Problem 28: Identification of Unknown Solid Samples

There are 12 unknown solid samples in vials numbered A01 to A12 on your table. Each vial contains about 100 mg of crystals or powder of one pure compound. The unknown samples are as following:

$NaCl$	$CdSO_4$	$Pb(NO_3)_2$	$Ba(OH)_2$	$Na_2S_2O_3$
$BaCl_2$	$FeSO_4$	KI	$NaHCO_3$	NH_4SCN

Note: (1) There are two duplicated unknown samples.

(2) The hydrated H_2O of crystal is omitted in the formulas listed above.

On your table, there are also 14 empty droppers, 12 empty vials, 12 coffee stirrers, and 5 droppers containing the following reagents:

0.1M $AgNO_3$	3% H_2O_2	0.1M Na_2S
1M HCl	0.01% phenolphthalein	

Procedure:

1. Use the coffee stirrers provided to transfer about 20 mg of each unknown sample into separate empty vial, add about 1 mL of distilled water to each vial to make the unknown solutions and label them appropriately.

2. Use the five reagents provided and mutual reactions between the unknown solutions to identify each unknown sample.

Note: (1) This practical exercise is a kind of spot test. You can do it on the provided pallet or on a sheet of white paper.

(2) Be sure to confirm your observations before writing your answers in the blanks of the Data Sheet.

Data Sheet 28

Compound	Code	Compound	Code	Compound	Code
KI	_____	$BaCl_2$	_____	$Na_2S_2O_3$	_____
NaCl	_____	$FeSO_4$	_____	NH_4SCN	_____
$Pb(NO_3)_2$	_____	$CdSO_4$	_____	$NaHCO_3$	_____
$Ba(OH)_2$	_____				

Problem 29: Identification of Unknown Solutions (I) – Spot Test without Electrolysis

1 This is a practical exercise best performed using spot test.

2 In a plastic bag, there are 12 unknown samples in droppers numbered X01 to X12. Each sample in the 1 mL droppers, contains a 0.1 M aqueous solution of a simple compound. A list of the compounds is given in the Data Sheet. There are also a dropper containing phenolphthalein, two empty droppers, a pallet, two coffee stirrers, a bottle of distilled water, and a small pack of tissue paper for your use.

3 Use the materials provided and mutual reactions of the unknown solution to identify each unknown sample and write your answer (code number) in the blank of the Data Sheet.

Note: (1) Three samples are duplicated.

(2) The volume of each sample is about 0.6 mL. No more solution will be provided.

(3) Each correct answer gets 8 points, and each incorrect answer will be penalized 2 points.

Data Sheet 29

Compound	Number	Compound	Number	Compound	Number
NaCl	_____	$AgNO_3$	_____	KI	_____
HCl	_____	$Pb(NO_3)_2$	_____	$BaCl_2$	_____
H_2SO_4	_____	Na_2CO_3	_____	NaOH	_____

Questions

29-1 How to find out the unknown sample of H_2SO_4 in this work?

29-2 How to confirm the H_2SO_4 solution in this work?

Problem 30: Identification of Unknown Solutions (II) – Spot Test with Electrolysis

Reagents and Equipment

Acid-base indicator	1	Simple electrolysis apparatus	1
Bromothymol Blue	1	Coffee stirrer	2
Distilled water	1	Tissue paper	1
Unknown samples	10		

1 Ten unknown samples are shown in the Data Sheet.

2 Simple electrolysis apparatus is shown in Fig 1.

3 Identify 10 unknown samples (code number: X01 ~ X10)

Note: (1) The compounds in the unknown solutions are given in the Data Sheet.

(2) Each unknown sample contains only one compound.

(3) The concentration of each unknown solution is about 0.1 mol/L.

(4) Write your answers (code number) in the blanks of your Data Sheet.

