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.**
- **Any form of academic dishonesty, including but not limited to the use of mobile phones, will result in disciplinary action.**

I. Choose the most accurate answer:

Circle the letter corresponding to your choice, or write the answer letter next to the question.
(maximum: 20 × 2 = 40 points)

1. What is the correct equation for Beer's law?
(A – absorbance, ε – molar absorptivity, b – optical pathlength, c – analyte concentration)
   a) $A = \varepsilon bc$
   b) $A = \varepsilon b \sin(c)$
   c) $A = \log(\varepsilon bc)$
   d) $A = \frac{\varepsilon}{bc}$
   e) $A = \frac{\varepsilon b}{c}$

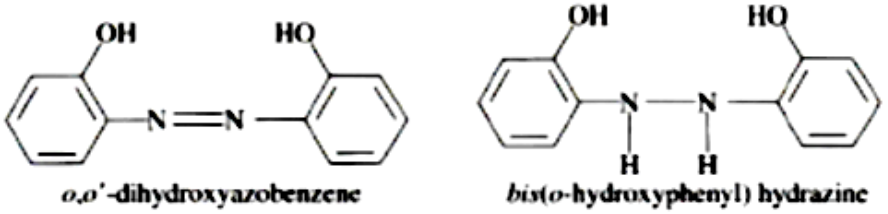
2. Which element can readily be analyzed by cold-vapor atomization atomic absorption spectrometry?
   a) silicon
   b) uranium
   c) sodium
   d) mercury
   e) cadmium

3. Which of the following statements about UV-Vis absorption spectroscopy is correct?
   a) Stray radiation improves absorbance accuracy by contributing additional light to the detector, compensating for signal loss at high concentrations and enhancing the reliability of quantitative measurements in complex samples.
   b) HOMO to LUMO transitions are rarely observed in UV-Vis spectroscopy because such electronic transitions typically violate molecular selection rules and are forbidden in most organic compounds under normal conditions.
   c) Only polychromatic radiation allows accurate application of Beer's Law because it illuminates the sample across a wider range of wavelengths, improving the response of chromophores with broad absorption features.
   d) Radiation can excite electrons to higher energy levels even when the photon's energy does not match the energy gap, as the molecule can redistribute excess energy through vibrational and rotational relaxation pathways.
   e) Transmittance is defined as the ratio of transmitted light intensity (P) to incident light intensity (P_0), used to determine absorbance in UV-Vis analysis.

4. Which device is used as a source of continuum UV radiation in molecular spectroscopy?
   a) hollow-cathode lamp
   b) deuterium lamp
   c) globar
   d) photoconductor
   e) phototube

5. 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) vibrational relaxation
   b) intersystem crossing
   c) predissociation
   d) fluorescence
   e) phosphorescence

6. Which compound would you expect to have a greater fluorescence quantum yield and why?



o,o'-dihydroxyazobenzene *bis*(*o*-hydroxyphenyl) hydrazine

   a) *bis*(*o*-hydroxyphenyl)hydrazine because it exhibits significant predissociation
   b) *bis*(*o*-hydroxyphenyl)hydrazine because the –NH–NH– group provides high rigidity that is absent in the –N=N– group
   c) *bis*(*o*-hydroxyphenyl)hydrazine because the –NH–NH– group decreases rigidity of the molecule
   d) *o,o'*-dihydroxyazobenzene because the –N=N– group provides high rigidity that is absent in the –NH–NH– group
   e) *o,o'*-dihydroxyazobenzene because it exhibits significant predissociation

7. Which technique is particularly useful in analysis of samples that contain low-molecular-weight compounds whose boiling points differ significantly?
   a) GC with temperature programming
   b) thin-layer chromatography
   c) ion-exchange liquid chromatography
   d) reversed-phase liquid chromatography
   e) UV-Vis absorption spectrometry

8. Which device is the key component in modern infrared spectrometers that enable recording infrared absorption spectra?
   a) Michelson interferometer
   b) prism
   c) diffraction grating
   d) ion source
   e) diffraction wedge

9. What is the main function of reflectron in time-of-flight mass analyzer?
   a) to compensate for mass dispersion
   b) to create ions
   c) to compensate for kinetic energy dispersion
   d) to reflect laser light
   e) to improve vacuum

