Student's name: _____ Student's ID No.: _____

Analytical Chemistry II – MIDTERM EXAM II

- **It is not allowed to put any additional items (*e.g.* cell phone) 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, 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 × 4 = 80 points)

1. If the transmittance has the value of 0.1, then what is the value of absorbance?
   a) 0.01
   b) 0.1
   c) 1
   d) 10
   e) 100

2. Which light source is suitable for molecular absorption spectroscopy in the visible range?
   a) argon lamp
   b) deuterium lamp
   c) tungsten lamp
   d) HCL lamp
   e) Globar

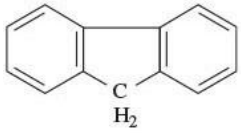
3. Which phototransducer would likely be used in portable photometers operating in the visible region?
   a) photovoltaic cell
   b) phototube
   c) photomultiplier tube
   d) electron multiplier
   e) LED

4. Which of the following is the characteristic of photodiode array detector?
   a) It cannot be used in the visible region.
   b) It enables recording full spectrum in a very short time.
   c) It has very slow response.
   d) It is much more sensitive to light then photomultiplier tube.
   e) It emits light at one wavelength only.

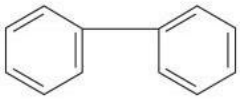
5. What is the typical effect of stray radiation on absorption measurements?
   a) No effect.
   b) Measured absorbance is equal to real absorbance.
   c) At low real absorbance, measured absorbance is much higher than real absorbance.
   d) At high real absorbance, measured absorbance is much higher than real absorbance.
   e) At high real absorbance, measured absorbance is lower than real absorbance.

6. By comparing UV absorption spectra of toluene and benzene, we can realize that the B band of toluene is at a different wavelength than the B band of benzene. How do we call this effect caused by the additional methyl group present in the molecule of toluene?
   a) violet shift
   b) blue shift
   c) hypsochromic shift
   d) bathochromic shift
   e) phase shift

7. Fluorene has higher quantum yield of fluorescence than biphenyl because



fluorene


biphenyl

   a) fluorene molecule has higher rigidity than biphenyl molecule
   b) fluorene molecule has lower rigidity than biphenyl molecule
   c) fluorene molecule exhibits significant intersystem crossing
   d) fluorene molecule exhibits significant predissociation
   e) fluorene molecule exhibits significant quenching

8. How many IR absorption bands result from stretching vibrations in CO_2 molecules?
   a) 0
   b) 1
   c) 2
   d) 3
   e) 4

9. Why do some IR spectrophotometers record white light interferogram?
   a) to define the movable mirror position corresponding to zero retardation
   b) to define the movable mirror position corresponding to maximum retardation
   c) to reduce absorbance in the IR spectrum
   d) to enhance transmittance in the IR spectrum
   e) to minimize reflection of the IR beam

10. Which transducer used in IR spectroscopy relies on change of electrical resistance of a metal element in response to temperature change?
   a) photoconductor
   b) thermocouple
   c) bolometer
   d) pyroelectric cell
   e) photodiode

11. Which material is not suitable for making optical elements of spectrophotometer operating in the wavelength range 7-10 μm?
    a) zinc selenide
    b) thallium bromide
    c) potassium bromide
    d) silicate glass
    e) sodium chloride

12. Which element of mass spectrometer is responsible for introduction of gas-phase ions from the high/intermediate-pressure zone into the vacuum compartment?
    a) quadrupole
    b) nebulizer
    c) skimmer cone
    d) lens
    e) electron multiplier

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

14. Which element can normally be found in atmospheric pressure chemical ionization source?
    a) corona electrode
    b) heated filament
    c) Taylor cone
    d) laser
    e) ion trap

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

16. What is the principle of the so-called ‘product-ion scan’ performed using triple quadrupole mass spectrometer?
    a) first, a quadrupole separates ions; second, the ions are fragmented in a collision cell; third, a quadrupole isolates one fragment ion
    b) first, a quadrupole isolates one ion; second, the ion is fragmented in a collision cell; third, a quadrupole separates the fragment ions
    c) first, a quadrupole converts one ion into product; second, a quadrupole separates the produced precursor ions
    d) first, a quadrupole scans substrate ions; second, a quadrupole isolates one precursor ion
    e) first, a quadrupole scans product ions; second, a collision cell and a quadrupole isolate one substrate ion

