

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 get 0 points from this exam.

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. What is the correct equation for Beer's law?

(A – absorbance, ε – molar absorptivity, b – optical pathlength, c – analyte concentration)

- a) $A = \log(\varepsilon bc)$
- b) $A = \frac{\varepsilon}{bc}$
- c) $A = \frac{\varepsilon b}{c}$
- d) $A = \varepsilon bc$
- e) $A = \varepsilon b \sin(c)$

2. Which element can readily be analyzed by cold-vapor atomization atomic absorption spectrometry?

- a) uranium
- b) sodium
- c) cadmium
- d) mercury
- e) silicon

3. Addition of potassium to sample can improve sensitivity in analysis of strontium by flame atomization atomic absorption spectrometry. In this case, potassium is:

- a) ionization suppressor
- b) releasing agent
- c) solute volatilization interferent
- d) protective agent
- e) radiation buffer

4. Which device is used as a source of continuum UV radiation in molecular spectroscopy?

- a) photoconductor
- b) hollow-cathode lamp
- c) globar
- d) phototube
- e) deuterium lamp

5. Which of the following is the characteristic of (photo)diode array detector?
- a) It has very slow response.
 - b) It cannot be used in the visible region.
 - c) It enables recording full spectrum in a very short time.
 - d) It emits light at one wavelength only.
 - e) It is much more sensitive to light than photomultiplier tube.
6. How do we call the process, in which a molecule changes from a higher electronic state to an upper vibrational level of a lower electronic state in which the vibrational energy is great enough to rupture the bond?
- a) intersystem crossing
 - b) predissociation
 - c) vibrational relaxation
 - d) phosphorescence
 - e) fluorescence
7. Which device is the key component in modern infrared spectrometers that enable recording infrared absorption spectra?
- a) ion source
 - b) prism
 - c) diffraction grating
 - d) diffraction wedge
 - e) Michelson interferometer
8. What is the main function of reflectron in time-of-flight mass analyzer?
- a) to create ions
 - b) to improve vacuum
 - c) to reflect laser light
 - d) to compensate for kinetic energy dispersion
 - e) to compensate for mass dispersion
9. Multiple charging of proteins is most prominent in
- a) electrospray ionization
 - b) electron ionization
 - c) inductively coupled plasma ionization
 - d) chemical ionization
 - e) matrix-assisted laser desorption/ionization
10. What is the characteristic feature of nanoelectrospray ionization?
- a) compatibility with inductively coupled plasma source
 - b) very high ionization efficiencies
 - c) very high limits of detection (in terms of total analyte mass)
 - d) very long desolvation times
 - e) use of very high pressures (several atmospheres)
11. Why do we need chromatographic separations?
- a) to speed up analysis
 - b) to increase the required sample volume
 - c) to decrease selectivity
 - d) to increase selectivity and reduce interferences
 - e) to miniaturize analytical systems

12. Which factor does not have strong influence on resistance to mass transfer in mobile phase?
- a) diameter of packing material
 - b) retention factor
 - c) linear velocity of mobile phase
 - d) diffusion coefficient in mobile phase
 - e) diffusion coefficient in stationary phase
13. What is the typical inside diameter of fused silica wall-coated open tubular column used in gas chromatography?
- a) < 0.2 µm
 - b) ~ 0.5-8 µm
 - c) ~ 10-50 µm
 - d) ~ 0.1-0.3 mm
 - e) > 2 mm
14. Which mobile phase gas can provide very low values of plate height at high average linear velocities?
- a) air
 - b) methane
 - c) nitrogen
 - d) helium
 - e) hydrogen
15. Which statement about flame ionization detector, used in gas chromatography, is true?
- a) Analytes have to be in ionic form before they enter the detector (*i.e.* already in the column).
 - b) It responds to the number of carbon atoms entering the detector per unit of time.
 - c) It selectively responds to halogen-containing compounds.
 - d) It relies on measurement of electrical resistance of a heated wire.
 - e) It is non-destructive.
16. Which transducer/detector uses radioactive β radiation emitter?
- a) flame ionization detector
 - b) atomic emission detector
 - c) electron capture detector
 - d) bolometer
 - e) thermocouple
17. Which statement about HPLC is true?
- a) To assure optimum separation, sample injection volume should be small (microliter range).
 - b) Large particles of column packing provide high column efficiency.
 - c) Gradient elution cannot be used to change polarity of mobile phase during separation.
 - 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.
18. In gradient elution,
- a) electric field gradient is applied to the column
 - b) temperature of the column is decreased
 - c) total flow rate of the mobile phase is decreased
 - d) all the compounds have the same retention time
 - e) the ratio of solvents is varied in a preprogrammed way

19. Which element is often placed between ion-exchange chromatographic column and conductometric detector?
- a) reversed-phase chromatographic column
 - b) ion-exclusion chromatographic column
 - c) micromembrane suppressor
 - d) ion source
 - e) ion trap
20. Stationary phase in HILIC chromatography has to contain
- a) polar moieties
 - b) non-polar moieties
 - c) polystyrene
 - d) polyimide
 - e) plate height

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 time-of-flight mass analyzer. Illustrate this explanation with a scheme.

