet or electromagnet.
- The ion beam enters a zone with magnetic field and the ions are deflected.
- The dispersed ions fall onto a photographic plate or an array transducer, and are recorded.
- Ions with different  $m/z$  can be scanned by varying the field strength of the magnet or the accelerating potential between slits (A and B). (In that case, one can use a single-point transducer, as shown in the figure below).

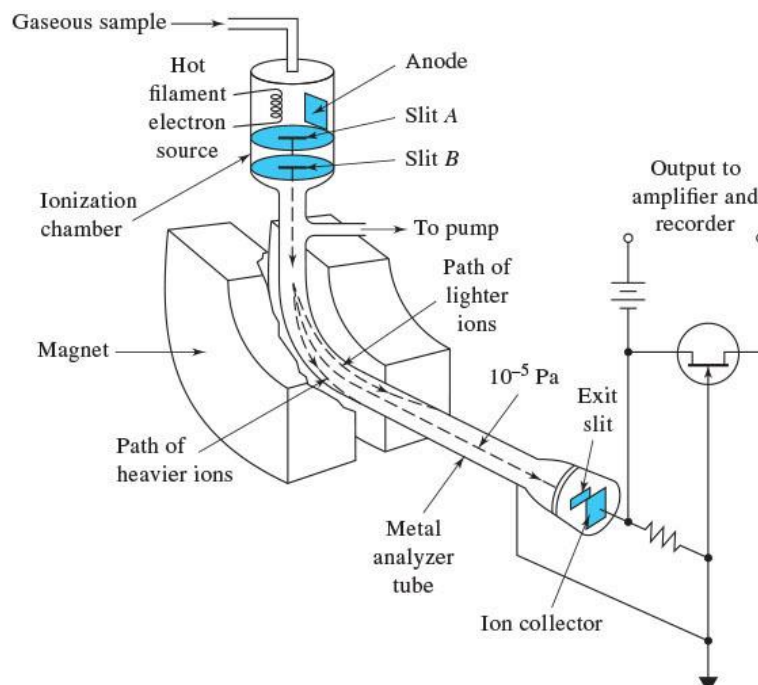
One can write one of these formulas introduced in the lecture:

$$r_B = \frac{mv}{qB}$$

$$\frac{m}{z} = \frac{B^2 r^2 e}{2V}$$



OR

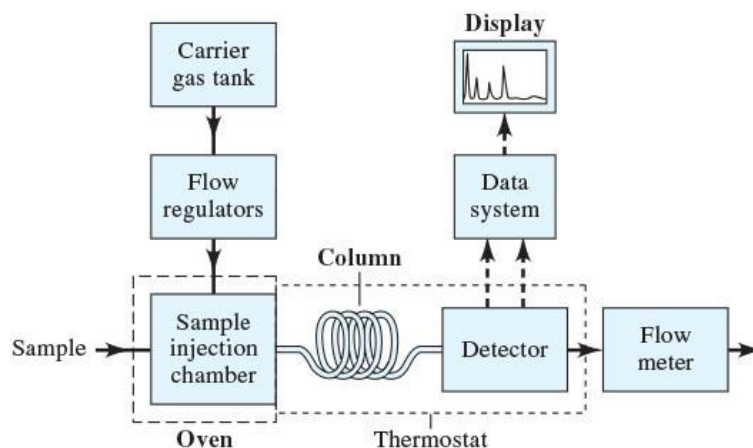


## C.

- (1) The *mobile phase* in chromatography is the one that moves over or through an immobilized phase that is fixed in place in a column or on the surface of a flat plate.

- (2) The *distribution constant*  $K$  in chromatography is the ratio of the concentration (strictly activity) of the analyte in the stationary phase to its concentration (activity) in the mobile phase when equilibrium exists between the two phases.
- (3) The *retention time* for an analyte is the time interval between its injection onto a column and the appearance of its peak at the other end of the column.
- (4) The *linear flow velocity* at the column outlet is measured in cm/s and is the volumetric flow rate per unit cross sectional area of the column. For a packed column the linear velocity is the volumetric flow rate divided by the cross sectional area and the fraction of the total column volume available to the liquid.
- (5) The *resolution*  $R_s$  of a column toward two species A and B is given by the equation:  $R_s = 2\Delta Z/(W_A + W_B)$ , where  $\Delta Z$  is the distance (in units of time) between the peaks for the two species and  $W_A$  and  $W_B$  are the widths (also in units of time) of the peaks at their bases.

#### D.



- In gas chromatograph, a chemically inert carrier gas (helium, argon, nitrogen, hydrogen) is applied at a pressure of 10-50 psi to move gaseous analytes along the column.
- The flow of the gas is regulated by a flow regulator. Typical flow rates: 25-150 mL/min (packed columns); 1-25 mL/min (capillary columns).
- Sample is injected to the column inlet.
- Sample injection chamber and column are thermostatted.
- Separated analytes are detected by a detector at the end of the column.
- Signal from the detector is recorded by data system, processed, and chromatogram is displayed.