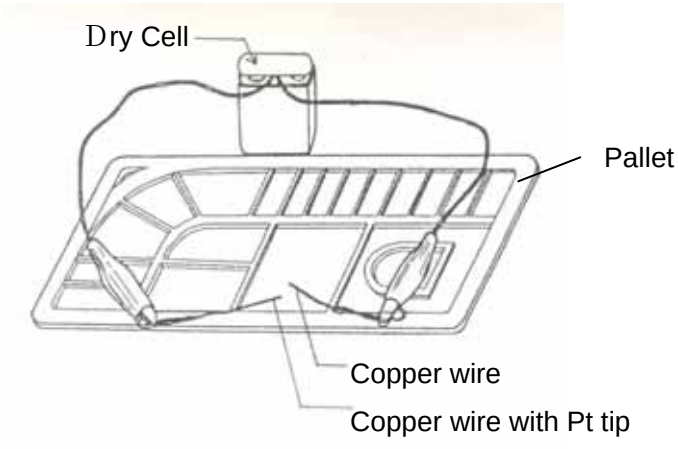


Fig 1. Simple Electrolysis Apparatus

Data Sheet 30

Compound	Number	Compound	Number	Compound	Number
$Cd(NO_3)_2$	_____	Na_2S	_____	H_2SO_4	_____
KI	_____	$Pb(NO_3)_2$	_____	NaOH	_____
$Na_2S_2O_3$	_____	HCl	_____	$Zn(NO_3)_2$	_____
NaCl	_____				

Problem 31: Quantitative Analysis of Ascorbic Acid in a Vitamin C Tablet

The major ingredient in commercial vitamin C is ascorbic acid ($H_2C_6H_6O_{27}$, FW = 176.12). It is acidic and a reductant, therefore, both acid-base and redox titrations can be used to measure the amount of ascorbic acid in commercial vitamin C tablets.

This experiment has two parts, the first part involves using an acid-base titration to determine the amount of ascribed acid in a vitamin C tablet. The second part involves using a redox titration to perform a similar determination.

The evaluation is based on accuracy. The acid-base titration accounts for 30%; the redox titration 60%; and a comparison of these two methods 10% of the final score.

CHECK REAGENTS AND APPARATUS BEFORE YOU START

Reagents	**Apparatus**	
NaOH Solution	Graduated Cylinder	
(concentration is shown on the label)	10 mL	x 1
	100 mL	x 1
Thiosulfate ($Na_2S_2O_3$) Solution	Beaker	
(concentration is shown on the label)	100 mL	x 2
Iodine Solution (0.01 M)	250 mL	x 2
Indicator	Erlenmeyer	
	125 mL	x 4
Phenonlphthalein Solution	250 mL	x 2
Methyl Red Solution	Filter Paper	x 10
	Weighing Paper	x 10
Starch Solution	Mold and Pastel	1 set
	Buret (1 rack)	x 2
	Buret Brush	x 1
	Volumetric Flask, 100 mL	x 1
	Spatula	x 1
	Funnel	x 1
	Pipette (20 mL) / Safety Bulb	1 set
	Pasteur Pipette (dropper)	x 6
	Brush	x 1

Procedure:

Dissolve the vitamin C tablet in water; filter if necessary. The final volume of the solution should be 100 mL.

Part 1: Acid-Base Titration

1-1 Pipette 10 mL of the above solution into an Erlenmeyer flask. Choose the appropriate indicator to perform titration.

1-2 Repeat step 2 a total of 3 times.

Part 2: Redox Titration

2-1 Determination of the concentration of the provided iodine solution using the standardized thiosulfate solution.

2-1-1 Pipette 20 mL of the iodine solution into an Erlenmeyer flask, and titrate by using standard $Na_2S_2O_3$ solution. Use starch as the indicator.

2-1-2 Repeat step 4 a total of 3 times.

2-2 Determination of the amount of ascorbic acid

2-2-1 Pipette 10 mL of the solution from step 1 into an Erlenmeyer flask. Add a few drops of starch as indicator and titrate with the iodine solution.

2-2-2 Repeat step 6 a total of 3 times.

Data Sheet 31

31-1 Acid-Base Titration

First titration Vitamin C solution _____mL; NaOH solution used _____mL

Second titration Vitamin C solution _____mL; NaOH solution used _____mL

Third titration Vitamin C solution _____mL; NaOH solution used _____mL

31-2 Redox Titration

31-2-1 Iodine concentration determination

First titration Iodine solution _____mL; $Na_2S_2O_3$ solution used _____mL

Second titration Iodine solution _____mL; $Na_2S_2O_3$ solution used _____mL

Third titration Iodine solution _____mL; $Na_2S_2O_3$ solution used _____mL

31-2-2 Ascorbic acid determination

First titration Vitamin C solution _____mL; Iodine solution used _____mL.

Second titration Vitamin C solution _____mL; Iodine solution used _____mL.

Third titration Vitamin C solution _____mL; Iodine solution used _____mL.

Questions

31-1 Assume ascorbic acid is a single protic acid, use the data from acid-base titration to calculate the amount of ascorbic acid in the whole vitamin C tablet.

31-2 The reaction of I_2 with $Na_2S_2O_3$ is as shown:

$$2\ S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Calculate the concentration of the iodine solution.

