THE OPEN UNIVERSITY OF SRI LANKA

BSc Degree Programme/ Stand Alone Courses in Chemistry

Level 5- Home Assignment II- 2019/2020

CYU5308- INSTRUMENTAL METHODS OF CHEMICAL ANALYSIS

ANSWER GUIDE

1.(a) Predict the elution order of the following in normal phase and in reverse phase chromatography: (i) n-heptane, heptanol, and toluene.
(ii) nitrobenzene, benzene and phenol
Give reasons for your answer. (20 marks)

In normal phase column chromatography, a polar stationary phase and a nonpolar mobile phase is used. Least polar compound binds least strongly to the stationary phase, so eluted first/moves fast; on the contrary, in reverse phase chromatography, stationary phase is nonpolar and mobile phase is polar. Here most polar compound is eluted first.

Order of polarity (i) n-heptane < toluene < heptanol
(ii) benzene < nitrobenzene < phenol

Elution order- Normal phase

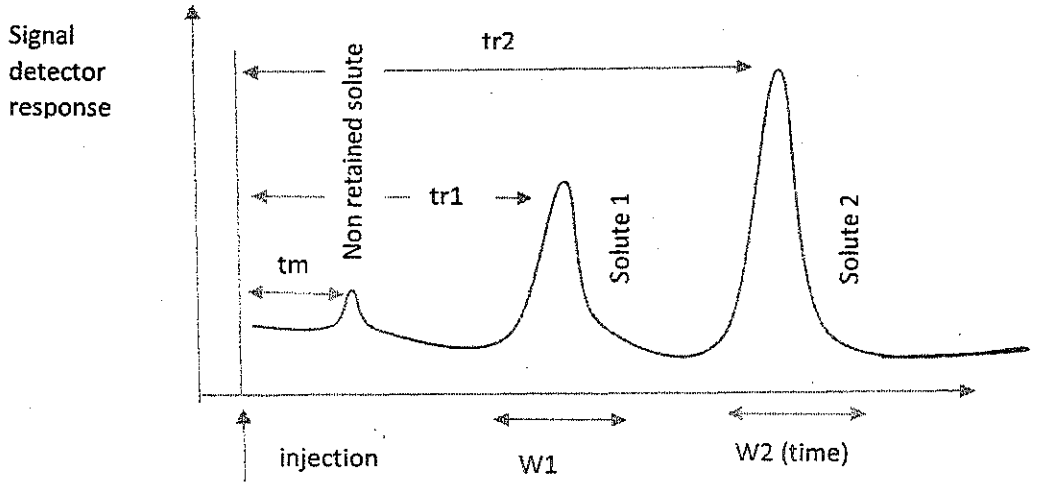
(i) n- heptane > toluene > heptanol
(ii) benzene > nitrobenzene > phenol

Reverse phase

(i) heptanol > toluene > n-heptane
(ii) phenol > nitrobenzene > benzene

(b) Heptane and toluene were separated with retention times of 15.4 and 16.5 min respectively on a 1.0 m packed column. An unretained species passed through the column in 1.8 min. The peak widths measured at the base were 1.15 min and 1.20 min for heptane and toluene respectively.

(i) Draw and label the chromatogram. What is the significance of t_o in gas chromatography?



t_m is the dead (or void) time; it is the time the void volume takes to pass through the column

(ii) Calculate:

(α) The resolution between the peaks.

$$R = \frac{2(16.5-15.4)}{1.15+1.2} = 0.94$$

(β) The average number of plates for the column.

$N = 16(15.4/1.15)^2 = 2869$ for heptane

$N = 16\,(16.5/1.2)^2 = 3025$ for toluene

$$N_{average} = \frac{2869+3025}{2} = 2947$$

(γ) The average plate height. (30 marks)

$$H = \frac{L}{N} = \frac{1.0\times10^3\,mm}{2869} = 0.35 \text{ mm for heptane}$$

$$H = \frac{1.0\times10^3\,mm}{3025} = 0.33\,mm \text{ for toluene}$$

$H_{average} = 0.34$ mm

(c) A sample of pesticide is analyzed by gas chromatography. A 0.1 ml injection of a standard containing 0.234 mg/L gives a peak of area 34873. The same size injection of an unknown sample solution gives an area of 39945. What is the concentration of the pesticide in the sample solution? (15 marks)

peak area α concentration

peak area = K x concentration; concentration of pesticide in unknown sample is x

$$\frac{39945}{34873} = \frac{x}{0.234}$$

$$x = \frac{39945}{34873} \times 0.234\,mg/L$$

(d) (i) What are some of the properties of a good chromatographic detector?

High sensitivity; linear dynamic range of 4 orders of magnitude or more; favorable signal to noise ratio; good long term stability; a small detector dead volume is also important

(ii) Briefly describe how the electron capture detector (ECD) functions

A diagram can help explanation.

