THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme
Level 5 –CYU 5302–ANALYTICAL CHEMISTRY
FINAL EXAMINATION PAPER 2020/21

Date: 2020.12.23 Duration: Two hours
Time: .1.30 p.m. – 3.30p.m.

Instructions to students

This question paper consists five pages having four questions. Answer all four questions.

1. A student was given a sample solution having 0.10 M of each ion X^{2+} and Y^{2+}. He was asked to confirm the concentration of Y^{2+} using Gravimetry by precipitating Y^{2+} as $Y(OH)_2$ with the base $B(OH)_2$. Both X^{2+} and Y^{2+} reacts with the base.

   Ksp of $X(OH)_2 = 4.0 \times 10^{-3}$ mol^3L^{-3}.
   Ksp of $Y(OH)_2 = 1.0 \times 10^{-9}$ mol^3L^{-3}.

   (i) Advise him on the following giving reasons.
   (a) Addition of $B(OH)_2$ to the sample solution.
   (b) Washing the precipitate
   (c) Drying the precipitate (30 marks)

   (ii) Do you think that selective precipitation of Y^{2+} is possible? Explain your answer. (10 marks)

   (iii) Calculate the pH of the solution at which selective precipitation of the maximum Y^{2+} amount is possible. (15 marks)

   (iv) The base $B(OH)_2$ (20.0 mL) was standardized with 0.02 M HCl solution using phenolpthalein as the indicator. The end point obtained was 20.00 mL.
   ($K_{b1} = 6.5 \times 10^{-1}$ mol L^{-1}, $K_{b2} = 1.5 \times 10^{-5}$ mol L^{-1})
   (a) Sketch and explain the titration curve of $B(OH)_2$ and 0.02 M HCl. (15 marks)
   (b) Calculate the concentration of $B(OH)_2$. (10 marks)

   (v) Comment on the following statements.
   (a) Precipitation of $Y(OH)_2$ can be obtained with lesser amount of $B(OH)_2$ if the sample solution was at a higher pH compared to a sample solution at a lower pH.
   (b) The minimum detection limit of gravimetric analysis can be improved if the molecular weight of the precipitate is increased. (20 marks)

2. (i) A sample solution having a trace amount of MZ (a strong electrolyte) was analyzed for Z^- by carrying out a photometric titration with a standard solution of R which is a chelating agent. The reaction of MZ and R is as follows:

Z^- (aq) + R(aq) → Q (aq)

Compound/ion	Λ_{max} (wavelength of maximum absorption) (nm)	Molar absorptivity coefficient ($mol^{-1}Lcm^{-1}$)
Z^- (aq)	510	5.32×10^8
R(aq)	210	1.35×10^4
Q (aq)	512	3.34×10^6

(a) At what wavelength will you carry out the photometric titration? Justify your answer. (10 marks)

(b) Sketch the titration curve accordingly (assuming that there is no dilution error). (10 marks)

(c) Suggest a chemical method to have a higher absorbance value for R(aq). (10 marks)

(d) Do you think a classical titration can be carried out between the above Z^- (aq) and R(aq)? Give reasons for your answer. (10 marks)

(ii) A 0.01 M solution of MZ gave a 30% transmittance at 510 nm. To a 50.0 mL sample solution having MZ, a 50.0 mL of H^+ just enough to complete the formation of the weak acid HZ ($K_a = 3 \times 10^{-4}$) was added. The resultant solution gave an absorbance of 0.250 in similar conditions of measuring the transmittance. Calculate the concentration of MZ in the sample solution. (20 marks)

(iii) A conductometric titration was carried out for 20.0 mL of 0.01 M the same MZ with 0.01 M HCl solution.

