SOME EXPERIMENTS OF PEDAGOGICAL VALUE IN INORGANIC CHEMISTRY

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CERTIFICATE

Certified that the work incorporated in the thesis entitled "SOME EXPERIMENTS OF PEDAGOGICAL VALUE IN INORGANIC CHEMISTRY" submitted by Mr. Sharad Ramchandra Pokharkar was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

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Research Guide

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S.R. POKHARKAR

RESEARCH PUBLICATIONS

1* Titrimetric Estimation of Calcium and Phosphate in Dietary Supplement Tablets - An Inorganic Analytical Undergraduate Experiment

Dr. V.D. Kelkar and S.R. Pokharkar

Indian J. Pharm. Educ., 23(1), March 1989.

2* Determination of Iron from Iron-supplement Tablets by Redox Titrations using Zinc Dust as Reductant - A General Chemistry Experiment

Dr. V.D. Kelkar and S.R. Pokharkar

Indian J. Pharm. Educ., 23(2), March 1989.

3** Preparation and Thermogravimetry of Ammonium Metallo--oxalates of Al(III), Fe(III) and Cu(II)

Dr. V.D. Kelkar, G.N. Natu and S.R. Pokharkar

Proc. 77th Ind. Sc. Cong. Part III (1990)

Chemistry Abstracts : Abstr-47 P. 25.

4 Paper Model of Twin Octahedra without Faces and having a common line

Dr. V.D. Kelkar and S.R. Pokharkar

Proc. 80th Ind. Sc. Cong. (1992)

(Communicated).

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* Reprint given in Appendix

** Abstract given in Appendix

contents

summary

desired ion (either Ca^{3+} or PO_4^{3-}) followed by titrimetric estimation of both.

Another similar experiment, namely, estimation of iron from iron supplement tablets by redox titrations, is mentioned in Chapter 4. In this experiment reduction of ferric ions is carried out using zinc dust in presence of dilute sulphuric acid.

In Chapter 5, a nonconventional experiment, preparation of paper models of the species containing octahedral units has been mentioned. The models given here, are of those species which are involved in the reactions studied in Chapter 2 to 4. Although this type of work is different from the usual type of research work, it gives simple and inexpensive methods of preparation of paper models which are very much useful for better understanding of the structure of complex species.

New contributions of the present work and their pedagogical value :

The experiments suggested in the present work are designed in such a way that they are useful to gain experience in the methods of synthesis, compositional study and various methods of titrimetric analysis. The contributions of the

present work to padagogy can be summarized as follows :

1. For metallo-oxalates, their ammonium salts rather than potassium salts are useful for the recovery and reuse of the metals. The present attempt is a step to introduce to the students the concept of recovery of chemicals that has gained significance today.

2. The analysis of any one of the metallo-oxalates reported here, introduces the students to at least three different types of titrimetric methods (complexometry / iodometry, redox titration and potentiometry).

3. In the thermogravimetry of any complex reported here, the students get not only the training of the technique but also its use for the calculation of parameters such as degree of decomposition (α) and energy of activation (Ea) for each step of decomposition.

4. In the experiment for estimation of calcium and phosphate in presence of each other, the students get experience of quantitative separation as well as the use of three methods of titrimetric analysis [alkalimetry, complexometry and redox (permanganometry)] .

5. In the estimation of iron from the drug,the discussion about the use of 'zinc dust method' instead of 'Sn-Hg method' for reduction, makes the students aware about

pollution problem and the remedies to minimise it.

6. The analysis of consumer product like drug requires complete disintegration of the sample. The students get training of it in the experiments mentioned above.

7. In the analysis of durg, the concentration of the constituent to be analysed is exactly known. Hence the comparison of the observed values with the results expected and therefore, the error analysis can be done.

8. The paper models of an octahedron and a tetrahedron without faces not only give the idea of the shape of the chemical species but can also indicate all the atoms and bonds. The two methods suggested, for getting such models are easy and inexpensive and they are of immense importance in teaching structural inorganic chemistry.

chapter 1

INTRODUCTION

Our experiments are not carried out to decide whether we are right, but to gain new knowledge. It is for knowledge's sake that we plough and sow.

— R. Willstatter

CHAPTER 1

INTRODUCTION

ABSTRACT

In practical courses of chemistry, experiment which helps in learning different concepts, techniques and skills in limited time has great significance. The designing of such experiments may, therefore, be treated as research in chemical education. Also, introducing new teaching aids is equally important. This view is discussed by giving appropriate examples from literature. The brief outline of the present work which includes some such ideas is given in this chapter.

1.1 LEARNING THROUGH EXPERIMENTS

"To hear is to forget
To see is to remember
To do is to learn".

This motto of Nuffield Foundation, the world-renowned organisation related to chemistry education, expresses rightly the necessity of doing practicals to learn chemistry. The practical should have a well-set procedure which can be completed in limited time and should have reproducible results. In chemistry practicals a gainful exercise is the one which would

1. teach the new skills in experimental work,
2. help the students to (a) draw justifiable conclusions from observations (b) realise that the chemical theory is derived from observations and (c) know that there are definite limitations in getting cent-per-cent accuracy, and
3. create interest for the subject.

With these criteria in mind we set some experiments which have pedagogical value in inorganic chemistry. As a prerequisite to this some such representative experiments reported earlier are mentioned.

1.2 SOME REPORTED EXPERIMENTS HAVING PEDAGOGICAL VALUE

The literature is cited in order to know different types of experiments such as :

(a) The customary single laboratory period (3-h) experiment such as estimation of a constituent from the solution containing it (e.g. estimation of copper from given volume of copper sulphate solution).

(b) The extended experiment requiring 2-3 laboratory periods such as preparation and purity of an inorganic complex e.g. preparation and purity of $\left[Ni(NH_3)_6\right]Cl_2$[1] or quantitative analysis of an ore or alloy or a synthetic mixture.

(c) The group experiment where students are divided into small groups, each responsible for only a portion of the total data ultimately shared by all, e.g. estimation of iron from Mohr's salt[2], $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, which can be done groupwise by titrimetry like permanganometry (group 1) and chelatometry (group 2) or by instrumental methods like colorimetry (group 3) and potentiometry (group 4).

(d) The project containing a series of experiments such as study of Reinecke's salt[3] which involves synthesis of the complex, its analysis for the components, ion exchange experiment, spectral studies and other measurements like conductance and magnetic susceptibility.

(e) The extended project containing a series of experiments which involve applications of usual methods for the analysis of unknown samples such as consumer products e.g. determination of iron from razor blade by two methods of redox titrations[4] or complete characterisation of unknown complex e.g. study of trans-$\left[Co(en)_2Cl_2 \right]_3 \left[Fe(ox)_3 \right] \cdot 4\frac{1}{2} H_2O$[5].

(f) The nonconventional experiments (which do not involve actual work in laboratory) such as interpretation of given data (e.g. interpretation of spectra), solution of the problems containing hypothetical data for analysis (e.g. estimation of phosphate from large vat containing boiling mixture of concentrated nitric and sulphuric acids, perhaps containing one dissolved human[6]) and preparation of models useful for the study of structural inorganic chemistry[7].

The approach forteaching of chemistry courses has, thus, changed in recent years from the conventional experiments to the use of more purposeful exercises. Although such an approach is gainful and stimulates much greater enthusiasm in the students, it presents the teacher with the problem of devicing various types of exercises to include in a course which familiarize the student with as wide a range of concepts, techniques and reactions as possible. This approach initiated us to set a few experiments based on some

recent literature data. For this, suitable modifications in the procedures mentioned in this data, have been done. The merits of these experiments have also been discussed.

1.3 NATURE OF THE PRESENT WORK

The thesis is divided into five chapters.

Chapter 1 describes the background for the present work with help of some appropriate references.

Chapter 2 deals with the synthesis and compositional study of ammonium salts of metallo-oxalates of Al(III), Cr(III), Fe(III), Ni(II), Cu(II) and Zn(II). The procedures for preparing these complexes are given. The compositions have been ascertained by chemical analysis and thermogravimetry. The study of thermograms, is extended further to find the procedural decomposition temperatures as well as energy of activation for different steps.

The pedagogical values of this experimental work are -

1. Information about the synthesis and merits of ammonium salts of metallo-oxalates as compared to those of conventional potassium metallo-oxalates
2. Introduction to different titrimetric methods of analysis Al(III), Ni(II) and Zn(II) - complexometry (EDTA method)

Cr(III) and Cu(II) - Iodometry

Fe(III) and oxalate - permanganometry

Ammonium ion - potentiometry

3. Study of the technique of thermogravimetry

Chapter 3 and 4 are related to the analysis of familiar samples of known compositions. They increase the awareness about the importance of chemistry of consumer products. The concept of errors in chemical analysis is also introduced by calculating different parameters like relative error, standard deviation and relative standard deviation. This is useful to increase the awareness about the precautions which are to be taken during different steps of chemical analysis in order to get accurate results.

In Chapter 3 a group experiment is given which involves two methods for estimation of calcium and phosphate from dietary supplement tablets. In both these methods PO_4^{3-} ions are precipitated as quinoline molybdophosphate and estimated by alkalimetry. In the first method Ca^{2+} ions are estimated by complexometry using EDTA solution (direct and back titration method) while in second method Ca^{2+} ions are precipitated as calcium oxalate and estimated by permanganometry.

This experiment has following pedagogical values -

1. Introduction to essential steps of analysis such as :
   (i) The preparation of the sample solution of consumer product by disintegration of the tablets,
   (ii) Quantitative precipitation of desired ions in presence of each other,
   (iii) Use of different titrimetric methods namely, alkalimetry, complexometry (direct as well as back titration method) and permanganometry.
2. Study of the comparison of two methods using calculations of error analysis.

Chapter 4 is related to methods of estimation of iron from iron supplement tablets. After disintegration of tablets, the ferric ions in the solution are reduced to ferrous ions using zinc dust as a reductant(in presence of sulphuric acid). The estimation of iron is done by redox titration method using potassium permanganate as well as potassium dichromate as titrant.

The pedagogical values of the experiment suggested are -

1. Introduction to the preparation of the sample solution of consumer product (disintegration of tablets).

2. Information about the method of reduction of ferric ions using zinc dust (in presence of dilute sulphuric acid) which is an alternative to "Sn-Hg method". [The Sn-Hg method involves use of $HgCl_2$ (which is not desirable due to pollution problem)].

3. Study of estimation of iron by redox titrations using two different types of titrant-potassium permanganate and potassium dichromate.

4. Calculations of error analysis.

In Chapter 5 a nonconventional experiment, namely, the construction of paper models of the species containing octahedral basic units has been mentioned. It involves two methods of construction of such models. The models of simple species (metallo-oxalates, metal-EDTA complex) as well as some polyanions containing octahedral units have been constructed (Refer photographs given in Chapter 5). These species are involved in the chemical reactions involved in earlier chapters.

The pedagogical values of this work are -

1. Simple and inexpensive methods for the construction of paper models.

2. Preparation of more meaningful models because of the formation of octahedral units without faces, which can show metal and ligating atoms, bonds, bond angles, bond lengths etc.

3. Use of models to explain structure, geometrical / optical isomerism for the complex species in a better way.

Thus the present research work seems to be an attempt of different approach in 'Chemistry-education'.

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chapter 2

SYNTHESIS AND SOME COMPOSITIONAL STUDIES OF AMMONIUM METALLO-OXALATES

The ingenuity and effective logic that enabled chemists to determine complex molecular structures from the number of isomers, the reactivity of the molecule and of its fragments, the freezing point, the empirical formula, the molecular weight etc., is one of the outstanding triumphs of the human mind.

— Henry Eyring

CHAPTER 2

SYNTHESIS AND SOME COMPOSITIONAL STUDIES OF AMMONIUM METALLO-OXALATES

ABSTRACT

The preparation, analysis and thermogravimetric study of ammonium salts of metallo-oxalates [M:Al(III), Cr(III), Fe(III), Ni(II), Cu(II) and Zn(II)] are reported here. The complexes are found to be of the type $(NH_4)_3[M^{III}(C_2O_4)_3] \cdot 3H_2O$ and $(NH_4)_2[M^{II}(C_2O_4)_2] \cdot 2H_2O$. The compositions have been ascertained from the analysis as : carbon and hydrogen (microanalysis); NH_4^+ (potentiometric titration); $C_2O_4^{2-}$ (permanganometry); and metal (complexometry/iodometry/redox titrations) as well as metal oxide and water (using thermogravimetry). The TGA curves are also studied to get degree of decomposition and hence energy of activation for each step of decomposition. The study of any of these complexes requires three laboratory periods (3-h each). Such experiments seem to be a purposeful investigation for postgraduate students of inorganic / analytical chemistry.

2.1 INTRODUCTION

In the experiments of synthetic inorganic chemistry, the complex selected should be such that, its preparation and analysis should be easy. The oxalato chelates seem to be ideal in this respect. The chelates like potassium salts of metallo-oxalates [Metal ion : Al(III), Cr(III) and Fe(III)] are common in the practical courses of inorganic chemistry. One can extend the study of the complex for its other properties also. e.g. Potassium salt of Bis oxalato-cuprate (II) dihydrate has been studied for its other properties such as TGA, spectra, magnetic moment etc.[1,2].

Our literature survey indicates that the study of ammonium salts of metallo-oxalates is limited as compared to the potassium salts.

