Write the answers at the back of the page unless space is provided

You are provided with the following :
A burette (50 ml ±0.05), a pipette (25 ml), volumetric flasks (500 ml), a funnel, filter papers, phenolphthalein, Analytical balance, Pure water

<u>PART ONE :</u>
In a rainy day, a truck carrying dichloroacetic acid ($Cl_2CHCOOH$) ran over the road and spilled part of its load over a cultivated land. The land turned muddy and it was decided to measure the acidity of the soil in order to raise its pH.
**The acid is assumed to behave as a strong acid**
a) With the apparatus provided above, describe how can you determine the amount (in moles) of acidity per 100g of soil (Max. 7 statements).

b) If the concentration of a standardised titrant NaOH (aq) is 0.0012 M, and the table of results obtained for a particular batch of mud (ClAc-1) of Weight = 211.26 g is :

TABLE - 1

2nd Reading-ml	7.75	14.30	20.90	27.35
1st Reading-ml	0.40	7.75	14.30	20.90
Vol. Titrant -ml				

i) Calculate the error propagated as you determine the average volume of the titrant ?
ii) Calculate the % by wt. of the acid in the mud using batch (ClAc-1) ? (Don't miss the stoichiometric eq.) ?

c) To assign a pH for the soil, a batch of mud of weight 115.87g was taken and dried in an oven.
i) What is the purpose of this drying procedure?
_____

ii) After drying and in order to determine the % by weight of water to mud the next step is to_____

iii) If the % by weight of water to mud is 35%, calculate the pH for the batch of soil,in part (b) ,i.e. (ClAc-1) ?

d) A bicarbonate solution [NaHCO$_3$ = 1.12 g/l] was used to neutralise the acid in the soil.

i) Calculate the volume of the bicarbonate solution required to neutralise the acid in the batch of mud (ClAc-1) ? (Don't miss the stoichiometric eq.)

ii) After sampling a large number of batches taken from different locations, a graph is plotted as shown in [fig-1]. For practical reasons, the batch of mud (ClAc-1)

Fig - 1
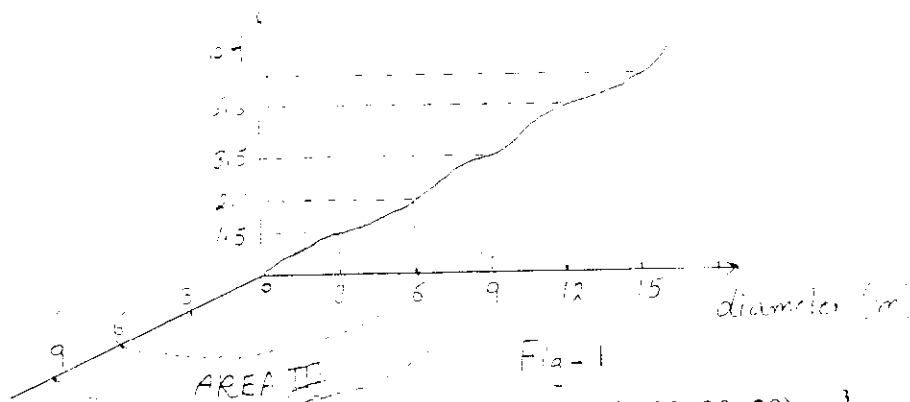
of a size of 100 cm^3 was taken from a larger cubical batch (20×20×20) cm^3 sampled from AREA III. Can you give an estimate of the volume of the bicarbonate solution required to neutralise the acid in AREA III ? Area of a circle = Πr^2 .

PART TWO :

A mixture of oxide salts PbO, Ag$_2$O, CuO and ZnO are mixed with silica. It is agreed that using a proper acidic solution the following general reaction can occur:

$$MO(s) + H^+ (aq) \rightarrow M^{n+} (aq) \quad \text{except for silica.}$$

Consider the following information:
a) Y^{2-} is known to chelate only to Zn^{2+} or Cu^{2+}, but the complex ZnY is more stable than CuY using buffer 'A' at pH = 10.
b) An indicator molecule T forms a complex only with Zn^{2+} which is less stable than Zn-Y complex where : Zn^{2+} (Orange) + T^{2-} → Zn-T(Green)
c) W^{2-} ,known to chelate to Cu^{2+} and Pb^{2+} , form the complexes CuW and PbW that are UV-Visible active and soluble in organic solvents.The complexes show the characteristics that appear in [fig-2],
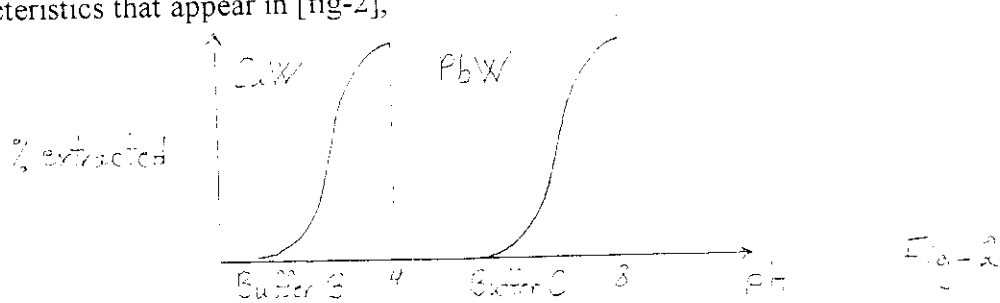
And their distribution coefficients are:
For CuW Korg/aq = 13.04,   for PbW Korg/aq = 8.15