Ion	Molar conductivity at 25°C ($\Omega^{-1}cm^2mol^{-1}$)	Ion	Molar conductivity at 25°C ($\Omega^{-1}cm^2mol^{-1}$)
M^+	45.6	H^+	349.8
Z^-	75.9	Cl^-	76.1

(a) Plot and explain the titration curve (assuming that there is no dilution error) (20 marks)

(b) In real conditions, the titration curve will not be linear due to dilution error. Suggest ways to improve the linearity. (10 marks)

(c) State two differences between conductometric titrations and photometric titrations. (10 marks)

3. (i) A sample solution was having Q^{2+}, T^{2+} and A^{2+} metal ions. The concentrations of T^{2+} and A^{2+} were the same. The following titrations were carried out for the solution:

Titration I

A 25.0 mL of a sample solution was titrated with 0.02 M EDTA solution at pH 9. The end point reading was 40.00 mL.

Titration II

Then to the same sample solution, an excess amount of 0.01 M NaF was added and the titration was carried out with 0.02 M X^{2+} solution at pH 9. The end point reading was 25.00 mL. The following information are available.

Metal-EDTA complex	K_{MY} *(at 0.1 ionic strength)*	pH range at which the complex exists	α_{Y4-} at the existing pH range	α_M at the existing pH range
QY^{2-}	5.1×10^{16}	7-9	5.2×10^{-2}	3.1×10^{-2}
TY^{2-}	3.3×10^{15}	7-9	5.2×10^{-2}	1
AY^{2-}	2.5×10^{15}	3-5	2.3×10^{-4}	1
XY^{2-}	3.0×10^{12}	7-9	5.2×10^{-2}	1

$TY^{2-} + NaF \rightarrow TF_2 + Y^{4-} + Na^+$

(a) In the titration I, which will react first with EDTA? Give reasons for your answer. (10 marks)

(b) Calculate the concentration of all three ions stating the assumptions made. (25 marks)

(c) If NaF is not available in the lab, suggest a method briefly with calculations to find the concentration of all three ions. (10 marks)

(d) The pH was maintained at 9 using a buffer. Calculate the concentration of HCl solution to be added to a 80.0 mL of a 0.1 M weak base solution, DOH (pK_a= 8.00) to prepare 100.0 mL of a buffer of pH 9. (15 marks)

(ii) To a 25.0 mL of a sample solution, having Q^{2+} (0.01M) and T^{2+}, a redox titration was carried out with a strong oxidizing agent E^{4+} (0.01 M) using a suitable indicator. The end point obtained was 30.00 mL.

$Q^{2+} \rightarrow Q^{4+} + 2e$ ($E^\circ = +1.61$ V)

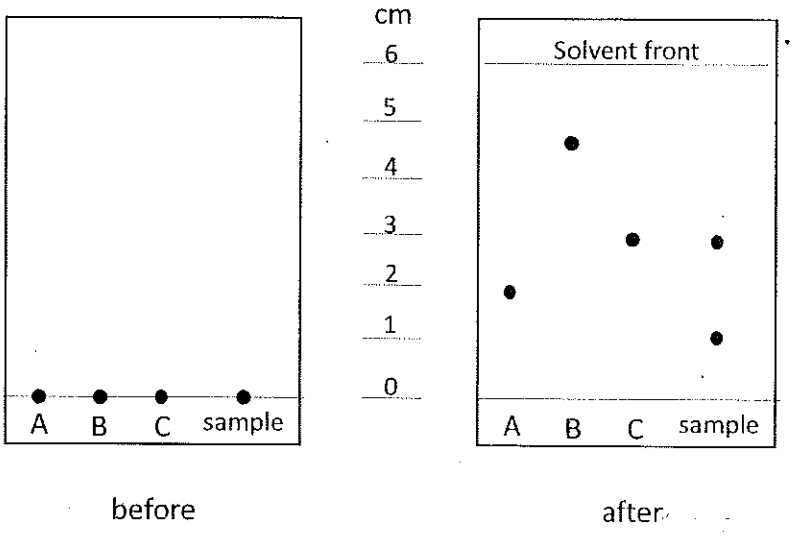
$T^{2+} \rightarrow T^{4+} + 2e$ ($E^\circ = +1.36$ V) $\qquad E^{4+} \rightarrow E^{2+} + 2e$ ($E^\circ = +2.00$ V)