The metallo-oxalates $M^{I}_{3}\left[M^{III}(C_2O_4)_3\right]\cdot xH_2O$ with $M^{I} = K, NH_4$; $M^{III} = Fe, Mn, Cr, Co$; $x = 3$ and $M^{I} = Na$; $M^{III} = Co$, $x = 4.5$ have been reported[3]. The study of X-ray and thermal decomposition[4] of $M^{I}_{3}\left[Fe(C_2O_4)_3\right]\cdot 3H_2O$ with M^{I} as K, Na and NH_4 is also reported. Paris et al[5] have reported the thermal decomposition of trioxalatometallates, $(NH_4)_3\left[M^{III}(C_2O_4)_3\right]\cdot 3H_2O$ where M = Fe, Cr and Al with M_2O_3 as final decomposition product. The preparation and thermal decomposition of ammonium trioxalato cobaltate (III) trihydrate,

$(NH_4)_3\left[Co(C_2O_4)_3\right]\cdot 3H_2O$ has also been reported[6]. The thermal investigations of sodium and ammonium metal-carboxylato complexes of the metals like Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) (with the carboxylate ligand : oxalate, malonate and succinate) in solid state, have been reported[7,8].

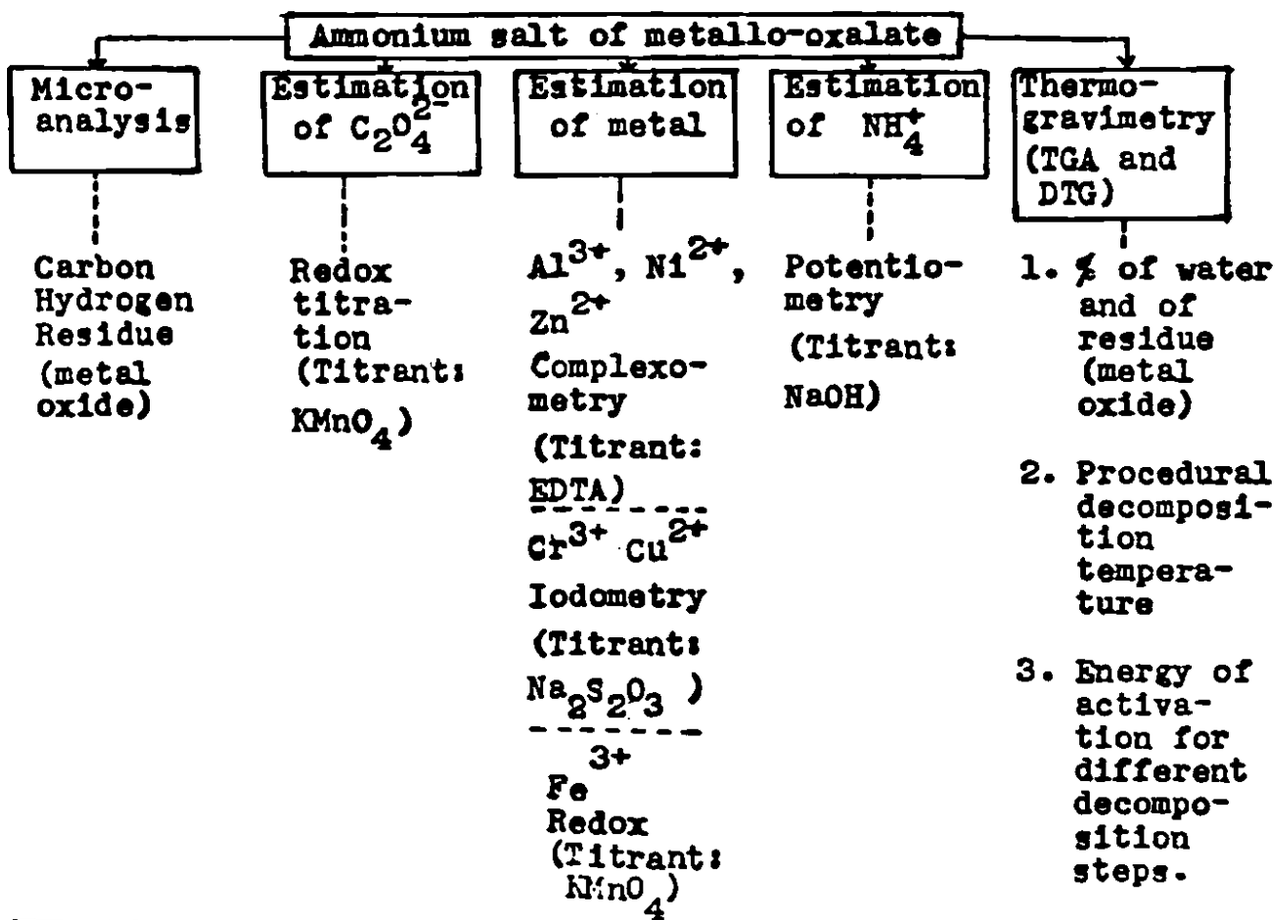
Using the information given in the earlier reports, the study of synthesis, analysis and thermogravimetry of ammonium salts of metallo-oxalates of Al(III), Cr(III), Fe(III), Ni(II), Cu(II) and Zn(II) is carried out. The compositions have been ascertained from the analysis for metals (by titrimetry), ammonium (by potentiometry[9,10]) as well as metal and water (using TGA). The preparation of any such complex, its analysis and TGA require about three laboratory periods (3-h each). This type of exercise, therefore, seems to be useful for the students to gain experience about the preparation of complex, standard titrimetric estimations of all its constituents and use of thermogravimetric analysis.

The plan of work and equations given herewith indicate that this work is useful to get the knowledge about various methods of analysis.

Based on the composition ascertained from analysis, these complexes seem to have octahedral geometry. To have better

idea about the structure, the models of these complexes have been prepared (refer Chapter 5).

Plan for analysis of ammonium salts of metallo-oxalates



Equations:

Synthesis of ammonium salts of metallo-oxalates

Al (III) :

$$Al_2(SO_4)_3 + 6\ NaOH \longrightarrow 2\ Al(OH)_3 + 3\ Na_2SO_4$$

$$2\ Al(OH)_3 + 3\ H_2C_2O_4 + 3(NH_4)_2C_2O_4 \longrightarrow 2(NH_4)_3\left[Al(C_2O_4)_3\right]\cdot 3H_2O$$

Cr (III) :

$$(NH_4)_2Cr_2O_7 + 7H_2C_2O_4 + 2(NH_4)_2C_2O_4 \longrightarrow 2(NH_4)_3\left[Cr(C_2O_4)_3\right]\cdot 3H_2O + 6\,CO_2 + H_2O$$

Fe (III) :

$$2\,FeCl_3 + 6(NH_4)_2C_2O_4 + 6H_2O \longrightarrow 2(NH_4)_3\left[Fe(C_2O_4)_3\right]\cdot 3H_2O + 6\,NH_4Cl$$

Ni (II) :

$$NiCl_2 + 2(NH_4)_2C_2O_4 + 2H_2O \longrightarrow (NH_4)_2\left[Ni(C_2O_4)_2\right]\cdot 2H_2O + 2\,NH_4Cl$$

Cu (II) :

$$CuSO_4 + 2(NH_4)_2C_2O_4 + 2H_2O \longrightarrow (NH_4)_2\left[Cu(C_2O_4)_2\right]\cdot 2H_2O + (NH_4)_2SO_4$$

Zn (II) :

$$ZnSO_4 + 2(NH_4)_2C_2O_4 + 2H_2O \longrightarrow (NH_4)_2\left[Zn(C_2O_4)_2\right]\cdot 2H_2O + (NH_4)_2SO_4$$

Analysis of metallo-oxalates

Estimation of oxalate

Standardization of $KMnO_4$

$$Na_2C_2O_4 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2C_2O_4$$

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10\,CO_2 + 8H_2O$$

Titration with $KMnO_4$

$$\text{Ammonium salt of metallo-oxalate} \xrightarrow{H_2SO_4} H_2C_2O_4$$

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8H_2O$$

<u>Estimation of metal ion</u>

Disintegration of metal complex

$$\text{Metal complex} \xrightarrow[2.\ H_2SO_4]{1.\ (HCl + HNO_3)} \text{M-sulphate + volatile products}$$

Al(III), Ni(II) and Zn(II) : by complexometry :

Standardization of EDTA

$$M^{2+} + In \longrightarrow MIn \quad \text{(wine red)}$$

Indicator

$$MIn + Na_2C_{10}H_{14}N_2O_8 \longrightarrow \left[M(C_{10}H_{12}N_2O_8)\right]^{2-} + 2H^+ + 2Na^+ + In^-$$

(Na_2 - EDTA) (dissociated) (blue)

(where M ≡ Zn^{2+} / Mg^{2+})

Back titration of excess (unused) EDTA with standard Mg^{2+} ion soln.

M^{n+} + EDTA (known excess) ⟶ M (EDTA) complex

EDTA (unused) + Mg^{2+} (std. soln.) ⟶ Mg(EDTA) complex

Mg^{2+} + In^- ⟶ MgIn

(blue) (wine red)

} (Back titration)

Mg^{2+} + EDTA (known excess as in back titration) $\longrightarrow$ Mg(EDTA) complex (Blank titration)

Cr(III) :

$$2\,Cr^{3+} + 3\,S_2O_8^{2-} + 7H_2O \xrightarrow{(AgNO_3)} Cr_2O_7^{2-} + 6\,HSO_4^- + 8H^+$$ (oxidation)

$2\,S_2O_8^{2-} + 2H_2O \longrightarrow O_{2\,(g)} + 4HSO_4^-$ (elimination of $S_2O_8^{2-}$) (unused)

$Cr_2O_7^{2-} + 6\,I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7\,H_2O$

$I_2 + 2Na_2S_2O_3 \longrightarrow 2\,NaI + Na_2S_4O_6$

} (iodometry / standardization of $Na_2S_2O_3$)

Cu(II) :

$2\,Cu^{2+} + 4\,I^- \longrightarrow Cu_2I_2 + I_2$

$I_2 + 2\,Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2\,NaI$

} (iodometry)

Fe(III) :

$$2\,Fe^{3+} + Zn \xrightarrow{H_2SO_4} 2\,Fe^{2+} + Zn^{2+}$$ (reduction)

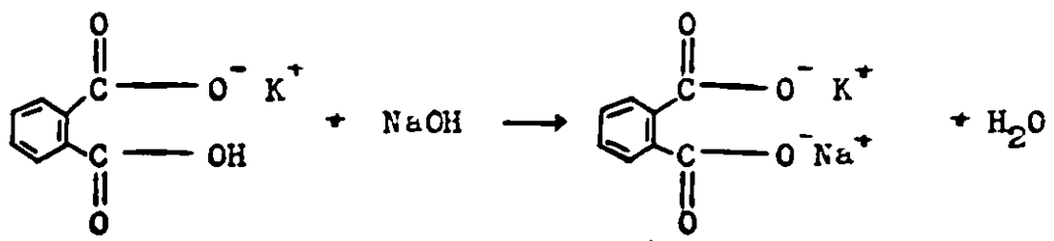
(dust)

$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2\,(g)$ (elimination of Zn) (unused)

$10\,Fe^{2+} + 2\,MnO_4^{2-} + 16\,H^+ \longrightarrow 10\,Fe^{3+} + 2\,Mn^{2+} + 8\,H_2O$ (titration with $KMnO_4$)

Estimation of NH_4^+

Standardization of NaOH



Potassium hydrogen phthalate

$$4\,NH_4^+ + 6HCHO \longrightarrow (CH_2)_6N_4 + 6H_2O + 4\,H^+ \quad \text{(reaction with HCHO)}$$

$$H^+ + OH^- \longrightarrow H_2O \quad \text{(Titration with NaOH)}$$

Decomposition of metallo-oxalates (Thermogravimetry)

For the complexes of M^{3+}:

$$(NH_4)_3\left[M(C_2O_4)_3\right]\cdot 3H_2O \xrightarrow{100\text{-}150\ ^\circ C} (NH_4)_3\left[M(C_2O_4)_3\right] + 3H_2O$$

$$2(NH_4)_3\left[M(C_2O_4)_3\right] + 3O_2 \xrightarrow{\text{upto } 500^\circ C} M_2O_3 + 6NH_3 + 12CO_2 + 3H_2O$$

For the complexes of M^{2+}

$$(NH_4)_2\left[M(C_2O_4)_2\right]\cdot 2H_2O \xrightarrow{125\ ^\circ C} (NH_4)_2\left[M(C_2O_4)_2\right] + 2H_2O$$

$$(NH_4)_2\left[M(C_2O_4)_2\right] \xrightarrow{280\ ^\circ C} MO + 2NH_3 + 4\,CO_2 + H_2O$$

2.2 SYNTHESIS OF AMMONIUM METALLO-OXALATES

All the chemicals used are of AnalaR or equivalent grade. The procedures are developed on the basis of those reported for potassium salts of metallo-oxalates.