31-3 The reaction of ascorbic acid with I_2 is

$$H_2C_6H_6O_6 + I_2 \rightarrow C_6H_6O_6 + 2\ I^- + 2H^+$$

Calculate the amount of ascorbic acid in the whole vitamin C tablet.

31-4 Compare the advantage and disadvantage of the two titration methods.

Problem 32: Determination of an Equilibrium Constant

Equilibrium constant is an important property of a chemical reaction. It indicates the direction of a reaction. The concentration of each reaction species can be calculated from the equilibrium constant. For a reaction of the type $aA + bB \leftrightarrow cC + dD$, the equilibrium constant, K_{eq}, is given by $([C]_{eq}^{c}[D]_{eq}^{d}) / ([A]_{eq}^{a}[B]_{eq}^{b})$. From the equation, K_{eq} can be easily computed if the concentrations of all species at equilibrium are known. Once the K_{eq} is determined, concentrations at equilibrium can be calculated from any given starting condition.

The aim of this experiment is to deduce the K_{eq} for the reaction of $Fe(NO_3)_3$ with KSCN. You are provided with 20 mL of a 0.1 M starter of each of the reactant: $Fe(NO_3)_3$ and KSCN. Three test

tubes containing the product from the reaction are also provided. Each of these contains a known concentration of the product: 3.214 x 10^{-3}, 1.360x10^{-3}, 1.375x10^{-4} M for tubes 1, 2, and 3; respectively. These standard solutions are used to be as colorimetric reference.

You have to design an experiment to determine the K_{eq} for the reaction of $Fe(NO_3)_3$ with KSCN using the given reagents. Your data should be listed in a table as shown below:

Starting conc. for reactant		Equilibrium conc. for reactant		Product conc.	Reaction equilibrium constant
$Fe(NO_3)_3$	KSCN	$Fe(NO_3)_3$	KSCN	?	K_{eq}
?	?	?	?	From colorimetric measurement	?

Carefully design your experiment before you start. More reagents can be obtained from the TAs upon request. However, 5 points will be deducted for each additional reagent. Marks for this experiment will be primarily awarded on the basis of the accuracy of the result.

Besides the reactants, the following equipment has also been provided on your bench:

1. Paper 3 sheets
2. Kimwipe 1 box
3. Labels
4. Test tubes (20 pieces) and a test tube rack
5. Safety bulb x 1
6. Rubber bulbs x 4
7. Pipette x 4
8. Glass rods x 2
9. Test tube brushes (thin and thick, one each)
10. Wash bottle x 1
11. Ruler (15 cm) x 1
12. Beaker 100 mL x 2
    250 mL x 2
    500 mL x 2

13.	Graduated cylinder	10 mL	x 1
		25 mL	x 1
14.	Volumetric	25 mL	x 2
15.	Erlenmeyer	100 mL	x 4
16.	Buret	5 mL	x 2
		1 mL	x 2

Data Sheet 32

Starting conc. for reactant		Equilibrium conc. for reactant		Product conc.	Reaction equilibrium constant
$Fe(NO_3)_3$	KSCN	$Fe(NO_3)_3$	KSCN		K_{eq}
				From colorimetric measurement	

Questions

32-1 Write a balanced equation for the reaction.

32-2 What is the expression for the equilibrium constant of this reaction?

K_{eq} =

32-3 What is the calculated value of K_{eq} from your data sheet?

Problem 33: Preparation of Acetylsalicylic Acid (Aspirin)

Acetylation of compounds containing the amino or hydroxyl group is usually accomplished by

means of acetyl chloride or acetic anhydride. The reaction is catalyzed by a catalyst such as pyridine or sulfuric acid.

Aspirin may be prepared from salicylic acid and acetic anhydride. Sulfuric acid is frequently used as a catalyst in this reaction.

$$HOC_6H_4COOH + (CH_3CO)_2O \xrightarrow{H^+} CH_3COOC_6H_4COOH + CH_3COOH$$

Procedure:

In a 125 mL Erlenmeyer flask place 3.5 g of salicylic acid, 3.5 mL of acetic anhydride (density: 1.08 g/mL), and 5 drops of concentrated sulfuric acid (some heat may be generated). Heat the flask in a hot water bath and stir for 5 minutes. During this time, the solid dissolve completely.

Remove the flask from the bath and add 15 mL of ice water to it. Cool the flask to crystallize the products. Collect the crystals by suction filtration.

