4C　機器分析 II　後期期末試験　　No._____　氏名_____

H28/2/16	10:40 – 12:10 (90 分)	問題 4 枚, 解答 4 枚	友野　和哲	A5 用紙･電卓･紙辞書

＊ 計算問題は途中式が記載できるものは記載すること。途中式がないものは減点とする。

1. **Fill in the blanks.**

【A】 analysis I and II are a field of analytical chemistry that investigates analytes using scientific instruments.

Perhaps the most functional definition of analytical chemistry is that it is “the qualitative and quantitative characterization of matter”. The word “characterization” is used in a very broad sense. It may mean the identification of the chemical compounds or elements present in a sample to answer questions such as “Is there any silicon in this shampoo as indicated on the label?” or “Is this piece of metal iron or nickel?” This type of characterization, to tell us “what” is present is called 【B】 analysis. Also, characterization may mean the determination of how much of a particular compound or element is present in a sample, to answer questions such as “How much sugar is in this Valentine’s chocolate cake?” or “How much nickel is in this steel?” This determination of “how much” of a species is present in a sample is called 【C】 analysis.

2. **Fill in the blanks.**

TOF－MS　is a method of mass spectrometry in which an ion’s mass to charge ratio is determined via a time measurement. The ions are accelerated by an electronic field of known strength. Ions are separated in the draft tube according to their velocities. The velocity of an ion, v, can be expressed as following formula;

$$v = \text{【D】}$$

where V is the accelerating voltage, m is the mass of the ion, Ze is the charge of the ion. If L is the length of the field-free drift tube and t is the time from acceleration to detection of the ion (the flight time of the ion in the tube),

$$v = \text{【E】}$$

therefore the flight time, t, of an ion is:

$$t = \text{【F】}$$

the equation can be used to calculate the difference in flight time between ions of two different masses. Actual time separations of adjacent masses can be as short as few nanoseconds, with typical flight times in microseconds.

3. Fill in the blanks.

(a) There is a definite relationship between the peaks at M+1 (【①】 peak) and M(; molecular ion peak) that is directly related to the number of carbons present in hydrocarbon molecules:

$$\frac{M+1}{M} = 1.1\ \% \times \text{number of carbon atoms in the molecule}$$

This relationship is very valuable in characterizing an unknown compound. The calculation just presented is for hydrocarbons (compounds containing only carbon and hydrogen) and ignores the contribution from the ^{2}H isotope (; deuterium) of hydrogen.

For example diethyl ether, in Fig. 1, the molecular ion m/z = 【②】, and the (M+1) m/z = 【③】. The relative abundance of the (M+1) peak is 4.5%; diving 4.5% by 1.1% confirms that there are 【④】 carbons in the molecule. Also, the base peak m/z = 【⑤】 is the most abundant peak in the spectrum.

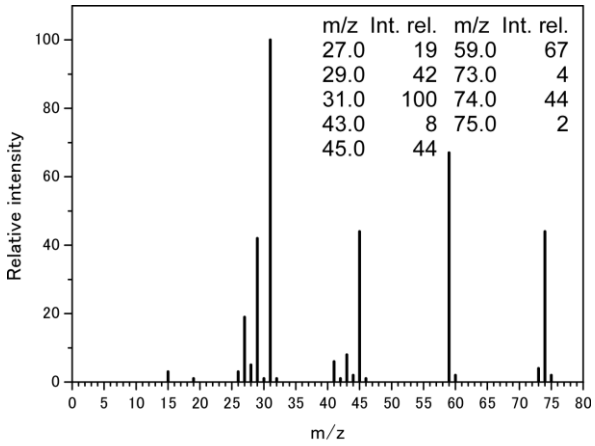
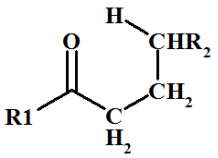


Fig. 1. A mass spectrum

(b) Ketones and aromatic aldehydes show strong molecular ion peaks, while aliphatic aldehydes give a weak but measurable molecular ion peak. Both ketones and aldehydes fragment by alpha cleavage.

A very important fragmentation with rearrangement occurs with aldehydes, ketones, and other classes of compounds. This is the 【⑥】 rearrangement. The ion must be able to form a six-membered cyclic transition state. A transfer of 【⑦; element】 to the oxygen atom occurs and an alkene molecule splits off.