Reagents :

Oxalic acid dihydrate

Ammonium oxalate monohydrate

Metal salt [Sulphate for Al(III), Cu(II) and Zn(II); chloride for Fe(III) and Ni(II); and ammonium dichromate for Cr(III)]

Sodium hydroxide

Methyl alcohol

Procedures :

Ammonium tris-oxalato aluminate (III) trihydrate :

In 30 mL of distilled water containing 2.50 g of NaOH (0.0625 moles) is added 7.00 g of $Al_2(SO_4)_3 \cdot 18\ H_2O$ (equivalent to 0.0210 moles of Al) with constant stirring. The precipitate of $Al(OH)_3$ is filtered through Whatman No. 41 filter paper and washed with distilled water till it is alkali free. In ~ 50 mL of hot distilled water are dissolved 3.75 g (0.0315 moles) of $H_2C_2O_4 \cdot 2H_2O$ and 4.48 g (0.0315 moles) of $(NH_4)_2C_2O_4 \cdot H_2O$. To this solution the precipitate of aluminium hydroxide is added

and the solution is boiled. The unreacted $Al(OH)_3$ is removed by filtration. The solution is concentrated to ~ 25 mL and ~ 2 mL of methyl alcohol is added. It is then cooled in ice bath. The colourless complex is separated by filtration, washed with small volume of ice cold 1:1 methyl alcohol and then dried.

Ammonium tris-oxalato chromate (III) trihydrate :

In 100 mL of hot water containing 17.50 g (0.1470 moles) of $H_2C_2O_4 \cdot 2H_2O$, 5.70 g (0.0401 moles) of $(NH_4)_2C_2O_4 \cdot H_2O$ is added. The solution is heated to get a clear solution. In 100 mL water 5.00 g (0.0198 moles) of $(NH_4)_2Cr_2O_7$ (equivalent to 0.0396 moles of Cr) is dissolved and this solution is added dropwise to the above oxalate solution with constant stirring. Then the solution is concentrated to ~ 10 mL. It is cooled and to it ~ 4 ml of methyl alcohol is added. The deep green crystalline product is filtered, washed with small volume of ice-cold 1:1 methyl alcohol and then dried.

Ammonium tris-oxalato ferrate (III) trihydrate :

In 5 ml of water is dissolved 3.20 g (0.0197 moles) of anhydrous $FeCl_3$ (equivalent to 0.0197 moles of Fe). In ~ 100 mL of hot water, is dissolved 9.25 g (0.065 moles) of $(NH_4)_2C_2O_4 \cdot H_2O$. To this solution is slowly added, the ferric

chloride solution with constant stirring. If ferric hydroxide precipitate is formed, it is removed by filtration. The solution is kept in ice bath. The pale yellow green precipitate of complex is filtered, washed with small volume of ice-cold 1:1 methyl alcohol and then dried.

Ammonium bis-oxalato nickelate (II) dihydrate :

In 20 mL of hot distilled water, 8.64 g (0.0363 moles) $NiCl_2 \cdot 6H_2O$ (equivalent to 0.0363 moles of Ni) is dissolved. In another beaker containing 100 mL of hot distilled water 20.74 g of $(NH_4)_2C_2O_4 \cdot H_2O$ (0.1459 moles) is dissolved. Both these solutions are mixed with constant stirring and the resultant solution is concentrated to ~ 50 mL. Then it is cooled in ice bath. The pale bluish green complex is filtered, washed with small amount of ice cold 1:1 methyl alcohol and dried.

Ammonium bis-oxalato cuprate (II) dihydrate :

In 10 mL of distilled water, is dissolved 4.10 g (0.0164 moles) of $CuSO_4 \cdot 5H_2O$ (equivalent to 0.0164 moles of Cu). In 45 mL of hot distilled water is dissolved in 9.50 g of $(NH_4)_2C_2O_4 \cdot H_2O$ (0.067 moles). These solutions are mixed together with constant stirring. The resulting solution is concentrated to ~ 10 mL.

It is then cooled in an ice-bath. The pale-skyblue precipitate of complex is filtered, washed with small volume of ice cold 1:1 methyl alcohol and then dried.

Ammonium bis-oxalato zincate (II) dihydrate :

In 50 mL of hot distilled water 9.50 g of $(NH_4)_2C_2O_4.H_2O$ (0.067 moles) is dissolved. To this solution 10 mL of aqueous solution containing 4.60 g (0.0160 moles) of $ZnSO_4 \cdot 7H_2O$ (equivalent to 0.0160 moles of Zn) is added dropwise with constant stirring. The solution is concentrated to ~ 10 mL. It is then cooled and to it 3 mL of methyl alcohol is added. The colourless product is filtered, washed with small volume of ice-cold 1:1 methyl alcohol and then dried.

The yields of the complexes are generally 50-60 per cent of theoretical yields. The complexes are recrystallised before use to make them free from ammonium oxalate. The recrystallization is carried out by using aqueous alcoholic medium.

2.3 ANALYSIS OF AMMONIUM METALLO-OXALATES

The results of analysis for carbon, hydrogen, oxalate, metal ion and ammonium ion are given in Table 2.1. The details of the observations and calculations for analysis of ammonium salt of oxalato complex of Ni(II) are given as a representative case.

2.3.1 Microanalysis

The analysis of carbon and hydrogen has been carried out on HOSLI-HOLLAND carbon-hydrogen analyser.

2.3.2 Estimation of oxalate

Analysis of $C_2O_4^{2-}$ is done by redox titrations (permanganometry).

Reagents :

Potassium permanganate solution (0.025 N)

Sodium oxalate (0.025 N) (Standard solution)

Sulphuric acid (3 M)

(Refer Chapter 4 for the preparation of these reagents and standardization of $KMnO_4$).

Procedure :

A definite quantity (about 0.1 g) of the complex is weighed and dissolved in distilled water. The solution is diluted to a known volume (100 mL). An aliquot of 10 mL of this diluted solution is mixed with 10 mL of H_2SO_4 (3 M) and then titrated against previously standardized $KMnO_4$ solution (0.025 N) until the end point faint pink colour is obtained.

From the titration reading percentage of $C_2O_4^{2-}$ is calculated by using the relation :

$$1\ mL\ \ 1\ N\ KMnO_4 \equiv 44.009\ mg\ of\ C_2O_4^{2-}$$

In case of estimation of $C_2O_4^{2-}$ from Cr(III)and Ni(II) complexes metal ions are removed by precipitating their hydroxides [by using KOH solution (10 %)] and the filtrate after neutralisation [by adding H_2SO_4 (3 M)] is used for estimation of $C_2O_4^{2-}$.

Estimation of $C_2O_4^{2-}$ from Ni(II) complex :

Weight of complex = 0.10600 g

Titration reading for 10 mL aliquot from 100 mL diluted solution of Ni(II) complex = 5.6 mL of $KMnO_4$ solution (0.02440N).

$$1\ mL\ \ 1\ N\ \ KMnO_4 \equiv 44.009\ mg\ of\ C_2O_4^{2-}$$

$\therefore$ 5.6 mL of 0.02440N $KMnO_4 \equiv$ 6.0134 mg of $C_2O_4^{2-}$ (in 10 mL aliquot)

$\therefore$ 100 mL diluted solution i.e. 0.10600 g of complex $\equiv$ 60.134 mg of $C_2O_4^{2-}$

$\therefore$ % of $C_2O_4^{2-}$ in Ni(II)-complex = 56.73

2.3.3 Estimation of metal ion

Disintegration of metal complex :

An accurately weighed amount (~ 0.1 g) of complex is disintegrated using 5 mL of $HCl-HNO_3$ (1:1 mixture of concentrated

acids) followed by 3 mL of concentrated H_2SO_4 solution. After complete evolution of brown fumes the solution is cooled and diluted to 100 mL exactly.

Estimation of Al^{3+}, Ni^{2+} and Zn^{2+} :

This is done by complexometry (EDTA titration method).

Reagents :

Zn^{2+} ion / Mg^{2+} ion solution (0.01 M) (standard solution) : For the present analysis Mg^{2+} ion solution is prepared by dissolving exactly weighed amount of pure magnesium wire (about 0.24312 g) in minimum amount of HCl (2 M) and diluting this solution to one litre exactly.

EDTA solution (0.01 M)

Buffer solution (pH 10) (ammonium chloride-ammonia)

Erichrome Black T indicator.

(Refer Chapter 3 for the preparation of these reagents and standardization of EDTA solution).

Procedure :

An aliquot of 10 mL of diluted metal ion solution is neutralized with dilute ammonia. To this solution is added known excess (25 mL exactly) of previously standardized EDTA solution (0.01 M) and ~ 5 mL of buffer solution (pH 10) are

added. The unused (excess) EDTA is back titrated with standard Mg^{2+} ion solution using Eriochrome Black T indicator until the end point blue to wine red colour is obtained. From the volume of Mg^{2+} ion solution required, the percentage of the metal ion is calculated using following relations :

$$\text{Volume of EDTA solution consumed by metal ion} = \frac{\text{Volume of } Mg^{2+} \text{ soln. x molarity}}{\text{Molarity of EDTA}}$$

1 mL 1 M EDTA ≡ 26.98 mg of Al^{3+} / 58.71 mg of Ni^{2+} / 65.37 mg of Zn^{2+}

Estimation of Ni^{2+} from Ni(II) complex :

Mean titration readings :

Blank titration : 23.1 mL of Mg^{2+} ion solution (0.01181 M)

Back titration : 20.6 mL of Mg^{2+} ion solution (0.01181 M)

∴ (Blank-Back) reading = 2.5 mL

Volume of EDTA (0.01092 M) consumed by Ni^{2+} ion

$$= \frac{2.5 \text{ (mL of } Mg^{2+} \text{ soln.) x 0.01181 (M of } Mg^{2+} \text{ soln.)}}{0.01092 \text{ (M of EDTA)}}$$

= 2.7 mL

1 mL of 1 M EDTA ≡ 58.71 mg Ni^{2+}

∴ 2.7 mL of 0.0192 M EDTA ≡ 1.731 mg of Ni^{2+} (in 10 mL aliquot)

∴ 100 mL diluted solution (i.e. 0.096 g of complex) ≡ 17.31 mg of Ni^{2+}

∴ % of Ni^{2+} in Ni(II) - complex = 18.03.

Estimation of Cr^{3+} and Cu^{2+}

This is done by iodometric method.

Estimation of Cr^{3+}

Using peroxodisulphate, Cr^{3+} ions are oxidized to Cr^{6+} and then estimated by iodometry[11].

Reagents :

Ammonium peroxodisulphate solution (10 %)

Silver nitrate solution (2 %) in distilled water

Potassium iodide solution (10 %)

Starch solution (freshly prepared 1 % solution)

Sodium thiosulphate solution (approx. 0.025 N): 6.20 g of $Na_2S_2O_3$ is dissolved in one litre of water

Potassium dichromate solution (0.025 N) (standard solution) : 1.225 g $K_2Cr_2O_7$ is dissolved in one litre of water

Procedure :

Standardization of $Na_2S_2O_3$ solution using standard $K_2Cr_2O_7$ solution :

An aliquot of 25 mL of $K_2Cr_2O_7$ (0.025 N) is mixed with 20 mL of HCl solution (1:1) and 20 mL of freshly prepared iodate free KI solution (10 %). The liberated iodine is titrated against $Na_2S_2O_3$ solution (approx. 0.025 N) using starch indicator (The end point is disappearance of blue colour).

Estimation of Cr (III) :

To an aliquot of the diluted Cr(III) solution, 10 mL of ammonium peroxodisulphate solution(10%) is added and solution is warmed to ~ 60 °C. To this solution 5 mL of silver nitrate solution (2 %) is added. The solution is boiled for 15 min. It is then cooled and diluted to ~ 50 mL. To this solution 20 mL of HCl solution (1:1) and 10 mL of KI solution (10 %) are added. The liberated iodine is titrated against standardized sodium thiosulphate solution (0.025 N) using starch indicator. From the titration reading percentage of Cr(III) is calculated using the relation :

$$1 \text{ mL of } 1 \text{ N } Na_2S_2O_3 \equiv 17.332 \text{ mg of } Cr^{3+}$$

Estimation of Cu^{2+}

Reagents :

Sodium thiosulphate solution (0.025 N)
Potassium dichromate solution (0.025 N) (standard solution)
Potassium iodide solution (10 %)
Starch solution (1 % freshly prepared solution)
Acetic acid (2 N)
Sodium carbonate solution (2 N)

Procedure :

An aliquot of 10 mL of diluted solution containing

Cu(II) ions is neutralised with Na_2CO_3 solution (2 N). Using acetic acid (2 N) the pH of the solution is adjusted to ~ 5 and then it is treated with 10 mL of KI solution (10 %). The liberated iodine is titrated with previously standardized $Na_2S_2O_3$ solution (0.025 N) using starch indicator. From the titration reading percentage of Cu(II) in the complex is calculated using the relation :

$$\underline{1 \text{ mL } 1 \text{ N } Na_2S_2O_3 \text{ solution} \equiv 63.50 \text{ mg of } Cu^{2+}}$$

Estimation of Fe^{3+}

Using zinc dust Fe^{3+} ions are reduced to Fe^{2+} and then estimated by using redox titration method (permanganometry).