10. Multiple charging of proteins is most prominent in
    a) matrix-assisted laser desorption/ionization
    b) electrospray ionization
    c) inductively coupled plasma ionization
    d) electron ionization
    e) chemical ionization

11. What is the characteristic feature of nanoelectrospray ionization?
    a) very high ionization efficiencies
    b) very high limits of detection (in terms of total analyte mass)
    c) very long desolvation times
    d) use of very high pressures (several atmospheres)
    e) compatibility with inductively coupled plasma source

12. Which of the following statements about matrix-assisted laser desorption/ionization is correct?
    a) It is mainly used for quantitative analysis.
    b) It requires vacuum ultraviolet (VUV) radiation.
    c) It predominantly generates singly charged ions.
    d) It does not require a matrix compound.
    e) It is only used for gas-phase samples.

13. Why do we need chromatographic separations?
    a) to increase selectivity and reduce interferences
    b) to decrease selectivity
    c) to miniaturize analytical systems
    d) to speed up analysis
    e) to increase the required sample volume

14. Which factor does not have strong influence on resistance to mass transfer in mobile phase?
    a) retention factor
    b) diameter of packing material
    c) linear velocity of mobile phase
    d) diffusion coefficient in stationary phase
    e) diffusion coefficient in mobile phase

15. What is the typical inside diameter of fused silica wall-coated open tubular column used in gas chromatography?
    a) < 0.2 nm
    b) ~ 0.5-8 μm
    c) ~ 10-50 μm
    d) ~ 0.1-0.3 mm
    e) > 3 mm

16. Which mobile phase gas can provide very low values of plate height at high average linear velocities?
    a) air
    b) hydrogen
    c) helium
    d) methane
    e) nitrogen

17. 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 selectively responds to halogen-containing compounds.
    c) It relies on measurement of electrical resistance of a heated wire.
    d) It responds to the number of carbon atoms entering the detector per unit of time.
    e) It is non-destructive.

18. Which of the following compounds would be most effectively detected by an electron capture detector in gas chromatography?
    a) benzene
    b) ethanol
    c) chloroform
    d) hexane
    e) acetone

19. Which statement about HPLC is true?
    a) Large particles of column packing provide high column efficiency.
    b) To assure optimum separation, sample injection volume should be small (microliter range).
    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.

20. In gradient elution,
    a) the ratio of solvents is varied in a preprogrammed way
    b) total flow rate of the mobile phase is decreased
    c) electric field gradient is applied to the column
    d) temperature of the column is decreased
    e) all the compounds have the same retention time

II. Answer the following questions: (maximum: 10 × 6 = 60 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. Convert each of the following decimal numbers into binary-coded-decimal (BCD) numbers:
(a) 3; (b) 7; (c) 37.
- answer length limit: 10 words

B. Please explain what an ionization suppressor is in the context of atomic spectrometry.
- answer length limit: 50 words

C. Draw block diagram of mass spectrometer. Indicate the main components of this instrument.
- answer length limit: 1 figure with labels

D. Please list the main processes performed by mass spectrometer.
- answer length limit: 5 items

E. Please compare hard and soft ionization sources used in molecular mass spectrometry.
- answer length limit: 100 words

F. Define the following terms used in chromatography field:
- answer length limit: 80 words per point
(1) selectivity factor
(2) column resolution
(3) longitudinal diffusion

G. What is the difference between packed columns and capillary columns used in gas chromatography? Consider the influence of column type on chromatographic peak shape, separation performance, and sample load capacity.
- answer length limit: 100 words

H. What are hyphenated GC methods? Briefly describe two hyphenated methods.
- answer length limit: 100 words

I. Draw a scheme illustrating interactions of analytes with mobile phase and stationary phase in liquid chromatographic separation, and explain it.
- answer length limit: 1 figure with labels, 100 words

J. Compare normal-phase chromatography and reversed-phase chromatography. For each type, describe the polarity of the stationary phase and the mobile phase, and indicate whether the compounds that elute first are of high or low polarity. When the polarity of the analyte increases, how does the retention time change?
- answer length limit: 100 words

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

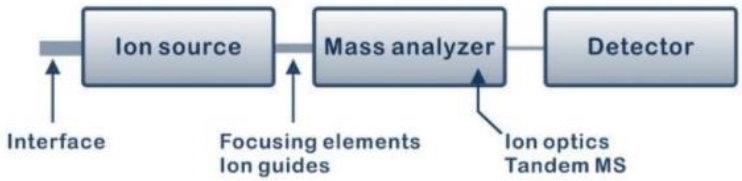
A.