→ 【A】 ＋ 【B】

The rearrangement product detected is the ionic product (an enol) shown; a neutral alkene is also produced. At least one of the alkyl chains on the ketone and the alkyl chain on the aldehyde must have three or more carbon atoms for the 【⑥】 rearrangement to occur. The mass spectrum of 2-pentanone is shown in Fig. 2. The peak at m/z = 【⑧】 is due to the enol type fragment ion of the 【⑥】 rearrangement; ethene (= ethylene) is the neutral alkene that splits off. The peak at m/z = 【⑨】 is due to alpha cleave on the right side of the carbonyl group as the structure is shown in fig. 2 to form (【⑩】)$^+$ or (【⑪】)$^+$; cleaving the bond gives two possible ions with the same m/z value. Alpha cleavage can also occur on the left side, forming $(CH_3)^+$ with m/z = 15 or $(C_4H_7O)^+$ with m/z = 71. Both ions are seen in the spectrum.

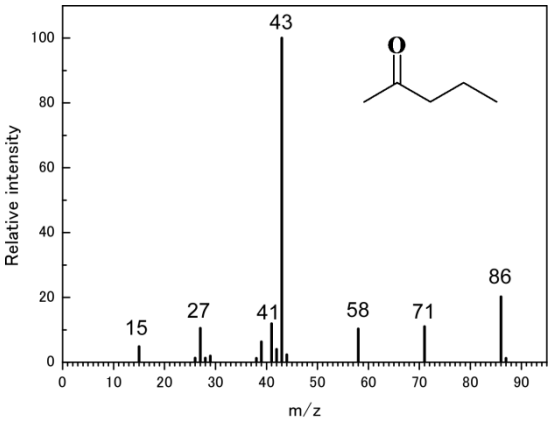


Fig. 2. A mass spectrum of 2-pentanone

4. Fill in the blanks

The Daniel cell is a type of electrochemical cell invented in 1836 by J. F. Daniell. One half-cell consists of a solid copper electrode immersed in an aqueous solution of copper sulfate, the other has a solid zinc electrode immersed in an aqueous solution of zinc sulfate. The two half-cell reaction and the net spontaneous reaction are shown the following;

Anode reaction: ①

Cathode reaction: ②

Net reaction: ③

The standard cell potential (E^0_{cell}) developed is calculated from the table of standard potentials.

E^0_{cell} = ④

Table. Selected standard reduction potentials

Redox equation	E^0 (V)	Redox equation	E^0 (V)
$Na + e^- = Na$	−2.7	$Cu^{2+} + 2e- = Cu$	+0.33
$Zn^{2+} + 2e- = Zn$	−0.76	$O_2 + 4H^+ + 4e^- = 2H_2O$	+1.2
$2H^+ + 2e- = H_2$	0.000	$S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$	+1.9

5. 以下の問いに答えなさい。

Shown in the following figure are the TG (solid line) and the DTA (dotted line) curves for copper sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$. Copper(II) sulfate pentahydrate decomposes before melting at 150°C, losing two water molecules at 60-80°C, followed by two more at 80-105°C and the final water molecule at 250-260°C. Dehydration proceeds by decomposition of the tetraaqua-copper(II) moiety, two opposing aqua groups are lost to give a diaqua-copper(II) moiety. The second dehydration step occurs with the final two aqua groups are lost. Complete dehydration occurs when the only unbound water molecule is lost. At 650°C, copper(II) sulfate decomposes (thermal decomposition) into X1(solid) and X2(gas). X2 is a significant pollutant, begin the primary agent in acid rain.

(Atomic weight; hydrogen 1.00, oxygen 16.00, copper 63.54, sulfur 32.10)