Reagents :

Sodium oxalate solution (0.025 N) (standard solution)
Potassium permanganate solution (approx. 0.025 N)
Sulphuric acid (3 M)
Zinc dust
(Refer Chapter 4 for the preparation of these reagents)

Procedure :

To 10 mL aliquot of the diluted solution of Fe(III) ions is added 5 mL of sulphuric acid solution (3 M). The solution is heated on water bath ~ 60 °C. Then ~ 0.5 g of zinc dust

is added (to reduce Fe^{3+} to Fe^{2+}). To the solution 5 mL of H_2SO_4 solution (3 M) is added. The flask is shaken until all the zinc dust is dissolved. This solution is titrated with previously standardized $KMnO_4$ solution (0.025 N). From this reading amount of Fe^{3+} is calculated using the relation

$$1 \text{ mL } 1 \text{ N } KMnO_4 \equiv 55.85 \text{ mg of } Fe^{3+}$$

2.3.4 Estimation of NH_4^+ from ammonium salts of metallo-oxalates :

Due to the limitation of conventional method (alkalimetry) of estimation of NH_4^+ in detecting the end point accurately the estimation is carried out by potentiometry[9,10]. The analysis is based on the reaction of NH_4^+ ions with formaldehyde. The liberated acid is titrated against standard sodium hydroxide solution potentiometrically using glass electrode and calomel electrode.

Reagents :

Sodium hydroxide solution (0.1 M)

Potassium hydrogen phthalate (0.1 M) (Standard solution)

Formaldehyde solution (2 %) : It is prepared by adding 6 mL of 36 % solution of formaldehyde to 100 mL distilled water. The solution is neutralised by adding few drops of NaOH (using phenolphthalein indicator). (Refer Chapter 3 for procedure of standardization of sodium hydroxide solution).

Procedure :

The accurately weighed amount of complex (~ 0.1 g) is transferred to a beaker. To this 20 mL of formaldehyde solution (2 %) is added and the solution is kept for sometime. The volume is adjusted to ~ 80 mL and the liberated acid is titrated potentiometrically with previously standardized NaOH solution (0.130M) using glass and calomel electrodes. Each time 0.3 mL of NaOH solution is added and the corresponding emf is measured.

The equivalence point of the titration is obtained by plotting graph of mL of NaOH added Vs. emf and also by plotting graph of $\Delta E / \Delta V$ Vs. mL of NaOH added. The amount of NH_4^+ is calculated using the relation :

$$1 \text{ mL } 1 \text{ M NaOH} \equiv 18.00 \text{ mg } NH_4^+$$

Estimation of NH_4^+ from Ni(II) complex (Refer Figure 2.1)

Weight of the complex = 0.0880g

From the graph, equivalence point of the titration = 4.1 mL of NaOH solution (0.130M).

$$1 \text{ mL } 1\text{M NaOH} \equiv 18.00 \text{ mg of } NH_4^+$$

$\therefore$ 4.1 mL 0.1300M NaOH = 9.594 mg of NH_4^+

$\therefore$ 0.0880g i.e. 88 mg of complex contains 9.594 mg of NH_4^+

$\therefore$ 100 mg of complex $\equiv$ 10.90 mg of NH_4^+

$\therefore$ % of NH_4^+ in Ni(II)- complex = 10.90.

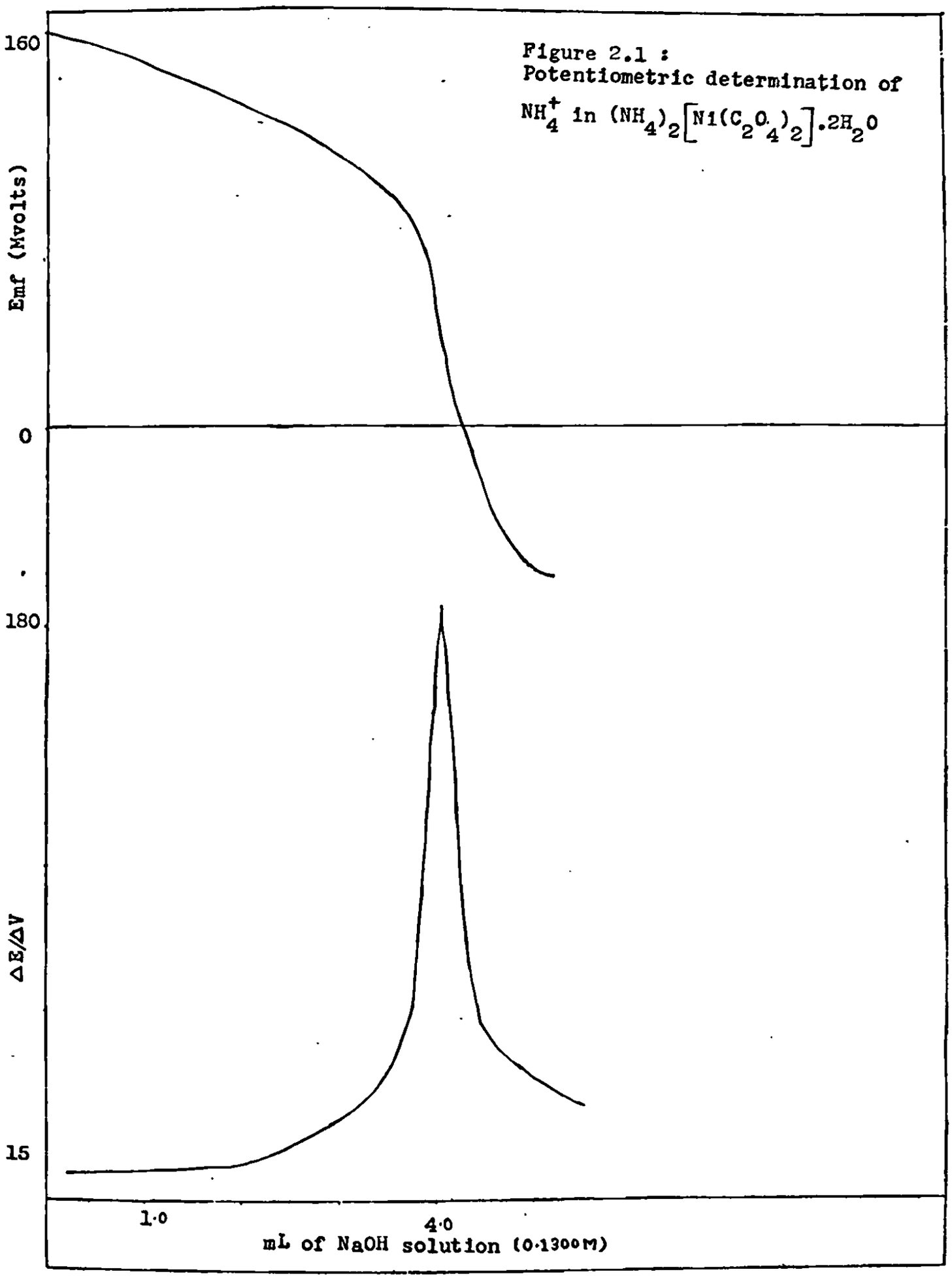


Figure 2.1 :
Potentiometric determination of NH_4^+ in $(NH_4)_2[Ni(C_2O_4)_2].2H_2O$

Table 2.1 : Analysis* of ammonium salts of metallo-oxalates

Analysis (%)		Ammonium salt of metallo-oxalate complex of					
		Al(III)	Cr(III)	Fe(III)	Ni(II)	Cu(II)	Zn(II)
C		14.68 (18.05)	19.03 (16.98)	17.74 (16.83)	17.62 (15.65)	15.71 (15.41)	16.47 (15.32)
H		4.91 (4.51)	3.86 (4.25)	4.46 (4.21)	4.65 (3.91)	3.83 (3.85)	4.68 (3.83)
$C_2O_4^{2-}$		63.70 (66.17)	59.77 (62.26)	65.00 (61.70)	56.73 (57.39)	57.73 (56.50)	55.50 (56.16)
Metal	(a)	6.01	14.58	13.04	18.03	19.55	21.47
	(b)	6.47	11.63	11.20	2.90	17.93	20.88
	(c)	7.86 (6.76)	13.94 (12.26)	12.92 (13.05)	2.16 (19.13)	20.47 (20.39)	17.35 (20.86)
NH_4^+		13.48 (13.54)	12.05 (12.74)	13.47 (12.62)	10.90 (11.74)	12.97 (11.56)	11.20 (11.49)

*The values in the parentheses indicate the calculated values.

(a) from titrimetric estimation (b) from the residue in TGA

(c) from the residue in microanalysis.

2.4 THERMOGRAVIMETRY OF AMMONIUM METALLO-OXALATES

2.4.1 Theoretical background

Thermogravimetry is a method that involves measurement of change in the weight (mass) of a sample as a function of change in its temperature[11,12]. It is done by using thermogravimetric balance where at a time, both weight and temperature of the sample are measured. The instrument consists of (1) a precision balance (accuracy 1 mg), (2) a sample holder (which is stable within temperature range of experiment) suspended from balance pan into the middle portion of furnace (3) a furnace for heating the sample (temperature of which can be programmed to increase linearly) and (4) temperature measuring equipment (thermocouple). The heating should be such that it should not affect functioning of the balance. The TGA curve (thermogram) is plotted as percentage mass loss against temperature. The accuracy of TGA experiment depends on the accuracy of balance, the particle size and amount of the sample, heating rate and type (static / dynamic) as well as nature (air/ nitrogen) of atmosphere.

From TGA it is possible to get information about the amount of water associated and of thermal decomposition of the complex. From the residue of the sample, metal content can also

be calculated. From TGA, it is possible to plot dm/dt i.e. derivative of mass change against temperature change (differential thermogravimetry DTG). From the DTG curve, temperature range for each step of decomposition is obtained. Also the exact temperature at which maximum decomposition occurs for that step can be found out.

From TGA curve, we can calculate the fraction of the sample undergoing decomposition in a particular step [i.e. degree of decomposition (α)]. It can be expressed as :

$$\alpha = \frac{\text{\% loss at time t}}{\text{Total \% loss for the step}}$$

For the reaction in which the order is unknown, Coats and Redfern derived the following expression[13]:-

$$-F(\alpha) = \ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)\,T^2}\right]$$

where $F(\alpha)$ is appropriate mechanistic function expressed in terms degree of decomposition (α), n is the order of reaction and T is temperature in ^{o}K at (α).

For the correct choice of $F(\alpha)$ and n the graph of $F(\alpha)$ against $1/T$ gives a straight line. The slope of this line gives the activation energy (E_a) for that particular step as per the relation :

$$Ea = - \text{slope} \times R$$

where R is Gas constant (8.314 $J\,K^{-1}\,mol^{-1}$).

In the calculations the value of n is varied such that the correlation coefficient is obtained close to $\pm$ 1.0 for the given set of data.

2.4.2 Procedure

The thermogravimetric analysis is done by using a laboratory-constructed thermobalance[14]. It is calibrated by using freshly prepared crystals of copper sulphate and calcium oxalate[11]. The following specifications are used for TGA :

Sample container : cylindrical cup of corning glass. [6 mm (id) x 20 mm (h)]

Particle size of sample : 150 mesh

Amount of sample : 50-100 mg

Precaution taken to reduce the sample-loss : On the top surface of the sample a layer of ~150 mg of dry silica gel (column grade) is applied. (Silica gel is an inert compound, soluble at high temperature).

Rate of heating : 3 $^{o}C\ min^{-1}$

Temperature range of study : room temperature to 700 ^{o}C

Atmosphere : dynamic air [Aspirator assembly is used for removing the evolved gases, with the flow of air at a rate of 6 litres per hour.]

For each metal complex TGA and DTG curves are plotted. From TGA curves percentage of water associated and of metal (from residue of metal oxide) are calculated. For the complexes under study two steps are observed in TGA, the first one being for dehydration while the second one being for decomposition. From the second step the procedural decomposition temperature is obtained[15].

From the DTG curves the exact temperature ranges for above mentioned steps are obtained. For these ranges where the accelerated weight loss is observed, the TGA curves are expanded.

For each curve the best fitting straight line is drawn for the region of maximum weight change. At least six points are selected on this straight line. The data of temperature (^{o}K) and corresponding weight loss (%) is tabulated. Using this data, the values of $F(\alpha)$ are calculated using Coats and Redfern equation.

The graph of $F(\alpha)$ against $1/T$ is plotted and from its slope energy of activation for that step is calculated.

Although all these calculations can be done manually, we have done this work using the computer programme (developed in our department by Dhar[16]) with the help of BBC microcomputer.

The thermograms of the complexes are shown in Figure 2.2.a and 2.2.b and the data obtained is summarized in Table 2.4.

As an illustration the graphs and calculations for Ni(II)-complex are shown in details. Figure 2.3 shows TGA and DTG for this complex. Figure 2.4 and 2.5 show the graphs required for finding out the energy of activation for the two steps of decomposition of the complex. Table 2.2 and 2.3 give the relevant information.

2.5 RESULTS AND DISCUSSION

The results of analysis as well as thermogravimetry for various constituents (Table 2.1 and 2.4) are in good agreement with the compositions $(NH_4)_3\left[M^{III}(C_2O_4)_3\right]\cdot 3H_2O$ (where M^{III} : Al, Cr, Fe) and $(NH_4)_2\left[M^{II}(C_2O_4)_2\right]\cdot 2H_2O$ (where M^{II} : Ni, Cu, Zn). These compositions are similar to those of reported metallo-oxalates[7,8,17,18] of the metal ions under present study. [There is, however, slight variation in number of water molecules in some of the reported compositions[7,8].]