(a) 0011; (b) 0111; (c) 0011 0111

B.

An ionization suppressor is more easily ionized than the analyte and provides a high concentration of electrons. These electrons suppress the ionization of the analyte.

C.



Minimum: The diagram should at least show ion source, mass analyzer, and detector.

D.

1) Production of ions
2) Separation (mass analysis)
3) Fragmentation
4) Detection
5) Processing the signals

E.

Hard ionization sources, such as electron ionization (EI), impart high energy to analyte molecules, leading to extensive fragmentation and the generation of low *m/z* fragment ions.
Soft ionization sources, such as chemical ionization (CI), transfer less energy, resulting in minimal fragmentation and preservation of the molecular ion.

F.

(1) 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.
(2) 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.
(3) *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.

G.

Packed columns are wider and shorter, filled with stationary-phase-coated solid particles, allowing higher sample loads but offering lower efficiency and broader peaks. Capillary columns are narrow and long, internally coated with stationary phase, providing sharper peaks, faster analysis, and superior resolution for complex mixtures, though they handle only small sample amounts. Packed columns suit bulk or preparative work, while capillary columns are preferred for high-resolution trace analysis. Overall, capillary columns excel in separation performance but have lower capacity.

H.

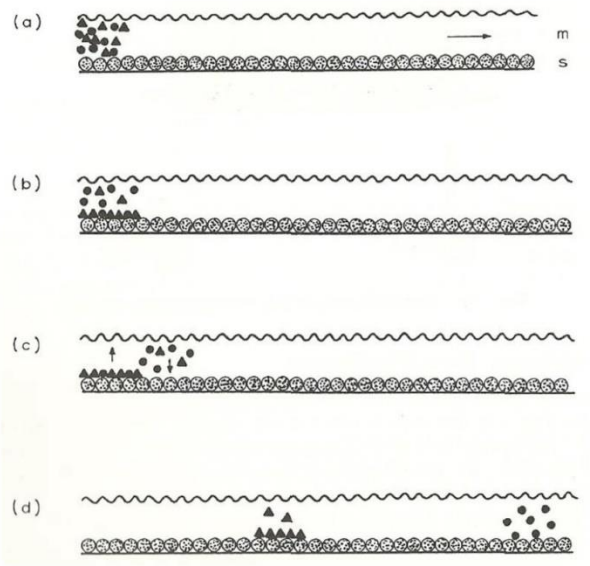
Hyphenated methods couple GC with a different instrumental technique such as mass spectrometry, FTIR, NMR spectroscopy, or electrochemical methods. Most modern hyphenated methods monitor the effluent from

the chromatographic column continuously by spectroscopic methods. Some computer-based GC instruments incorporate large databases for comparing spectra and identifying compounds.

or, simply:

Hyphenated methods couple GC with a different instrumental technique such as mass spectrometry, FTIR, NMR spectroscopy, or electrochemical methods. The effluent from the GC column is either continuously monitored by the second technique or collected and measured.

I.



A mixture of solutes is brought by mobile phase to stationary phase. Solutes migrate to the stationary phase. Some of them interact strongly with the stationary phase while others interact weakly. The solutes that have higher affinity to the mobile phase move faster along the chromatographic column.

or, simply:

Phases involved:

- stationary phase
- mobile phase

Behavior:
(a) All components are introduced at the start.
(b) Components interact differently with the stationary and mobile phases.
(c) Some move faster due to stronger affinity for the mobile phase.
(d) By the end, components are fully separated based on their interactions.

J.

Normal-phase chromatography:

- Stationary phase: polar
- Mobile phase: non-polar
- Elution order: low-polarity compounds elute first.
- Effect of increasing polarity: analytes with higher polarity have stronger interactions with the polar stationary phase, so their retention time increases.

Reversed-phase chromatography:

- Stationary phase: non-polar
- Mobile phase: polar
- Elution order: high-polarity compounds elute first.
- Effect of increasing polarity: analytes with higher polarity interact less with the non-polar stationary phase, so their retention time decreases.