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

18. How does selectivity factor (α) depend on retention factors (k_B, k_A) of two solutes?
(B – more strongly retained species, A – more rapidly eluted species)
   a) $\alpha = k_A k_B$
   b) $\alpha = \frac{k_B}{k_A}$
   c) $\alpha = \left(\frac{k_B}{k_A}\right)^2$
   d) $\alpha = k_A - k_B$
   e) $\alpha = k_A + k_B$

19. Theoretical plate height (H) is affected by several processes taking place in chromatographic column according to this equation:

$$H = A + \frac{B}{u} + (C_S + C_M)u$$

(u – average linear velocity of the mobile phase)

What are these processes?
   a) A – multiple flow paths (eddy diffusion), B/u – longitudinal diffusion, $C_S u$ – resistance to mass transfer to and from stationary phase, $C_M u$ – resistance to mass transfer in mobile phase
   b) A – longitudinal diffusion, B/u – multiple flow paths (eddy diffusion), $C_S u$ – resistance to mass transfer to and from stationary phase, $C_M u$ – resistance to mass transfer in mobile phase
   c) A – resistance to mass transfer, B/u – longitudinal diffusion, $C_S u$ – multiple flow paths (eddy diffusion) in stationary phase, $C_M u$ – multiple flow paths (eddy diffusion) in mobile phase
   d) A – multiple flow paths (eddy diffusion), B/u – longitudinal diffusion, $C_S u$ – concentration of analyte in stationary phase, $C_M u$ – concentration of analyte in mobile phase
   e) A – advective flow constant, B/u – longitudinal diffusion, $C_S u$ – resistance to mass transfer to and from stationary phase, $C_M u$ – resistance to mass transfer in mobile phase

20. How do we define chromatographic resolution?
($(t_R)_A$ and $(t_R)_B$ – retention times of two analytes, W_A and W_B – the corresponding peak widths at base)
   a) $R_S = \frac{(t_R)_A}{W_A}$
   b) $R_S = (t_R)_B - (t_R)_A$
   c) $R_S = \frac{2[(t_R)_B + (t_R)_A]}{W_A - W_B}$
   d) $R_S = \frac{2[(t_R)_B + (t_R)_A]}{W_A + W_B}$
   e) $R_S = \frac{2[(t_R)_B - (t_R)_A]}{W_A + W_B}$

II. Answer the following questions: (maximum: 4 × 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 5 points may be deducted per question for exceeding the length limits.
- Handwriting must be clear.
- Schemes and graphs must be labeled.

A. Explain the difference between fluorescence and phosphorescence. Support this explanation with the Jablonski diagram.
- answer length limit: 150 words, 1 figure with labels

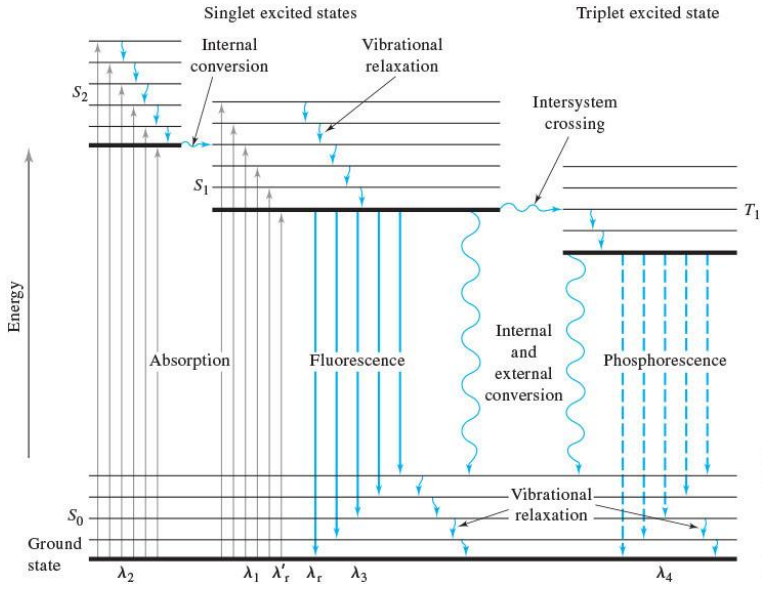
B. Explain the operational principle of portable IR photometer for gas analysis. Illustrate this explanation with a scheme of the device.
- answer length limit: 150 words, 1 figure with labels