The analyses also indicate that the adsorbed water is not associated with these salts.

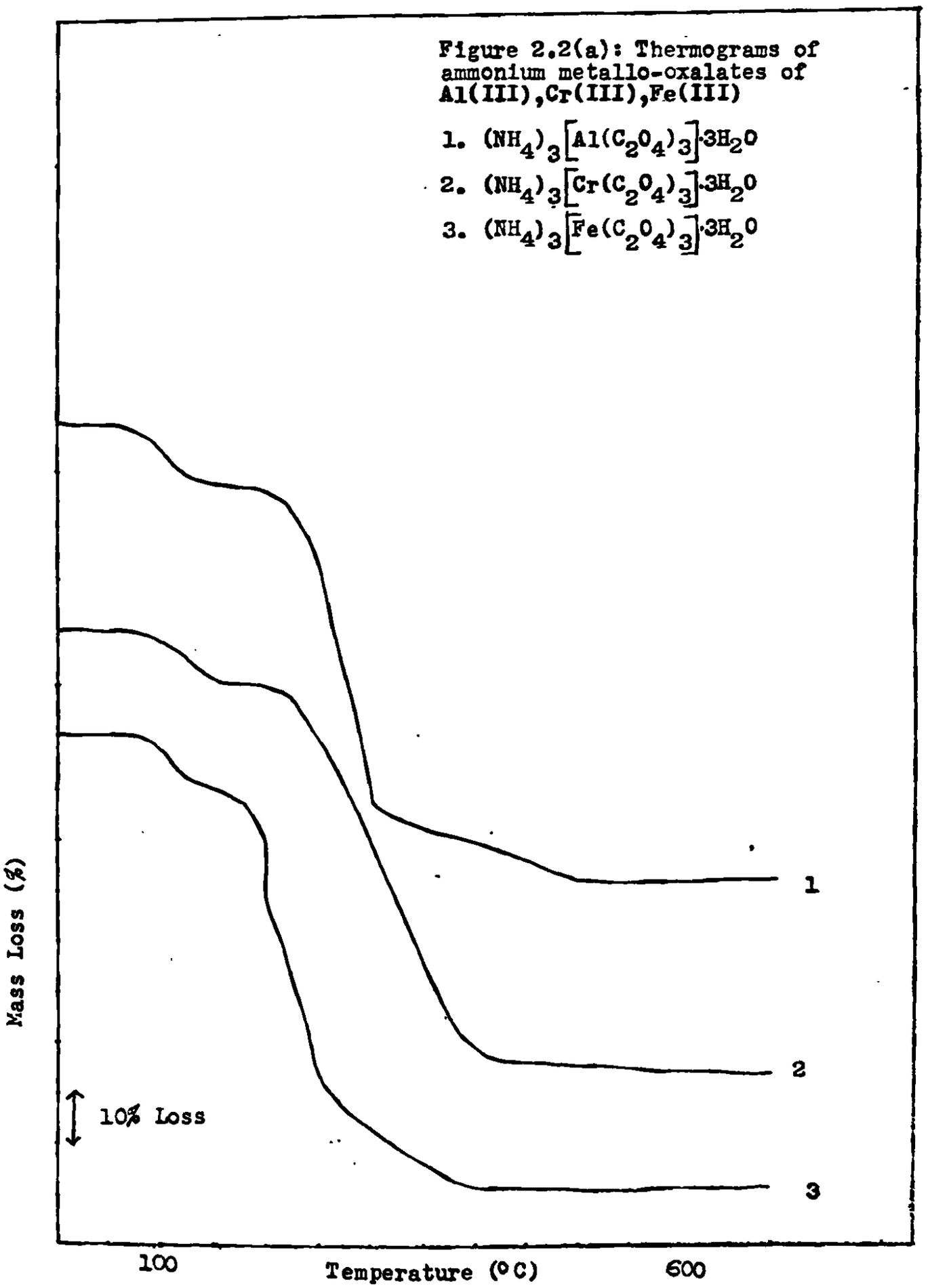


Figure 2.2(a): Thermograms of ammonium metallo-oxalates of Al(III),Cr(III),Fe(III)
1. $(NH_4)_3[Al(C_2O_4)_3]\cdot 3H_2O$
2. $(NH_4)_3[Cr(C_2O_4)_3]\cdot 3H_2O$
3. $(NH_4)_3[Fe(C_2O_4)_3]\cdot 3H_2O$
Mass Loss (%)
10% Loss
1
2
3
100
Temperature (°C)
600

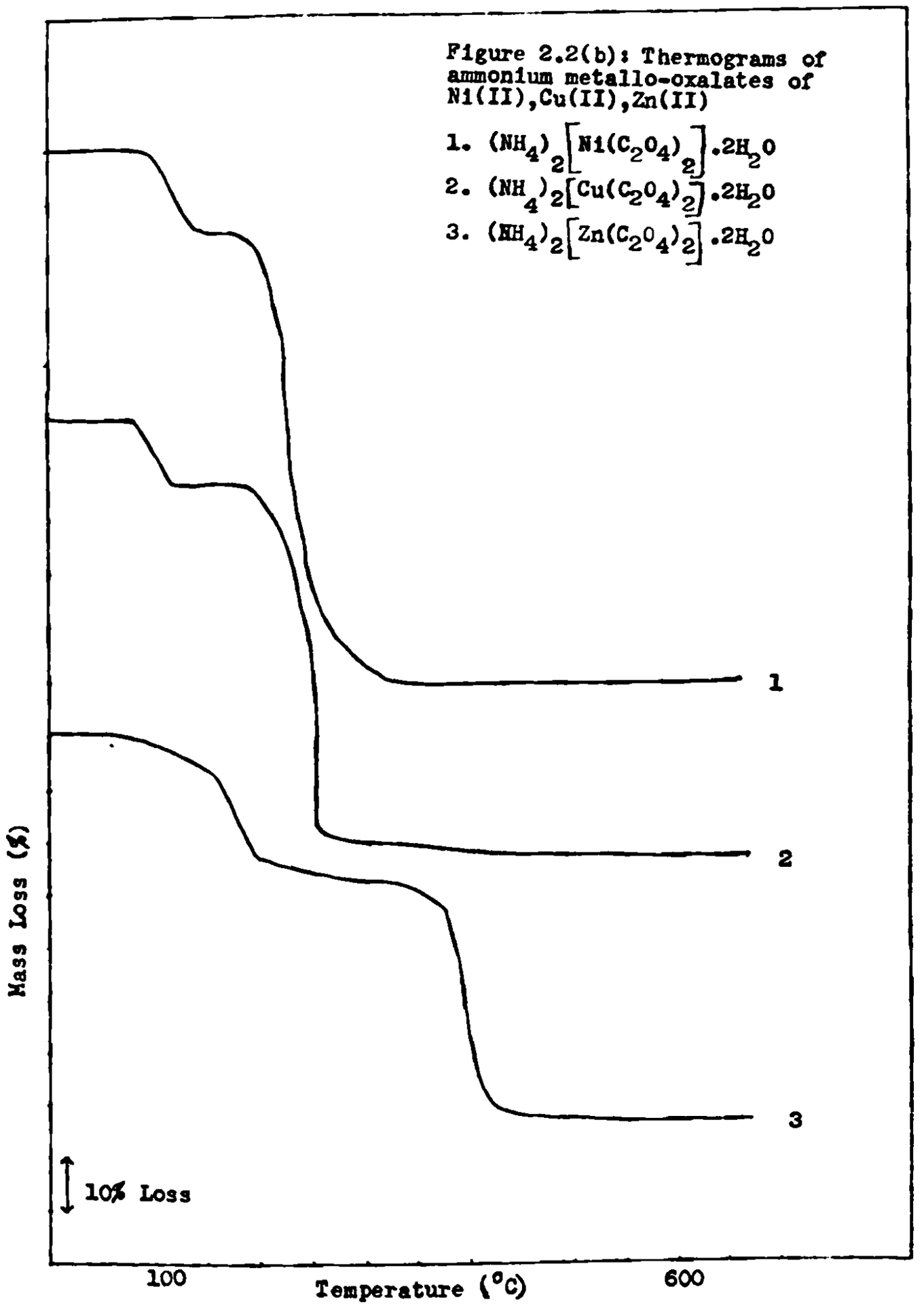


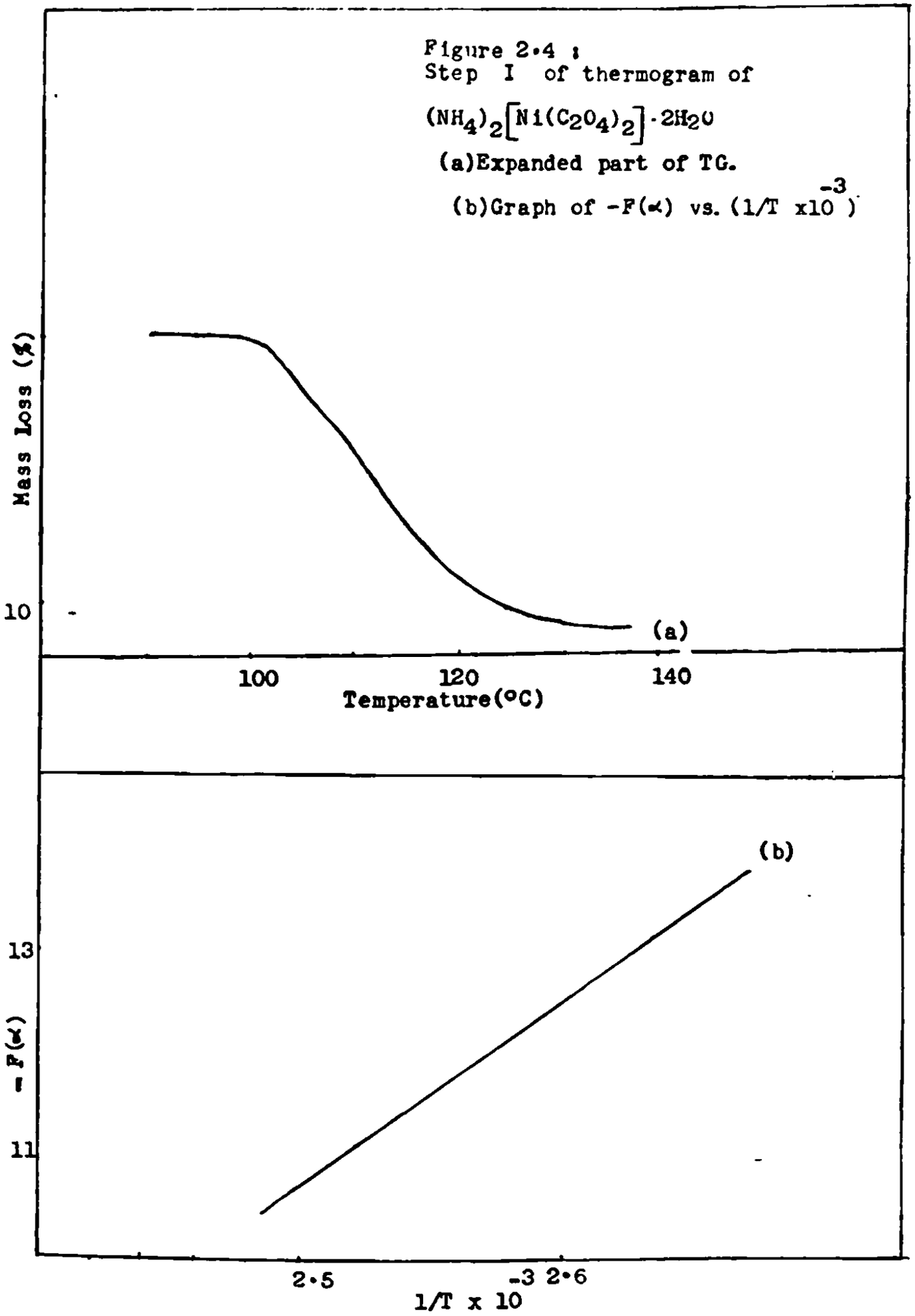
Figure 2.2(b): Thermograms of ammonium metallo-oxalates of Ni(II),Cu(II),Zn(II)
1. $(NH_4)_2[Ni(C_2O_4)_2].2H_2O$
2. $(NH_4)_2[Cu(C_2O_4)_2].2H_2O$
3. $(NH_4)_2[Zn(C_2O_4)_2].2H_2O$
1
2
3
Mass Loss (%)
10% Loss
100
Temperature (°C)
600

Figure 2·4 :
Step I of thermogram of

$(NH_4)_2[Ni(C_2O_4)_2]\cdot 2H_2O$

(a)Expanded part of TG.

