Analytical Chemistry Cumulative --- January 2016
by Yoshitaka Ishii

Total 100 points. The pass line is ~70 points. Points may be scaled by an adequate scaling function. Unless specified, answer each question concisely using no more than one paragraph and 5 equations.

1. Answer the following questions. Total 25 points (a 4 points, b 5 points, c 10 points, d 6 points)

(a) Suppose that the S/N of a ^{1}H NMR spectrum for a sample A is 10 for 1024 scans. How much S/N do you expect in the NMR spectrum if you accumulate 10240 scans?
(b) State the reason of your expectation in (a). Mention how noise level and signal intensity depends on the number of scans.
(c) Describe how you measure the noise or the noise level in NMR even though the noise intensity fluctuates between positive and negative?
(d) State two other ways to increase S/N of the NMR spectrum with concise reasoning.

2. Answer the following questions. Total 25 points (5 point each)

(a) Describe the relationship between spin angular momentum and spin magnetic moment using equations with the angular momentum $\boldsymbol{I}$ and the magnetic moment $\boldsymbol{\mu}$, where $\boldsymbol{I}$ and $\boldsymbol{\mu}$ are generally vector values.
(b) Describe the Zeeman energy that accounts for the energy due to the interaction between a static magnetic field $\boldsymbol{B}_0$ and a spin magnetic moment $\boldsymbol{\mu}$. Assume that $\boldsymbol{B}_0$ is parallel to the z-axis.
(c) Draw an energy diagram of the Zeeman energy for a spin 1 system ($I = 1$).
(d) Describe the transition energy for the system (c). Define an adequate constant and give a formula that corresponds to the energy.
(e) Explain why NMR transition frequencies depend on a type of the nucleus. What is the reason why a nucleus having a smaller mass generally has a higher frequency?

3. Answer the following questions.
Bloch equation describes a motion of a magnetic moment **M**(t) in a magnetic field **B**(t). The equation is given by $(d\mathbf{M}(t)/dt) = \mathbf{M}(t) \times \gamma\mathbf{B}(t)$. What is the expected motion of **M**(t) under the following **B** and **M**(0) defined in (a) and (b)? Explain the motions with equations and draw a vector motion. (a) 6 points (b) 6 points (c) 13 points.

(a) $-\gamma\mathbf{B} = [0, 0, \Omega]$ & $\mathbf{M}(0) = [0, 0, M_0]$

(b) $-\gamma\mathbf{B} = [0, 0, \Omega]$ & $\mathbf{M}(0) = [0, M_0, 0]$

(c) $-\gamma\mathbf{B} = [0, 0, \Omega]$ & $\mathbf{M}(0) = [M_1, M_2, M_3]$

4. Answer the following questions. 25 Points

Q1-Q7: 2 point each; Q9: A 6, B5

Q1-Q8. Choose right answers from the multiple choices (not necessarily one.)

Q1 Choose two factors that do NOT affect a signal-to-noise ratio in NMR from the following multiples.

(a) Gyromagnetic ratio (b) Temperature (c) Sample size
(d) Static magnetic field (e) Signal assignment (f) Fourier transform
(g) Relaxation time

Q. 2 ^{1}H natural abundance is (Q3A)% while ^{13}C natural abundance is about (Q3B)%.

(Q3A, Q3B) =

a. (98%, 0%) b. (100%, 10%) d. (98%, 10%) d. (100%, 1%)

Q. 3 J coupling is independent of [Q4A]. Hence, it is constant in a unit of [Q4B] at any MHz.

a. (a static field, ppm) b. (chemical structure, ppm)
c. (static field, Hz) d. (chemical structure)

Q4. Chemical shift is proportional to a static field in a unit of [Q5A], but it is constant in a unit of [Q5B].

a. (ppm, Hz) b. (Hz, ppm) c. (chemical structure, ppm) d. (a static field, Hz)

Q5. Inversion recovery experiment is performed for measuring (Q6) of NMR signals.

(a) T_1, (b) T_2, (c) S_0, (d) S_1

Q6. The rate of the NOE effect is generally proportional to (Q7)

(a) R, (b) R^2, (c) R^3, (d) R^6, (e) R^{-1}, (f) R^{-2}, (g) R^{-3}, (h) R^{-6}, (i) 0, (j) None of (a-i)

where R is the inter-nuclear distance between the nuclei at which spins of interest are located.

Q7. What does "O" of NOE stand for?

(a) Oppenheimer, (b) Opella, (c) Overweiss, (d) None of (a-c)

Q8. Answer the following questions (A: 6points; B:5 points)

A. Explain the principle of Fourier Transform (FT) NMR. (Use at least 3 equations.)

Hint: use terms such as spin, magnetization, equilibrium, RF pulse, excite, free induction decay (FID), time-domain signal, frequency-domain signal, Fourier Transform (FT), spectrum, and bandwidth.

B. Briefly explain principle of cw NMR, and describe major advantage of FT NMR over cw NMR.