Transfer the crystals to a 125 mL Erlenmeyer flask, add 8 mL of ethanol. Heat the flask in a water bath until the solid has dissolved. Add 20 mL of hot water to the flask and heat it until the solution clears. Remove the flask from the bath, cover it, and allow it to cool at room temperature. Collect the needle-like crystals by suction filtration. Wash the crystals with cold water and allow it to dry thoroughly.

Weight the crystals obtained and calculate the percentage yield of this experiment. Determine the melting points of the products.

Questions

33-1 What is the purpose of adding ice water?

33-2 Why the crystals was needed to wash with water?

33-3 Calculate the percentage yield of this reaction.

33-4 What is the melting point of aspirin you obtained?

Problem 34: Analysis of Aspirin Tablets

For many reasons, materials packaged for domestic use are often “diluted” by inert substances, often referred to as fillers. In the case of drugs, one reason for this procedure is to provide the correct dosage in a tablet of acceptable size. For example, aspirin, acetylsalicylic acid, is often mixed with a filler in commercial preparations. The aim of this experiment is to determine the percentage of aspirin in a readily available tablet.

Aspirin or acetylsalicylic acid can be considered to be the product of reaction of acetic acid (CH_3COOH) and salicylic acid (HOC_6H_4COOH). When treated with a solution of sodium hydroxide, aspirin is hydrolyzed and the two acids are simultaneously neutralized.

$$CH_3COOC_6H_4COOH + 2NaOH \rightarrow CH_3COO\ Na + HOC_6H_4COONa + H_2O$$

If an excess of NaOH solution is used in this reaction, the amount of excess can be determined by a back titration with H_2SO_4. It is essential, however, that the H_2SO_4 used in this titration does not also react with sodium acetate and sodium salicylate, both of which contain basic anions. This can be avoided by the selection of either phenol red (pH range 6.8–8.4) or phenolphthalein (pH range 8.3-10.0) as the indicator.

Procedure:

Accurately weigh out sufficient aspirin tablets to give a mass of about 1.5 g. Record the number of tablets and the mass.

Transfer the tablets to a 150 mL conical flask. Add a 25 mL aliquot of a carefully prepared NaOH solution together with a similar volume of water. Heat gently for about 10 minutes to hydrolyze the acetylsalicylic acid, according to the equation above. Cool the reaction mixture by holding the flask under running water and carefully transfer the contents, without loss, to a 250 mL volumetric flask. Rinse the reaction vessel several times with water, adding the washings to the volumetric flask. Dilute the solution to the calibration mark and mix well by shaking.

Take a 25 mL aliquot of the diluted reaction mixture and transfer it to a clean conical flask.

Titrate the aliquot with 0.05 M H_2SO_4 solution using phenol red (or phenolphthalein) as the indicator. Record the actual molarity of the acid and the titre obtained. Repeat the determination until consistent titres are determined. Calculate the average titre.

Using a pipette and a volumetric flask, dilute a sample of the 1 M NaOH solution to 0.1 M.

Titrate 25 mL aliquots of the dilute solution with 0.05 M H_2SO_4 using the same indicator as before.

Questions

34-1 Why was it essential to cool the reaction mixture？

34-2 Why was it essential to mix thoroughly?

34-3 With what should the pipette first be rinsed？

34-4 With what should the flask have been rinsed？

34-5 Why was it necessary to dilute the NaOH solution？

34-6 Record the titres of acid and determine the molarity of the original NaOH solution, showing all steps in your calculation.

34-7 Determine the number of moles of NaOH originally added to the aspirin sample and the number of moles of NaOH used in the hydrolysis step.

34-8 Calculate the number of moles of acetylsalicylic acid present in the titre sample.

34-9 Calculate the mass of acetylsalicylic acid in each tablet and compare this with the specification shown on the package.