(b)Graph of $-F(\alpha)$ vs. $(1/T \times 10^{-3})$



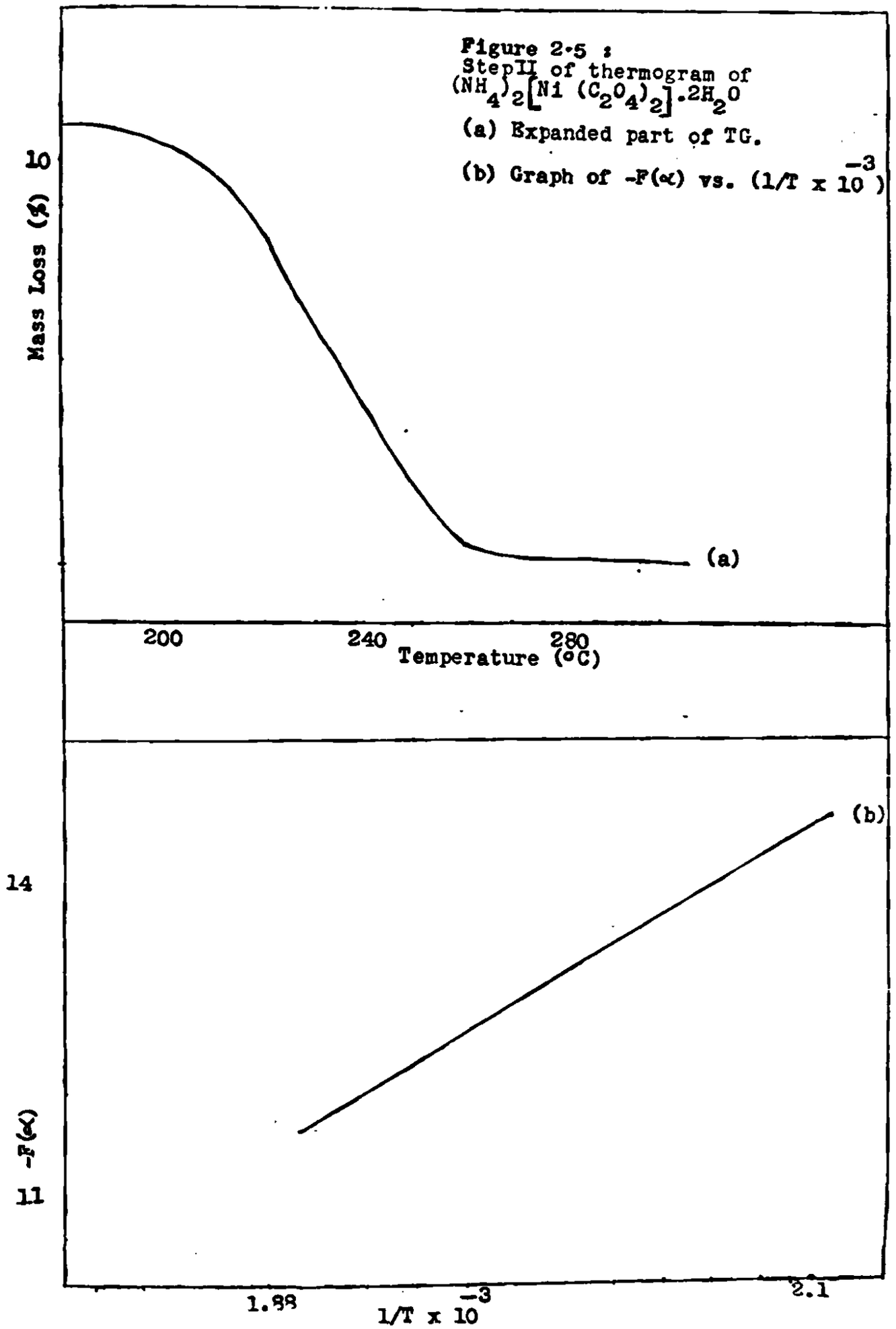


Figure 2·5 :
Step II of thermogram of $(NH_4)_2[Ni(C_2O_4)_2].2H_2O$

(a) Expanded part of TG.

(b) Graph of $-F(\alpha)$ vs. $(1/T \times 10^{-3})$

Table 2.2 : Information obtained for the first step of thermogram [Region I : 100-140 ^{o}C (dehydration)] for ammonium salt of oxalato nickelate (II)

Information obtained using computer programme:

Order = 0.95 Intercept = 4.183×10^{1}

Corr. coefficient = -9.792×10^{-1}

Activation energy E_a = 174.0 kJ mol^{-1}

No.	% wt.loss	T ^{o}C	$(1/T \times 10^{-3})^{*}$	F(α)
1	1.0	102.5	2.663	- 14.21
2	4.4	110	2.611	- 12.58
3	7.2	115	2.577	- 11.89
4	8.4	117.5	2.561	- 11.60
5	9.8	122.5	2.528	- 11.22
6	10.4	125	2.513	- 10.98

*Calculated after converting temperature into ^{o}K

Information obtained from graph :

$$\text{The slope of graph of } [F(\alpha) \text{ Vs. } 1/T] = \frac{-2.0}{0.1 \times 10^{-3}}$$

$$\therefore E_a = -\text{slope} \times R = 2.0 \times 10^{4} \times 8.314 = 16.628 \times 10^{4} \text{ J mol}^{-1}$$

$$= 166.28 \text{ kJ mol}^{-1}$$

Table 2.3 : Information obtained for the second step of thermogram [Region II : 200-280 ^{o}C (decomposition)] for ammonium salt of oxalato nickelate (II)

Information obtained using computer programme:

Order = 0.95 Intercept = 1.6212×10^{1}

Corr.coefficient = $- 9.981 \times 10^{-1}$

Activation energy 121.6 kJ mol^{-1}

No.	% Wt. loss	T ^{o}C	$(1/T \times 10^{-3})^{*}$	F(α)
1	18	200	2.114	- 14.79
2	23	210	2.070	- 14.26
3	36	220	2.028	- 13.48
4	53	230	1.988	- 12.86
5	69	240	1.949	- 12.39
6	91	255	1.894	- 11.62

*Calculated after converting temperature to ^{o}K

Information obtained from graph :

The slope of graph of [F(α) Vs 1/T] $= \frac{-2.0}{0.14 \times 10^{-3}}$

$= - 1.43 \times 10^{4}$

$\therefore E_a$ = - slope x R = $1.43 \times 10^{4} \times 8.314 = 11.89 \times 10^{4}$ J mol^{-1}

$= 118.9$ kJ mol^{-1}

Table 2.4 : Thermogravimetric study of ammonium salts metallo-oxalates

Complex (Composition based on the analysis)	Temperature (^{o}C)	% loss	Tentative assignment	Energy of activation (E_a) $kJ\ mol^{-1}$
$(NH_4)_3[Al(C_2O_4)_3] \cdot 3H_2O$	62-175	12.00	Loss of coordinated water (Calc.* : 13.54 %)	a. 76.4 b. 79.8
	200.525	76.00	Decomposition	a. 36.5 b. 30.7
	240***		Residue : 12.22 % (calculated** = 12.77 %)	
$(NH_4)_3[Cr(C_2O_4)_3] \cdot 3H_2O$	100-197	11.00	Loss of coordinated water (Calc.* : 12.74 %)	a. 18.9 b. 23.9
	300-362	74.00	Decomposition	a.133.4 b.129.3
	220***		Residue : 15.00 % (Calculated** = 17.92 %)	
$(NH_4)_3[Fe(C_2O_4)_3] \cdot 3H_2O$	65-145	10.00	Loss of coordinated water (Calc.* : 12.62 %)	a. 77.5 b. 69.3
	162-375	73.00	Decomposition	a. 37.4 b. 31.6
	220***		Residue : 16.00 % (Calculated** = 18.65 %)	

Contd ...

Table 2.4 (contd.)

Complex (Composition based on the analysis)	Temperature (°C)	% loss	Tentative assignment	Energy of activation (E_a) kJ mol^{-1}
$(NH_4)_2[Ni(C_2O_4)_2] \cdot 2H_2O$	100-125	15.00	Loss of coordinated water (Calc.*: 11.74 %)	a. 174.0 b. 166.3
	200-255	75.00	Decomposition	a. 121.6 b. 118.9
			Residue : 2.75 % (Calculated** = 24.35 %)	
	195***			
$(NH_4)_2[Cu(C_2O_4)_2] \cdot 2H_2O$	100-125	12.00	Loss of coordinated water (Calc.*: 11.56 %)	a. 192.4 b. 189.2
	200-280	72.0	Decomposition	a. 28.4 b. 27.7
			Residue : 22.51 (Calculated** = 25.53 %)	
	225***			

Contd ...

Table 2.4 (contd.)

Complex (Composition based on the analysis)	Temperature (^{o}C)	% Loss	Tentative assignment	Energy of activation (E_a)
$(NH_4)_2[Zn(C_2O_4)_2] \cdot 2H_2O$	150-185	16.00	Loss of coordinated water (Calc.* : 11.49 %)	a. 67.6 b. 66.5
	375-405	48.00	Decomposition	a. 89.5 b. 91.5
			Residue : 26.00 % (Calculated** = 25.97 %)	
	375***			

*Loss calculated for coordinated water ($3H_2O$ for M^{III}- complex and $2H_2O$ for M^{II}- complex)

**% of Residue calculated assuming metal oxide.

***Procedural decomposition temperature

a. E_a calculated using computer programme.

b. E_a calculated using graph of $F(\alpha)$ Vs. $1/T$.

For the analysis of Fe(III) or Cu(II) complex, instead of using separate amounts of the complex for estimating $C_2O_4^{2-}$ and M^{n+} individually, one can use the same amount for the estimation of both as per the following method[1,2,18].

The exactly weighed amount of complex is dissolved in water and diluted to known volume. The aliquot of this solution is used for estimating $C_2O_4^{2-}$ by permanganometry. After the end point the addition of $KMnO_4$ is stopped. The same solution is utilized further for estimating metal [Fe(III) by permanganometry while Cu(II) by iodometry] by following proper precautions of redox conditions and pH. We have tried this procedure of estimation also and got good results.

The TGA curves indicate that the salts loose water molecules in the temperature range 60 - 200 ^{o}C and then starts their decomposition to give metal oxides by loosing probably ammonia and carbon dioxide (Refer the equations given). The E_a values for dehydration and decomposition are found to be 18 to 190 and 27 to 130 kJ mol^{-1} respectively for these complexes. The procedural decomposition temperatures indicate that the metal ions can be arranged as per the increasing thermal stability of the complex in the order as :

$$Ni(II) \leqslant Fe(III) < Cr(III) < Cu(II) < Al(III) < Zn(II).$$

An abnormal observation is noted in case of Ni(II)--complex where we get the percentage of residue very much less than the expected value. Such loss is, however, not seen complexes such as $NiC_2O_4 \cdot 2H_2O$ or $Ni\left[Ni(C_2O_4)_2\right] \cdot 2H_2O$[19]. This observation, thus, seems to be an interesting thing which requires further detailed investigation.

2.6 MERITS OF THE STUDY

Our study suggests that ammonium salts of metallo--oxalates may be better than potassium salts. The probable reasons for this are as follows: (i) The thermal decomposition gives pure metal oxide. One can recover the metal from it. (ii) The thermogram obtained is useful for calculation of percentage of metal (iii) During TGA of potassium salts, the sample holder is affected (due to formation of K_2O). This drawback is eliminated when ammonium salt is used. (iv) The analysis of NH_4^+ can be easily performed.

The experimental work suggested in this chapter is useful to gain experience in the preparation of some metal complexes, their analysis (involving different types of titrimetric methods) and their thermogravimetric study. The study of any one of these complexes gives experience of using different techniques and utilizing the experimental data obtained for purposeful investigation within reasonable time.

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chapter 3

TITRIMETRIC ESTIMATION OF CALCIUM AND PHOSPHATE IN DIETARY SUPPLEMENT TABLETS

If from any art you take away that which concerns weighing, measuring and arithmetic, how little is left of that art !

— Plato

CHAPTER 3

TITRIMETRIC ESTIMATION OF CALCIUM AND PHOSPHATE IN DIETARY SUPPLEMENT TABLETS

ABSTRACT

An experiment involving estimation of calcium and phosphate is suggested which enables the student to gain experience in three types of standard titrimetric estimations, namely, neutralisation method (alkalimetry), redox method (permanganometry) and complexometry (EDTA titrations). It also gives two methods for separating and estimating one of these constituents in presence of other, which otherwise is erroneous. The results show accuracy and reproducibility. The methods have been used for the estimation of calcium and phosphate from salts and some dietary supplement tablets.

3.1 INTRODUCTION

The teaching of titrimetric analysis has now introduced purposeful exercises involving analysis of consumer products such as drugs. This necessiates the setting of experiments which familiarize the students with as wide a range of titrimetric reactions as possible. The experiment for estimation of calcium and phosphate in dietary supplement tablets is suggested here. It is profitable as it adds to variety in the laboratory programme, enables the students to gain experience in analysis of a familiar sample of known composition and increasestheir awareness about the importance of chemistry of consumer products.

For estimation of Ca^{2+} and PO_4^{3-} from dietary supplement tablets, they are disintegrated using nitric acid (1:1) and concentrated hydrochloric acid (so that organic matter is removed). The solution is diluted to a known volume and aliquots from it may be used for the analysis by either of the two methods suggested here.

Any of these methods for the estimation of calcium and phosphate involve separation and combined use of different types of titrimetry, namely, acid-base, redox and complexometry. This otherwise, is not possible due to the precipitation of their salt. The analysis of a sample using both the methods

will require three 3-h laboratory periods.

