



THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 –Continuous Assessment Test– 2011 / 2012

1

CMU 3123/CME 5123 – Analytical Chemistry

Duration: One and half hours

Date and time: 25th September, 2011 from 4.00 p.m. to 5.30 p.m.

Reg. No.....

Question number	Max. marks	marks
1	50	
2	24	
3	26	
Total		

Instructions to students

Answer all questions in the spaces given. Additional sheets will not be marked.

(1). A random sample of well water from Anuradhapura area was analyzed for Mg^{2+} by titrating 25.0 cm^3 of the sample solution with 0.02 M EDTA at $\text{pH} = 9$ using Eriochrome Black T as the indicator.

(i) How do you prepare a random water sample from a well? (05 marks)

(ii) Why did you maintain the pH at 9? (03 marks)

(iii) This titration was repeated five times and the readings obtained were $15.60, 15.65, 15.55, 15.60$ and 18.00 cm^3 .

(a) Can you reject the result 18.00 cm^3 statistically? (for 5 observations $Q = 0.717$ at $p = 0.5$) (show all the steps clearly)

(10 marks)

(b) Why do you reject any outliers in a set of results? (02 marks)

(c) Considering the decision made in (iii) (a), calculate the concentration of Mg^{2+} in the sample. Show all the steps clearly.

(05 marks)

(iv) Another student commented saying that the results are not reliable since background interference is not eliminated.

(a) What is meant by background interference in this experiment? (02 marks)

(b) Suggest a method to eliminate background interference. (03 marks)

(v) (a) Derive an equation to show the relationship between the formation constant and the conditional formation constant of a metal EDTA complex.

(08 marks)

(b) Calculate the conditional formation constant of Mg- EDTA complex at pH 9. ($\log K_{MY} = 8.7$, at pH 9 $\alpha_{Y4-} = 5.2 \times 10^{-2}$, $\alpha_{Mg^{2+}} = 2.0 \times 10^{-4}$)

(04 marks)

- (vi) Give two significant differences between acid- base titration and complexometric titrations.

(08 marks)

2. An analyst was given an impure salt of barium (1.000g) to analyze the amount of barium in it. He decided to do a gravimetric analysis by precipitating barium with 0.01 M potassium chromate solution.

- (i) Give two important parameters that should be satisfied in order to do a gravimetric analysis.

(04 marks)

- (ii) Write two important practices he should follow in order to filter the precipitate easily.

(04 marks)

- (iii) The weight of the precipitate obtained was 0.6940g. Calculate the percentage of barium in the sample. (Ba = 137.3g, Cr = 52.0g, O = 16.0g)

(10 marks)

- (iv) Although it was found that lead was also present in the barium salt as an impurity, lead chromate precipitate was not formed until the barium chromate precipitation was completed.
- (a) What could have been the reason for not getting the barium chromate precipitate? (K_{sp} of barium chromate at 25° C = $1.7 \times 10^{-10} \text{ mol}^3 \text{ dm}^{-9}$, K_{sp} of lead chromate at 25° C = $1.8 \times 10^{-14} \text{ mol}^3 \text{ dm}^{-9}$)

(02 marks)

- (b) Considering the information given in question 2 part (iv), suggest a method that can be used to analyze the amount of lead present in the sample giving the reason for selecting that method.

(04 marks)

3. An aqueous solution mixture having X^{3+} and Y^{2+} was titrated with a standard solution of Z^{2+} .
($E_{X^{3+}/X^{2+}}^\circ = 0.20 \text{ V}$, $E_{Y^{3+}/Y^{2+}}^\circ = 0.30 \text{ V}$, $E_{Z^{2+}/Z^\circ}^\circ = 1.02 \text{ V}$)

- (i) Which will be oxidized by Z^{2+} first? Why?

(04 marks)

(ii) Sketch and label the expected titration curve.

(10 marks)

(iii) Out of the following redox indicators, which can be used for this titration?
Give reasons for your answer.

Diphenylamine - $E_m^\circ = 0.76 \text{ V}$ Ferroin - $E_m^\circ = 1.06 \text{ V}$

(04 marks)

(iv) Give two differences of redox titrations when compared with acid base titrations.

(08 marks)

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 CMU 3123 - Assignment Test I
Answer Sheet

1. (i) Collect water samples from different levels (surface, middle and bottom) of different wells in different areas of Anuradhapura. Then either mix and take a sample for the analysis or analyse separately and average the results.

(ii) To make EDTA selective for Mg^{2+}

(iii) (a) Q Test for the result 18.00cm^3

$$Q_{\text{cal}} = \frac{\text{Suspected value} - \text{Nearest Neighbor}}{\text{Range}} = \frac{(18.00 - 15.65)}{(18.00 - 15.55)} = \frac{2.35}{2.45} = 0.959$$

$$Q_{\text{calculated}} > Q_{\text{critical}} \\ 0.959 > 0.717$$

Therefore we can reject the result 18.00 cm^3 at 95% confidence level. (P=0.5)

(b) To improve precision.