(a) Sketch and explain the titration curve according to the expected observations. (15 marks)

(b) Calculate the concentration of T^{2+}. (15 marks)

(c) If the above titration was a potentiometric titration, what differences Would you have observed? (10 marks)

4. (i) It was suspected that a particular mixture of chemicals contained three components: A, B, and C. To check this, the mixture was analyzed by thin layer chromatography (TLC). In this experiment a nonpolar solvent was used with a polar stationary phase and the following results were obtained when the sample was chromatographed along with the standards:



(a) Which suspected components (out of A, B and C) are present in the mixture? (20 marks)

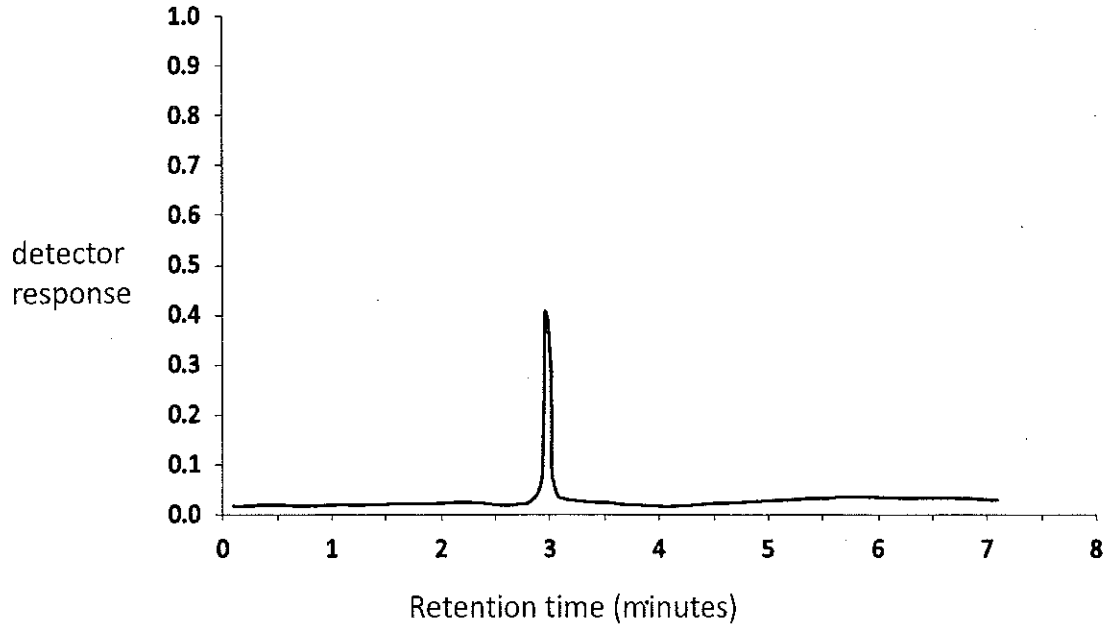
(b) Are there other components in the sample? (10 marks)

(c) What is the R_f value of the unidentified component? (10 marks)

(d) Which of the suspected components is the most polar? and least polar? (20 marks)

(e) What type of TLC is this? (10 marks)

(ii) High-performance liquid chromatography (HPLC) was used to determine the amount of caffeine in a sample of a soft drink. The chromatogram below shows the detector response when a standard solution of caffeine with a concentration of 200 mg L^{-1} is measured using the instrument.



(a) What is the retention time of caffeine in this experiment? (10 marks)

(b) On the chromatograph above, sketch the detector response when a commercial soft drink with a caffeine content of 350 mg L-1 is measured using the same instrument?

(20 marks)