When only the carrier gas (N_2, Ar) flows into the ECD, it is exposed to a radioactive source (^{63}Ni) which gives off β particles (fast moving electrons) which ionize carrier gas giving electrons, A steady current passes between electrodes. When a carrier gas contains a component (organic molecule with an affinity for electrons), they capture electrons. In the presence of a component, current is reduced. Reduced current is recorded as a signal.

(ii) What is the advantage in using the ECD in environmental analyses?

(35 marks)

ECD is sensitive to electrophilic organic molecules (halogenated and S-containing compounds, poly nuclear compounds). Ttherefore widely used to detect trace pollutants in the environment (insecticides and pesticides) Added advantage is sample is no destroyed.

2.(a) Write nuclear equations for the following radioactive decays:

$^{238}_{92}u \longrightarrow {}^{4}_{2}\propto + {}^{234}_{90}Th$

$^{131}_{53}I \longrightarrow {}^{0}_{-1}\beta + {}^{131}_{54}Xe$

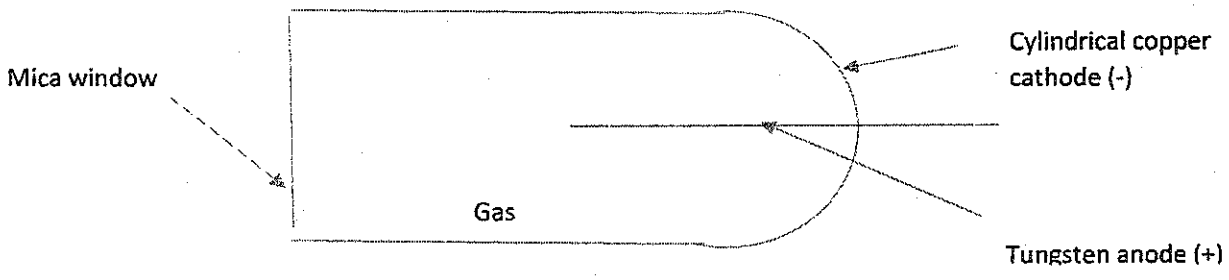
$^{11}_{6}C \longrightarrow {}^{0}_{+1}\beta + {}^{11}_{5}B$

$^{7}_{4}Be + {}^{0}_{-1}e \longrightarrow {}^{7}_{3}Li$ (12 marks)

(b)(i) Briefly explain the principle behind Gas Ionization detectors for measuring radiation.

Radiation enters a chamber filled with a gas (Ar, CH_4) at low temperature through a "mica" window. When ionizing radiation passes through the gas, ions and electrons (ion pairs) are formed. They travel towards electrodes of opposite charge, resulting in a current. Thus, every time radiation enters the chamber, a brief current (pulse) flows in the external circuit.

(ii) Draw a schematic diagram of a Geiger Müller counter and briefly explain how radiation is detected by this counter.



Radiation enters through the mica window, collides with gas atoms/moles, ionize them- primary electrons are produced which are accelerated towards the strong electrodes. The energetic electrons collide with other gas molecules creating further electrons (secondary), thus the cascade of ions and electrons create a pulse of current which can be counted.

(iii) Compare and contrast the Geiger Muller Counter and the Gas Flow counter.

(48 marks)

GM counter	Gas flow counter
Simple and effective	Expensive
Only high energy β and low energy γ and x-ray are determined; α and slow β particles cannot pass through the mica window; therefore not determined	α and slow β particles can be determined
Cannot distinguish between radiation of different energies	Can get some idea of energy of each particle/ ray

(c) Briefly describe how neutron activation analysis (NAA) is used in both qualitative and quantitative analyses. (20 marks)

The element present in a sample are activated or made radioactive by irradiating with neutrons; stable target nuclei capture neutrons and give radioactive isotopes, which decay, giving off γ radiation of energy characteristics of the emitting isotope- can be used is identify isotope (qualitative).

By counting the emitted radiation we can determine the number of radioactive nuclei formed, which is proportional to the amount of original element present in the sample (quantative)

(d) In an isotope dilution analysis of a fertilizer sample for arsenic, 40.00 mg of $^{76}_{33}As$ with an activity of 1200 cpm was added to a 1.00 g of the fertilizer sample. After mixing, 20 mg of arsenic was isolated and purified. The activity measured using a Gas Ionization detector was 400 cpm.

(i) Briefly explain the principle behind isotope dilution analysis.

To determine the unknown mass (m_x) of analyte in a mixture (without completely isolating in pure form), a tracer (radioactive form, R_t) of analyte (m_t) is added to the mixture. Tracer becomes evenly distributed (homogeneously) within the analyte. From the counting rate (R_s) of a small amount (m_s) of pure analyte separated, mass of unknown (m_x) is determined.

$$\frac{R_s}{R_t} = \frac{m_s}{(m_x + m_t)}$$

$$m_x = \frac{R_t}{R_s} m_s - m_t$$

(ii) Calculate the weight of As in the original sample. (20 marks)

$$m_x = \frac{1200}{400} \times 20 - 40\ mg$$

m_x = 60-40 mg = 20 mg

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