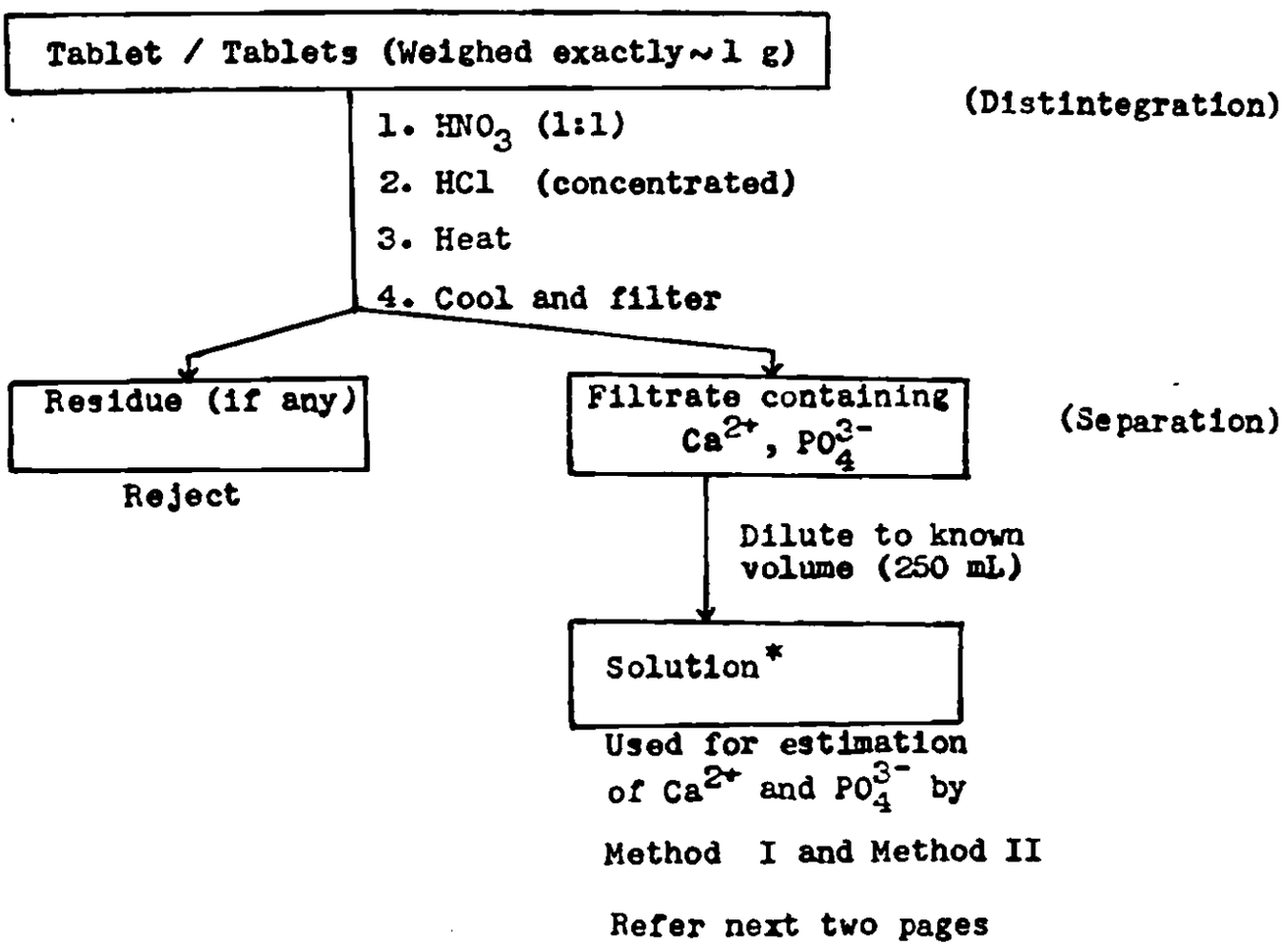
The flow sheet and reactions for the experiment are given herewith.

Method I

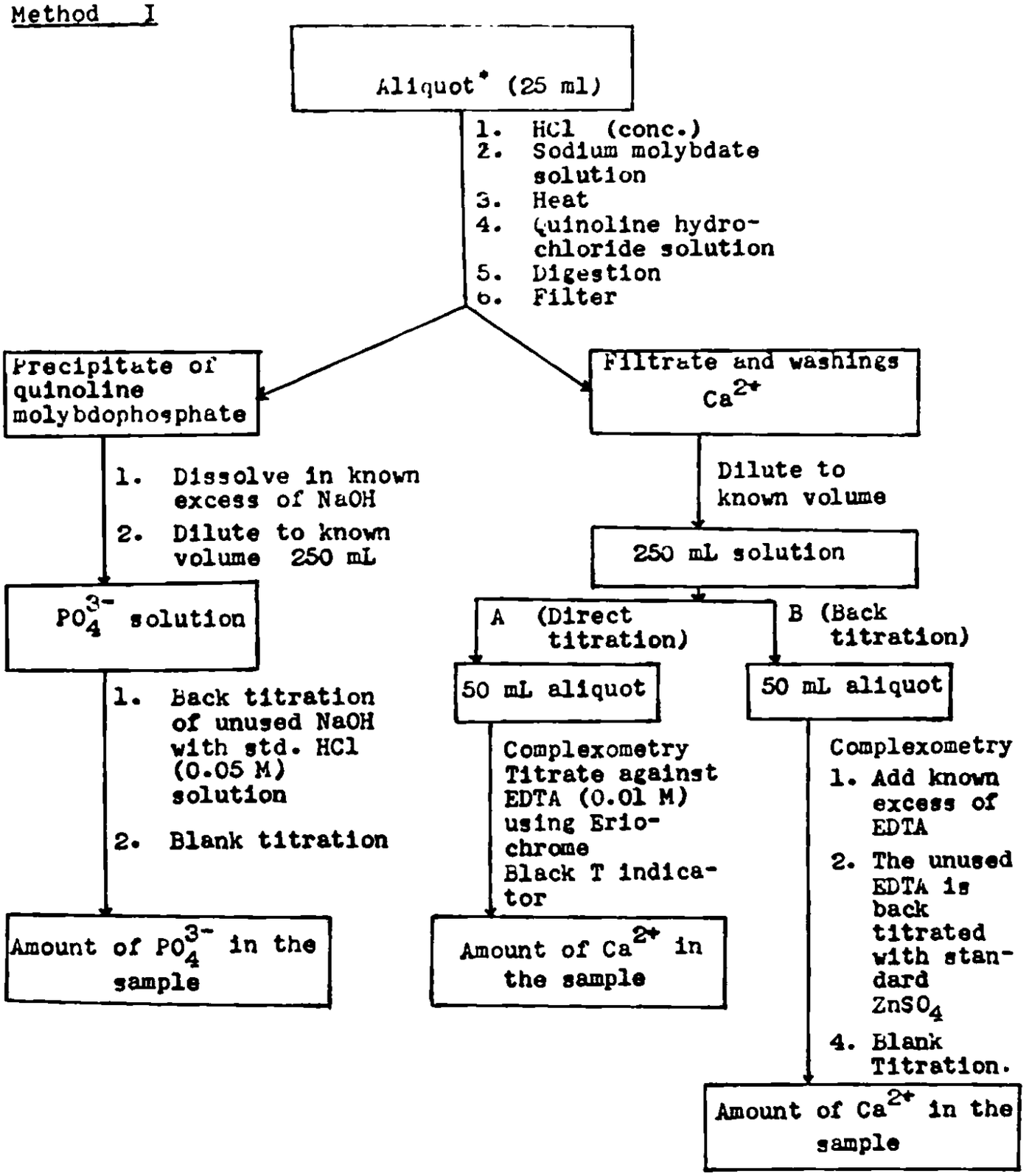
In this method phosphate is separated as quinoline molybdophosphate precipitate[1]. For this, to the solution containing Ca^{2+} and PO_4^{3-}, concentrated hydrochloric acid, sodium molybdate and quinoline hydrochloride reagent are added successively. The yellow precipitate is digested on waterbath. It is filtered through Whatman filter paper No. 41. The precipitate is dissolved in known volume of standard solution of sodium hydroxide. The excess of sodium hydroxide is back titrated with standard hydrochloric acid using phenolphthalein indicator.

The filtrate and washings obtained after removing the precipitate of quinoline molybdophosphate, are collected together. To this solution liquor ammonia is added dropwise till the white turbidity dissolves and pH of the solution becomes about 10. Then the solution is diluted to definite volume with distilled water. The aliquots from this solution are used for estimation of calcium using EDTA solution (either directly or by back titration with standard zinc sulphate solution[2]).

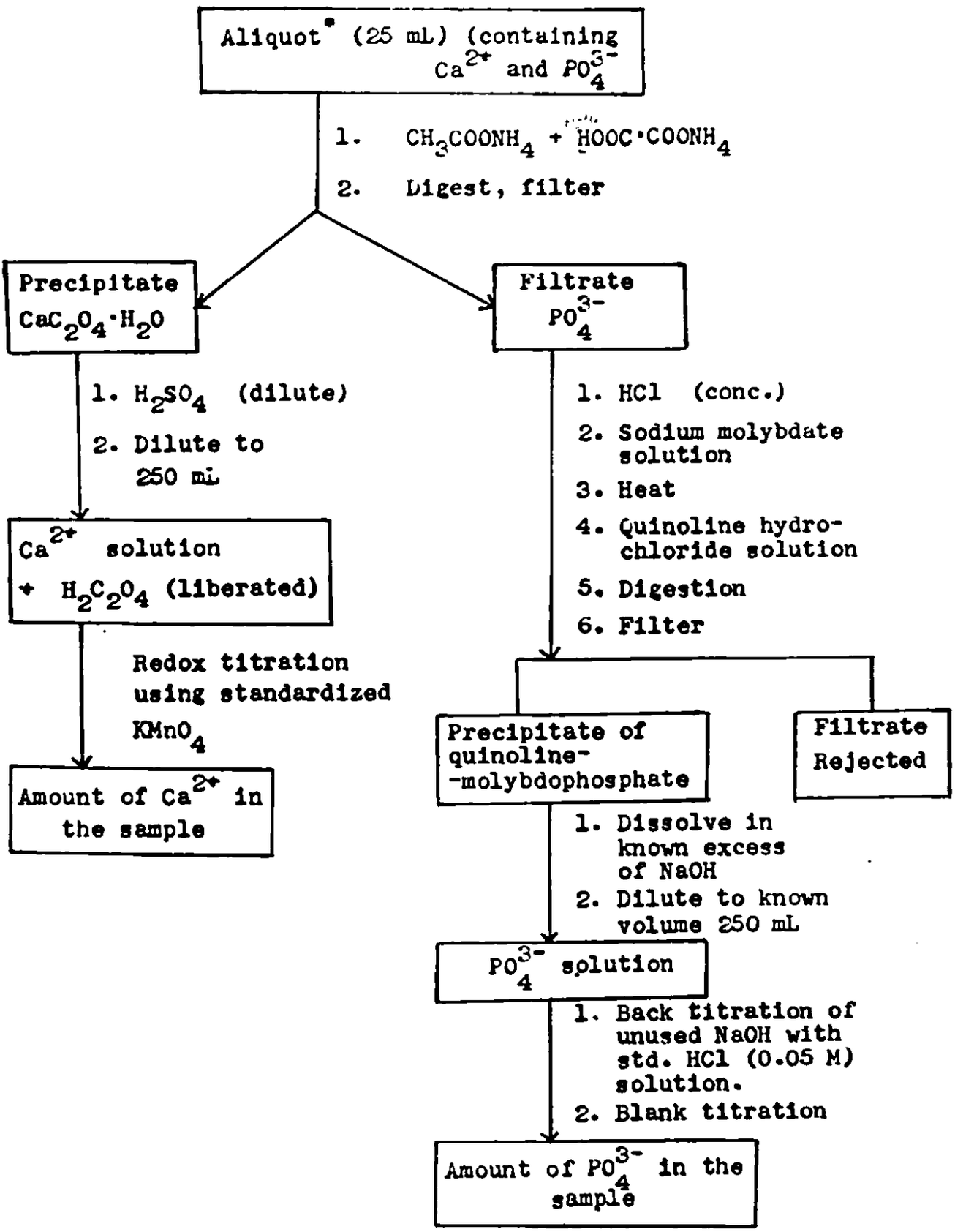
Flow sheet


Tablet / Tablets (Weighed exactly ~ 1 g)
(Distintegration)
1. HNO_3 (1:1)
2. HCl (concentrated)
3. Heat
4. Cool and filter
Residue (if any)
Reject
Filtrate containing Ca^{2+}, PO_4^{3-}
(Separation)
Dilute to known volume (250 mL)
Solution*
Used for estimation of Ca^{2+} and PO_4^{3-} by
Method I and Method II
Refer next two pages

Method I


Aliquot* (25 ml)
1. HCl (conc.)
2. Sodium molybdate solution
3. Heat
4. Quinoline hydrochloride solution
5. Digestion
6. Filter
Precipitate of quinoline molybdophosphate
Filtrate and washings Ca^{2+}
1. Dissolve in known excess of NaOH
2. Dilute to known volume 250 mL
Dilute to known volume
PO_4^{3-} solution
250 mL solution
A (Direct titration)
B (Back titration)
1. Back titration of unused NaOH with std. HCl (0.05 M) solution
2. Blank titration
50 mL aliquot
50 mL aliquot
Complexometry Titrate against EDTA (0.01 M) using Eriochrome Black T indicator
Complexometry
1. Add known excess of EDTA
2. The unused EDTA is back titrated with standard $ZnSO_4$
4. Blank Titration.
Amount of PO_4^{3-} in the sample
Amount of Ca^{2+} in the sample
Amount of Ca^{2+} in the sample

Method II

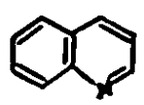

Aliquot* (25 mL) (containing Ca^{2+} and PO_4^{3-}
1. CH_3COONH_4 + $HOOC \cdot COONH_4$
2. Digest, filter
Precipitate $CaC_2O_4 \cdot H_2O$
Filtrate PO_4^{3-}
1. H_2SO_4 (dilute)
2. Dilute to 250 mL
1. HCl (conc.)
2. Sodium molybdate solution
3. Heat
4. Quinoline hydrochloride solution
5. Digestion
6. Filter
Ca^{2+} solution + $H_2C_2O_4$ (liberated)
Redox titration using standardized $KMnO_4$
Amount of Ca^{2+} in the sample
Precipitate of quinoline-molybdophosphate
Filtrate Rejected
1. Dissolve in known excess of NaOH
2. Dilute to known volume 250 mL
PO_4^{3-} solution
1. Back titration of unused NaOH with std. HCl (0.05 M) solution.
2. Blank titration
Amount of PO_4^{3-} in the sample

Equations

Disintegration to tablet $PO_4^{3-} \xrightarrow[\text{acid}]{3H^+} H_3PO_4$

Organic matter $\xrightarrow[2.\ HCl]{1.\ HNO_3}$ volatile products.