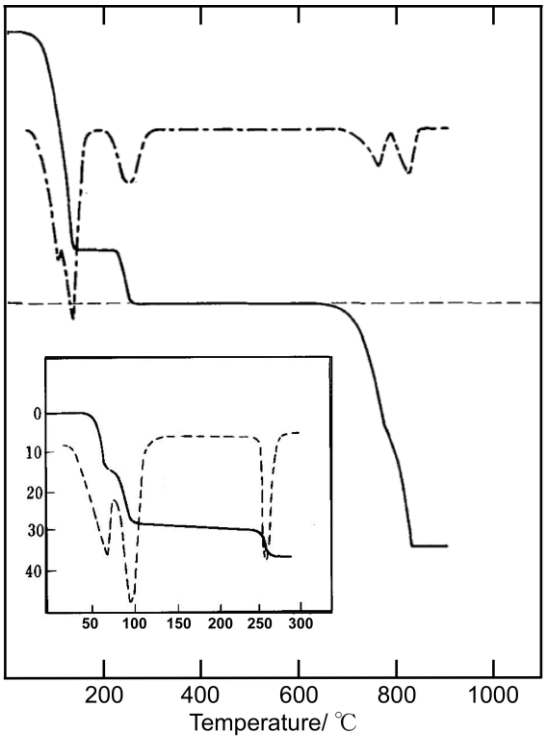


Fig. 3. TG and DTA curves of $CuSO_4 \cdot 5H_2O$ in 100 mL/min air flow

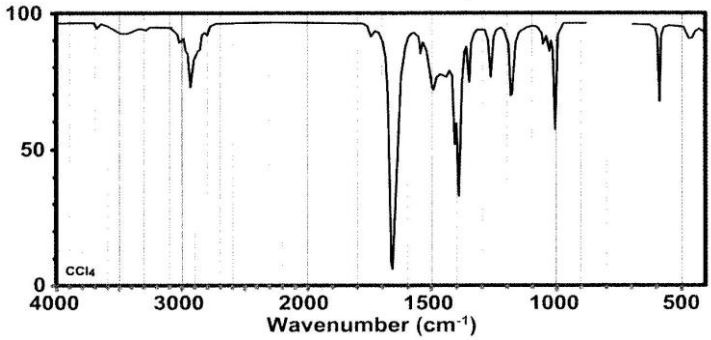
(a) 0℃～300℃において，観測される３つの吸熱反応に対応する重量減少(%)を算出しなさい。

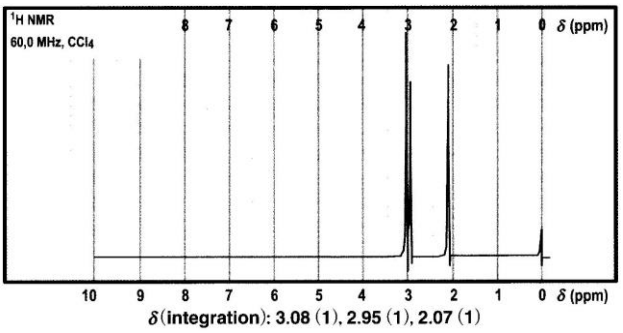
(b) 500℃以上において，二つの吸熱反応が観測される。重量減少率は，それぞれ 32.74%と 32.74%であった。反応式を答えなさい。

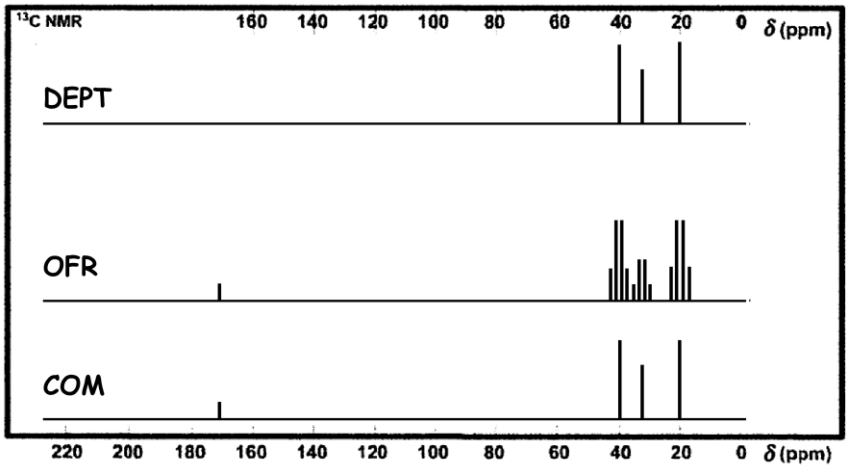
＊縦軸のスケールは中央の点線で変化します。よって，(a)と(b)の値は，比較できません。

6. Explain the principle of MALDI method by using the following words ①～⑤. (; MALDI 法の原理について，以下の語句①～⑤を用いて説明しなさい。）
（① MALDI 法の正式名称は，②グリセロールとコバルト，③窒素レーザー，④熱，⑤田中耕一）

7. Identify the following compound from their IR, NMR, MS spectra and the data provided.
Hint: The “Nitrogen rule” can be used to help decide if a peak is molecular ion peak. Because of the atomic weights and valences of elements commonly present in organic molecules, it transpires that the m/z value of the molecular ion is always an even number if the molecular ion contains either no nitrogen atoms or an even number of nitrogen atoms. If the molecular ion contains an odd number of nitrogen atoms, the m/z value must be an odd number. (Atomic weight; nitrogen 14.00)
*各スペクトルの解釈が正しければ，部分点を与えます。







δ: 170.49, 38.00, 35.03, 21.51