C. Explain the operational principle of electrospray ionization source used in mass spectrometry. Illustrate this explanation with a scheme of the device.
- answer length limit: 150 words, 1 figure with labels

D. Explain the operational principle of time-of-flight mass analyzer. Illustrate this explanation with a scheme of the device.
- answer length limit: 150 words, 1 figure with labels

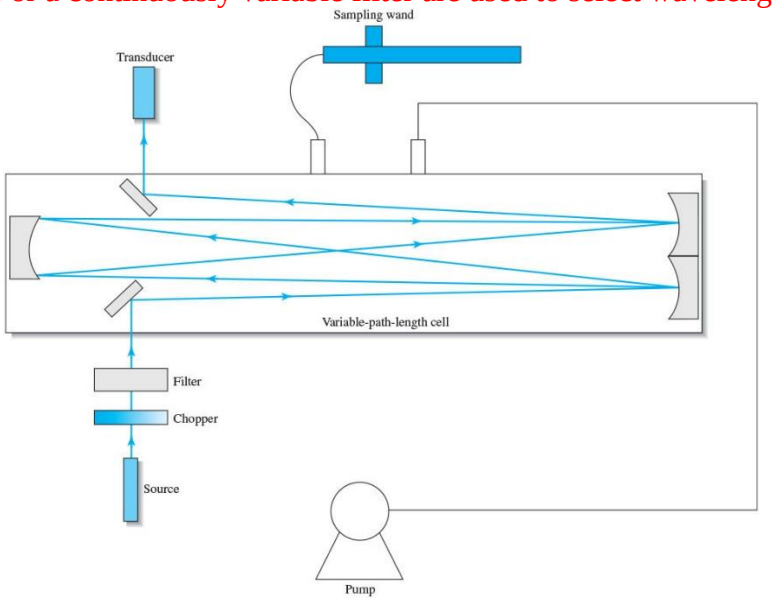
ANSWERS:

A.
- Photoluminescence encompasses fluorescence and phosphorescence.
- In both cases, excitation is brought about by absorption of photons.
- The excited molecule makes the transition via a series of vibrational relaxations, internal conversion, and further relaxations.
- In fluorescence, the molecule undergoes de-excitation from the excited singlet state.
- In phosphorescence, the electronic energy transitions involve a change in electron spin.
- After intersystem crossing to the triplet state, further deactivation can occur either by internal or external conversion or by phosphorescence.
- Transition probability and excited-state lifetime are inversely related.
- For that reason, the average lifetime of the excited triplet state ranges from 10^{-4} s to 10 s or more.



B.

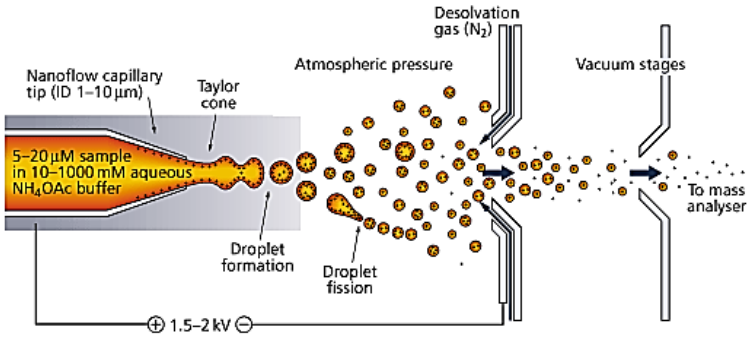
- The gaseous sample is brought into the cell by means of a pump.
- Mirrors are used to increase the optical pathlength.
- The source is a nichrome-wire filament, and the transducer is a pyroelectric device.
- Fixed bandpass filters or a continuously variable filter are used to select wavelengths.



C.