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

B. Discuss the major differences between a tandem-in-space mass spectrometer and a tandem-in-time mass spectrometer. Include the advantages and disadvantages of each type.

- answer length limit: 150 words

C. Define the following terms used in chromatography field:

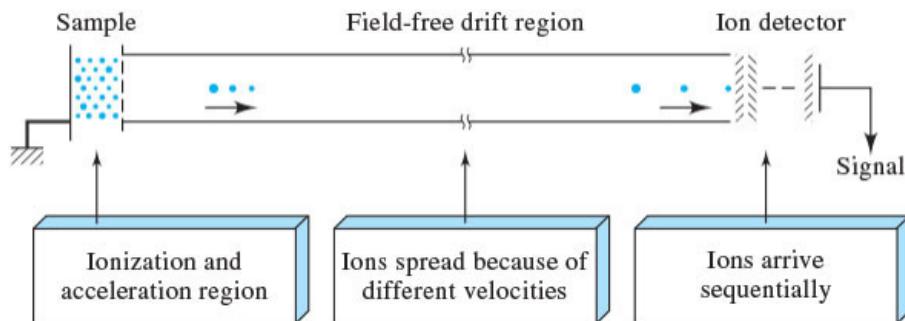
- answer length limit: 80 words per point

- (1) stationary phase
- (2) retention factor
- (3) selectivity factor
- (4) column resolution
- (5) longitudinal diffusion

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.

- Ions are produced in the ion source and accelerated.
- The ions enter a field-free drift tube (ca. 1-2 m).
- The ions with different mass-to-charge ratios move with different velocities.
- The lighter ions arrive at the detector earlier than the heavier ions.

B.

In tandem in space instruments, two independent mass analyzers are used in two different regions in space. This is a rather straight-forward way to do tandem MS and some conventional mass spectrometers can be converted to tandem instruments. The advantages are that it is relatively easy to take all the different types of spectra (product ion, precursor ion, neutral loss, multidimensional). The disadvantages are that the efficiency can be very low and thus the sensitivity can be low. Tandem in time instruments form the ions in a certain spatial region and then at a later time expel the unwanted ions and leave the selected ions to be dissociated and mass analyzed in the same spatial region. The efficiency can be fairly high and the process can be repeated many times. It is, however, only straight forward to take product ion spectra. Both approaches require quite expensive instrumentation.

C.

- (1) The *stationary phase* in a chromatographic column is a solid or liquid that is fixed in place. The mobile phase then passes over or through the stationary phase.

- (2) The *retention factor* k is defined by the equation

$$k = K_A V_S / V_M$$

where K_A is the distribution constant for species A and V_S and V_M are the volumes of the stationary and mobile phases respectively.

- (3) The *selectivity factor* α of a column toward species A and B is given by $\alpha = K_B / K_A$, where K_B is the distribution constant of the more strongly held species and K_A is the distribution constant for the less strongly held species.

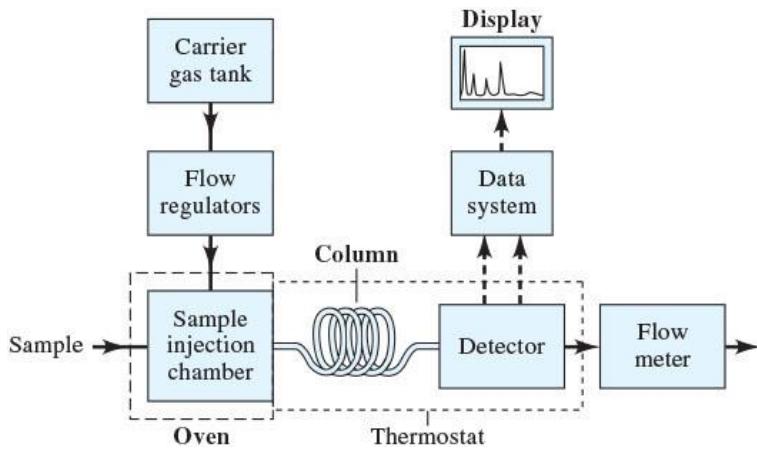
- (4) The *resolution* R_s of a column toward two species A and B is given by the equation

$$R_s = 2\Delta Z / (W_A + W_B)$$

where ΔZ 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.

- (5) *Longitudinal diffusion* is a source of band broadening in a column in which a solute diffuses from the concentrated center of the band to the more dilute regions on either side.

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.