(c) Average burette reading of four results = 15.60cm^3

Number of moles of EDTA reacted = $(0.02 \times 15.60) / 1000$

EDTA: Mg^{2+} = 1:1

Number of moles of Mg^{2+} reacted = $(0.02 \times 15.60) / 1000$

Concentration of Mg^{2+} = $\frac{0.02 \times 15.60 \times 1000}{1000 \times 25.0} = 0.012M$

(iv) (a) The analyte response is either hindered or enhanced by the presence of other ions in the sample solution.

(b) Addition of masking agents or standard addition method

(v) (a) $M^{n+} + y^{4-} \leftrightarrow MY^{n-4}$

$$K_{\text{my}} = \frac{[MY^{n-4}]}{[M^{n+}][y^{4-}]} \\ \alpha_{M^{n+}} = \frac{[M^{n+}]}{[M']} \quad \alpha_{y^{4-}} = \frac{[y^{4-}]}{[y']}$$

$[M']$ = Concentration of all forms of metal ion except those which complexed with EDTA

$[y']$ = Concentration of all forms of EDTA except those which complexed with metal ion.

$$K_{\text{my}} = \frac{[MY^{n-4}]}{\alpha_{M^{n+}} [M'] \alpha_{y^{4-}} [y']} \\ K_{\text{my}} \cdot \alpha_{M^{n+}} \cdot \alpha_{y^{4-}} = \frac{[MY^{n-4}]}{[M'] [y']} = K'_{m'y'}$$

(b) $K'_{\text{my}} = K_{\text{my}} \alpha_{M^{n+}} \alpha_{y^{4-}} = 5.1 \times 10^8 \times 5.2 \times 10^{-2} \times 2.0 \times 10^{-4} = 5.2 \times 10^3$

(vi)

Acid – base titrations	Complexometric titrations
Selectivity-low	High
Indicators-acids or bases	Metal ion indicators
Use to determine the $[H^+]$ or $[OH^-]$	$[M^{n+}]$
Variable-pH or $[H]^+$	pM or metal ion concentration

2. (i) The precipitate
1. should have a low solubility.
 2. should be able to wash and filter easily.
 3. should be able to get in pure form.
 4. should have a constant stoichiometry or molecular formula.

- (ii)
1. Add dilute solutions
 2. Stir while adding the precipitating agent.
 3. Add the precipitating reagent drop wise.
 4. Allow the precipitate to form at high temperature.
 5. Apply the method "Precipitation from homogeneous solution" (PFHS) if possible.

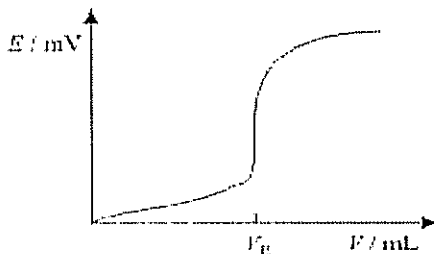
(iii)

Molecular weight of BaCrO ₄	= 253.3 g
No of moles of BaCrO ₄	= (0.694 / 253.3) mol
No of moles of Ba in it	= (0.694 / 253.3) mol
Weight of Ba	= 137.3 x (0.694 / 253.3) g
Percentage of Ba present	= $\frac{37.3 \times (0.694 / 253.3)}{1.000} \times 100 \%$
	= 37.6 %

- (iv)
- (a) Since there is an error in the part (a), marks allocated for part (a) was added for part (b).
 - (b) Any instrumental method with high sensitivity and low minimum detection limit.

3. (i) X³⁺
- The reducing agent having a low formal potential will be oxidized first. Therefore, X³⁺ has the highest tendency to be oxidized and will be oxidized first. Here, the oxidation of Y²⁺ will start before the oxidation of X³⁺ is over since the difference of the two redox couples, (Z²⁺ and X³⁺, Z²⁺ and Y²⁺) is less than 0.4 V.

(ii)



- (iii) Diphenyl ammine.
- E°_{in} of Diphenyl ammine falls between the E° values of the analyte ion (Y⁺³/Y⁺²) and the titrant (Z²⁺/Z⁺).

(iv)

Acid – base titrations	Redox titrations
Selectivity-low	Comparatively high
Indicators-acids or bases; no self indicators used.	Redox indicators; self indicators also can be used.
Use to determine the [H ⁺] or [OH ⁻]	Use to determine the [M ⁿ⁺]
Variable-pH or [H ⁺]	Variable-E _{cell}
One product is always water (H ₂ O)	The products are reduced and oxidized species.