- Liquid sample is infused through a metal capillary.
- Electric voltage is applied to the capillary and a counter electrode (near the MS orifice).
- The liquid meniscus forms Taylor cone, and microdroplets detach from its apex.
- The microdroplets undergo desolvation (evaporation of solvent).
- Electric charge density on the surface of droplets increases.
- Because surface tension forces cannot balance electrostatic repulsion forces, the microdroplets undergo fission.
- Finally, all the solvent molecules evaporate leaving behind gaseous ions of analyte species.
- Multiply charged species are formed from large molecules.
- Ionization typically follows any of the following pathways:
    - protonation
    - deprotonation

- formation of adducts



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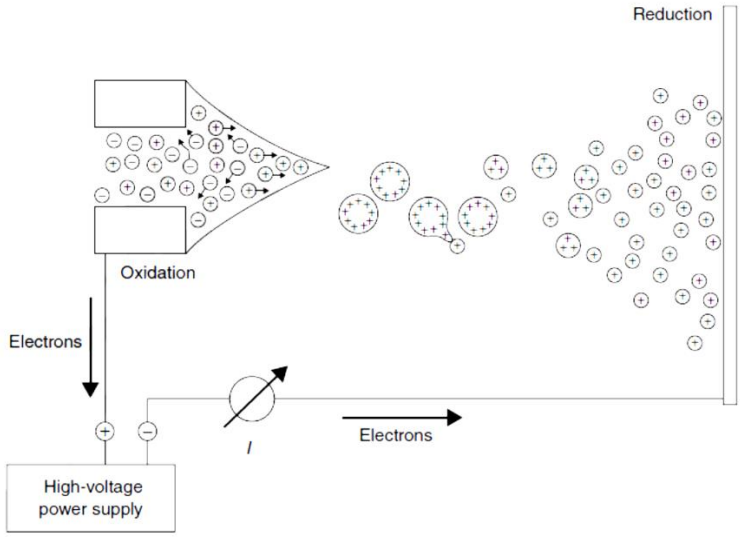
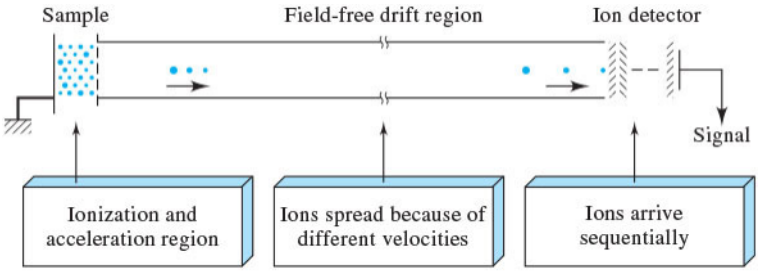


D.

- The time required for ions to travel from an ion source to a detector is measured.
- The ions receive approximately the same kinetic energy during ionization and acceleration.
- The accelerated ions pass to a field-free drift tube (ca. 1-2 m).
- The lighter ions arrive at the detector earlier than the heavier ions.



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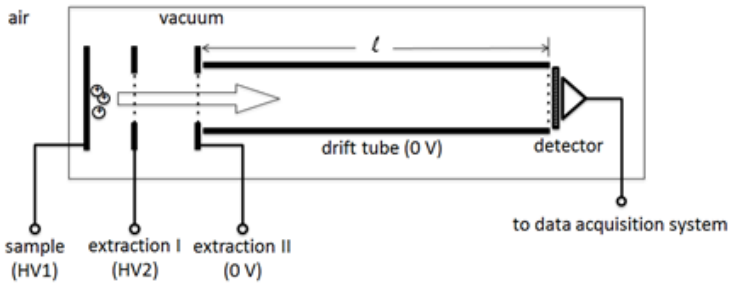
air
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drift tube (0 V)
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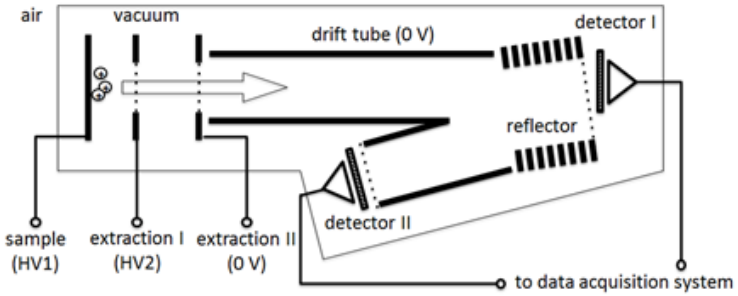
to data acquisition system
sample
(HV1)
extraction I
(HV2)
extraction II
(0 V)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to data acquisition system