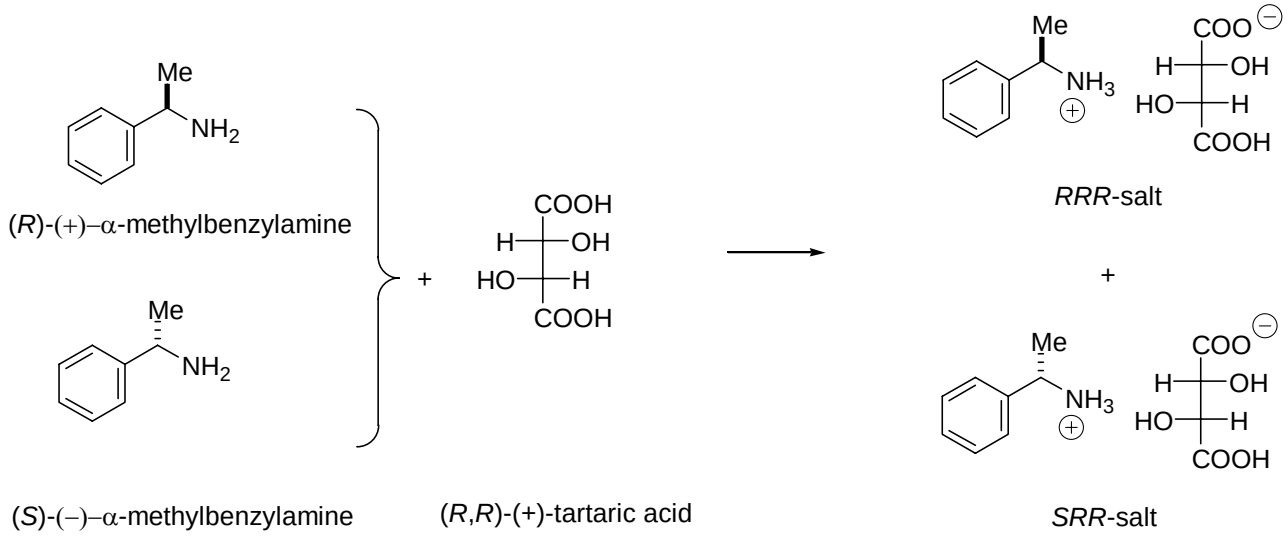
34-10 Analyze your own technique and assumptions in the experiment. List, in estimated order of importance, various sources of error which could arise in this analysis.

Problem 35: Resolution of (±) - α - Methylbenzylamine and Determination of the Optical Purity

The traditional method for resolving a racemic mixture into its enantiomers is to use an enantiomerically pure natural product that bonds with the compound to be resolved. The enantiomers in the racemic mixture bond with the optically pure resolving agent to form two diastereomers. The diastereomers are separated, and then the resolving agent is cleaved from the separated enantiomers. The optical purity of a compound is defined as the ratio of its optical

rotation to the rotation of a pure enantiomer.

A racemic mixture of α-methylbenzylamine is readily resolved by (*R*,*R*)-(+)-tartaric acid. The resulting (*S*)-(-)-α-methylbenzylaminium (*R*,*R*)-(+)-tartrate salt, *SRR*-salt, has a lower solubility than its diastereomeric counter part, (*R*)-(+)-α-methylbenzylaminium (*R*,*R*)-(+)-tartrate salt, *RRR*-salt. The *SRR* salt is induced to crystallize, whereas the *RRR* salt stays in solution. The crystals are removed by filtration and purified, and (S)-(-)-α-methylbenzylamine is regenerated by treatment with a base.



Procedure and Questions:

In an Erlenmeyer flask (250 mL) are placed (*R*,*R*)-(+)-tartaric acid (7.8 g, 52.0 mmol) and methanol (125 mL). The mixture is heated on a hot plate until the solution is nearly boiling. A racemic mixture of α-methylbenzylamine (6.25 g, 51.6 mmol) is added slowly over a period of 5 minutes to the solution. (*Caution: at this step, the mixture is very likely to froth and boil over*) Stopper the flask and let it stand overnight (18 hours). Formation of prismatic crystals indicates a complete resolution of enantiomers, whereas impure isomers will appear in needles. Needles should be dissolved by careful heating, and crystallized again on cooling slowly. A seed of prismatic crystal can be added to induce the recrystallization.

The crystals are filtered through a Büchner funnel, and rinsed with a few portions of cold methanol. The crystals are transferred to a preweighed Erlenmeyer flask (50 mL), and purged with a stream of nitrogen. The dry crystals are weighed, and the yield is calculated. The crystals in the flask are treated with water (25 mL), and 50% aqueous sodium hydroxide solution (4 mL) is added slowly. The mixture is extracted with 10 mL of methylene chloride for three times using a separatory funnel. The organic layers from each extraction are combined in a

stoppered flask, and dried over anhydrous sodium sulfate (1.0 g) for about 10 minutes. The dried solution is decanted into a round-bottom flask (50 mL), and methylene chloride is removed by rotary evaporation. The residual α-methylbenzylamine is weighed, and the yield is calculated. Every effort should be taken to avoid prolonged exposure of the amine to air. Transfer the α-methylbenzylamine into a polarimeter tube cell, and measure its optical rotation. The reported specific rotation of (*S*)-(-)-α-methylbenzylamine is $[\alpha]_D^{23} = -40.3^o$ (neat). Calculate the percentage for each of the enantiomers in the resolved sample.