d) No chelating agent is provided for Ag⁺ ions. Silver can be quantitatively determined by depositing the Ag⁺ ions on a clean weighed Pt electrode using an electrochemical cell.

Questions :

1) What technique is used to separate silica from the soluble salts ?
_____

2) For the extraction of *copper ions* the following were mixed :
a) 25 ml withdrawn from the salt solution mixture.
b) 10 ml of a buffer
c) 25 ml of a chelating agent.
d) 40 ml of distilled water.
e) 92 ml of CCl_4 divided into *four* portions.

i) Name the piece of glassware where these reagents are mixed ?
_____

ii) In part(b) which one of the above buffers is used ?
_____

iii) In part(c) which one of the above chelating agents is used ?
_____

iv) Calculate the % of copper extracted into the CCl_4 solvent ?
v) By referring to the table shown below, determine the concentration of copper[in ppm] in the original sample, knowing that :

a) Standard $[Cu^{2+}] = 5.65 \times 10^{-3}$ M.
b) The volume of extracts taken from this standard solution are 15 ml,25 ml and 35 ml respectively for photometric studies.
c) The organic extracts are transferred to a 100 ml volumetric flask.

TABLE-2

Mixture	Volume of Extracts	Absorbance
Standard 1	15.00 ml	0.48
Standard 2	25.00 ml	0.81
Standard 3	35.00 ml	1.13
Reference	-	0.00
Unknown (1ˢᵗ run)	25.00 ml	0.65
Unknown (2ⁿᵈ run)	25.00 ml	0.63

(**Should plot a graph and everything that goes with it**).

vi) At this stage, which metallic ions are left in the aqueous phase ?
_____

vii) Following the above scheme (i.e. (a)…(e)), what modification is done in order to extract another metallic ion ? Name this metallic ion ?

3) Having extracted the 2nd ion, which metallic ions are left in the aqueous phase ?

_____.

4) One of these metallic ions can be quantified using the other chelating agent. Name the titration method used in this case ?

_____

i) Write down the chemical reaction that occurs long before the end point, indicating the color of the solution ?

_____.

ii) Depict the chemical reaction that occurs right at the end point, indicating the change in color ?

_____.

iii) At the end point there is a neutral chemical species and a charged one, name them ?

_____

5) Electric currents do not affect the neutral species, but the charged one gets reduced to free metal.
i) Write down the half reaction ?

_____.

ii) By picking up the right standard electrode potential from table-3, calculate the Nernst potential at a concentration of $[M^{q-}] = 10^{-4} M$?

TABLE-3

Reaction	E 0 (V) vs SHE
$Zn^{2+} + 2e- \rightarrow Zn^{0}$	-0.763
$Pb^{2+} + 2e- \rightarrow Pb^{0}$	-0.126
$Cu^{2-} + 1e- \rightarrow Cu^{-}$	+0.167
$Cu^{2-} + 2e- \rightarrow Cu^{0}$	+0.337
$Cu^{+} + 1e- \rightarrow Cu^{0}$	+0.521
$Ag^{-} + 1e- \rightarrow Ag^{0}$	+0.799

Please write your answer in this space :

4

6) Using an ammeter the current was measured against time and the results shown in table-4 were obtained.

TABLE - 4

Time (seconds)	Current (Amps)
0	1.20
5	1.15
10	1.05
15	0.85
20	0.65
25	0.50
30	0.35
35	0.25
40	0.15
45	0.10
50	0.05
55	0.02
60	0.00

i) What makes the current goes to zero as time goes to infinity ?

_____

ii) If you plot Current (I) vs Time (t) a nearly decaying feature is obtained. Connect the data points by straight lines. Calculate the area of the individual trapezoids, then find their summation. Their summation $(I \times t)$ represents the

_____

If the amount (in moles) of M^{q-} deposited is determined using $n = (I \times t) / (q \times F)$
Where, $F = 96485$ C,
and   q   is the number of e- in a half reaction

iii) Calculate the concentration of M^{q-} in the original solution ?