Estimation of Phosphate (Quinoline molybdate method)



Quinoline

$+ HCl \longrightarrow [(C_9H_7N)H]^+ Cl^-$

Quinoline hydrochloride

$H_3PO_4 + 12\ Na_2MoO_4 + 3\ (C_9H_7N)H^+Cl^- + 24\ HCl \longrightarrow$

sodium molybdate

$(C_9H_7N)_3H_3[PO_4 \cdot 12MoO_3] + 24\ NaCl + 12\ H_2O + 3HCl$

Quinoline molybdophosphate (yellow)

$(C_9H_7N)_3H_3[PO_4 \cdot 12\ MoO_3] + 26OH^- \longrightarrow 3\ (C_9H_7N) +$

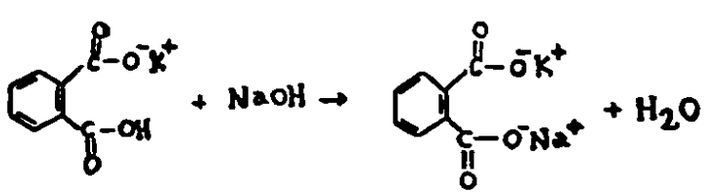
(known excess of NaOH)

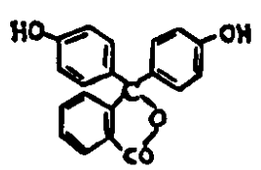
$12\ MoO_4^{2-} + HPO_4^{2-} + 14\ H_2O$

Titration : $NaOH + HCl \longrightarrow NaCl + H_2O$

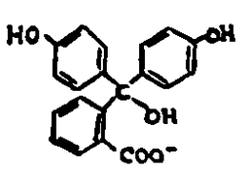
(unused) (std.soln.)

Standardization of NaOH using Potassium-hydrogen phthalate

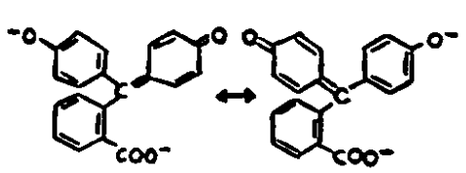




Phenolphthalein (colourless)



triphenyl carbinol ion



Phenolphthalein ion (Red)

Estimation of calcium

Standardization of EDTA : M^{2+} + In ⟶ MIn (wine red)
Indicator

$$MIn + Na_2C_{10}H_{14}N_2O_8 \longrightarrow \left[M(C_{10}H_{12}N_2O_8)\right]^{2-} + 2H^+ + 2Na^+ + In^-$$

Na_2- EDTA; M - EDTA; (dissociated) (blue)

(where M ≡ Zn^{2+}, Mg^{2+})

Method I A

Direct titration of Ca^{2+} with EDTA using Eriochrome Black T indicator.

$$Na(C_{20}H_{12}N_2O_7S) \xrightarrow{pH \sim 10} (C_{20}H_{11}N_2O_7S)$$

$Na - H_2D$; HD^{2-}

Eriochrome Black T

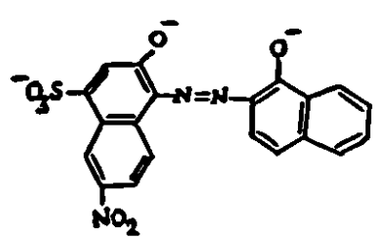
$$M^{2+} + HD^{2-} \xrightarrow{pH \sim 10} MD^- + H^+$$

blue ; red

where M^{2+} ≡ Ca^{2+}, Zn^{2+}

and

D ≡ $C_{20}H_{10}N_2O_7S$ ≡



Method I B

Back titration of excess (unused) EDTA with standard zinc sulphate solution.

Ca^{2+} + EDTA (known excess) $\longrightarrow$ Ca(EDTA) complex

EDTA unused + Zn^{2+} (std.soln.) $\longrightarrow$ Zn(EDTA) complex

} (Back titration)

Zn^{2+} + EDTA (known excess as in back titration) $\longrightarrow$ Zn(EDTA) complex (Blank titration)

Method II

Oxalate method, titration with standard $KMnO_4$ solution

Standardization of $KMnO_4$:

$$Na_2C_2O_4 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2C_2O_4$$

$$5\ H_2C_2O_4 + 2MnO_4^- + 3\ H_2SO_4 \longrightarrow 2\ Mn^{2+} + 3\ SO_4^{2-} + 8\ H_2O + 10\ CO_2$$

Precipitation of Ca^{2+} ions as calcium oxalate.

$$Ca^{2+} + 2\ C_2O_4^{2-} \longrightarrow CaC_2O_4$$

$$CaC_2O_4 + H_2SO_4 \longrightarrow CaSO_4 + H_2C_2O_4$$ (dissolution of ppt. of CaC_2O_4)

$$5\ H_2C_2O_4 + 2\ MnO_4^- + 3\ H_2SO_4 \longrightarrow 2\ Mn^{2+} + 3\ SO_4^{2-} + 8\ H_2O + 10\ CO_2$$

(titration with $KMnO_4$).

Method II

In this method, from the solution containing Ca^{2+} and PO_4^{3-} ions, Ca^{2+} ions are separated as calcium oxalate precipitate, which is then dissolved in hot dilute sulphuric acid solution. Oxalic acid produced is titrated with previously standardized potassium permanganate solution. From the volume of potassium permanganate solution, amount of Ca^{2+} ions is calculated. From the filtrate (obtained after removing precipitate of calcium oxalate), PO_4^{3-} ions are precipitated as quinoline molybdophosphate and estimated by alkalimetry (as described in Method I).

3.2 THEORETICAL BACKGROUND

Disintegration of drug sample

In the disintegration the use of acid mixture is found to be necessary in order to get clear solution and to remove the organic matter (which may interfere in $KMnO_4$ - titration).

Estimation of PO_4^{3-}

In the proposed methods, phosphate is estimated[1] by "Quinoline molybdophosphate method" which is better than the conventional "Ammonium molybdophosphate method". In the conventional method, PO_4^{3-} ions are precipitated as ammonium

molybdophosphate complex. The precipitate of $(NH_4)_3\left[PO_4 \cdot 12(MoO_3)\right]$ is treated with standard solution of sodium hydroxide. The excess of sodium hydroxide is back titrated with standard hydrochloric acid solution using phenolphthalein indicator. However, the results are less accurate due to liberation of ammonia.

The advantages of the reagent containing sodium molybdate and quinoline are - (i) the precipitate formed, quinoline molybdophosphate is less soluble and has a constant composition (ii) Quinoline is a weak base and does not interfere in the titration.

Estimation of Ca^{2+}

Complexometric (i.e. EDTA) titrations :

Direct method :

When Ca^{2+} ions are titrated with EDTA solution, a relatively stable calcium-complex is formed.

$$Ca^{2+} + H_2Y^{2-} \rightleftharpoons CaY^{2-} + 2\,H^{+} \quad \text{(where } Y \equiv \text{EDTA)}$$

With Ca^{2+} ions alone, end point with Eriochrome Black T indicator is not sharp. The EDTA complex formed by Mg^{2+} ions is less stable.

$$Mg^{2+} + H_2Y^{2-} \rightleftharpoons MgY^{2-} + 2H^{+}$$

Also magnesium - indicator complex is more stable than calcium - indicator complex but less stable than magnesium - EDTA complex. Therefore, during the titration of a solution containing Ca^{2+} and Mg^{2+} ions with EDTA, using Eriochrome Black T indicator, EDTA reacts first with Ca^{2+} ions, then with Mg^{2+} and finally with magnesium - indicator complex. Since magnesium - indicator complex is wine red and free indicator is blue (in the pH range 7 to 11), the colour of the solution changes from wine red to blue.

$$\underset{\text{(red)}}{MgD^-} + H_2Y^{2-} \rightleftharpoons MgY^{2-} + \underset{\text{(blue)}}{HD^{2-}} + H^+$$

(where D is Eriochrome Black T indicator).
If Mg^{2+} ions are not present in a solution containing Ca^{2+} ions, then they are added in one of the following manners - (i) little $MgCl_2$ is added to EDTA solution before it is standardized or (ii) little Mg-EDTA solution (1 %) is added to buffer solution or (iii) little Mg-EDTA (MgY^{2-}) solution is added to Ca^{2+} ion solution.

The interference due to metal ions like Cu^{2+}, Mn^{2+} etc. in this method can be overcome by using suitable masking agents[1].

Back titration method :

To the aliquot containing Ca^{2+}, a known excess of EDTA

solution is added and the unreacted EDTA is estimated using standard Zn^{2+} or Mg^{2+} solution using Eriochrome Black T indicator[1].

Redox titrations (i.e. permanganometry) :

From an aliquot containing Ca^{2+}, calcium is precipitated as calcium oxalate using ammonium oxalate. The precipitate is filtered, washed with water and then dissolved in hot dilute sulphuric acid. The liberated oxalic acid is estimated using standardized potassium permanganate solution.

3.3 EXPERIMENTAL

The setting of the procedure is done by using standard solutions of Ca^{2+} and PO_4^{3-}, their synthetic mixtures and a salt of known composition. The detailed procedure is given below and the results are given in Table 3.1 to 3.3. Some of the well-known dietary supplement tablets containing calcium and phosphate are used for the analysis. All the reagents and chemicals used are of Analar or equivalent grade.

1. Estimation of PO_4^{3-}
2. Estimation of Ca^{2+}
3. Estimation of PO_4^{3-} and Ca^{2+} together from synthetic mixture and a salt.
4. Estimation of PO_4^{3-} and Ca^{2+} from dietary supplement tablets.

3.3.1 Estimation of PO_4^{3-}

Reagents

Aqueous solution of sodium molybdate dihydrate (15 %) : 75 g of Na_2MoO_4, $2H_2O$ in 500 mL.

Quinoline hydrochloride solution : 20 mL of redistilled quinoline solution is added to 800 mL hot water containing 20 mL concentrated HCl. The solution is stirred well, cooled and filtered. It is then diluted to one litre with distilled water.

HCl solution (0.05 M) : 4.5 mL of concentrated hydrochloric acid per litre.

NaOH solution (0.5 M) : 20 g of sodium hydroxide per litre.

NaOH solution (0.05 M) : 100 mL of NaOH (0.5 M) diluted to one litre.

Stock solution of PO_4^{3-} (1 mg PO_4^{3-} / mL) : 1.4330 g of potassium dihydrogen phosphate (KH_2PO_4, molecular weight 136.09) is dissolved in one litre of distilled water.

Standard aqueous solution of potassium hydrogen phthalate (0.05 M) : 2.5525 g per 250 mL.

Phenolphthalein indicator : Alcoholic solution (1 %).

Procedures :

Standardization of sodium hydroxide solution (approx. 0.05 M): An aliquot of 25 mL of potassium hydrogen phthalate solution (0.05 M) is titrated against sodium hydroxide solution (approx. 0.05 M) using phenolphthalein indicator till the end point colourless to pink is obtained.

Mean titration reading = 22.8 mL of NaOH
Exact molarity of NaOH solution = 0.05485

Standardization of hydrochloric acid solution (approx 0.05 M) : An aliquot of 25 mL of HCl solution (approx. 0.05 M) is titrated against standard NaOH solution (0.05485 M) using phenolphthalein indicator till the end point colourless to pink is obtained.

Mean titration reading = 24.4 mL of NaOH solution
Exact molarity of HCl solution = 0.05357

Determination of concentration of stock solution of PO_4^{3-} : An aliquot of 25 mL of PO_4^{3-} solution (1 mg PO_4^{3-} / mL) is taken in the beaker and 25 mL of concentrated HCl and 18 mL of sodium molybdate solution are added to it. The solution is heated and quinoline reagent (35 mL) is added slowly with constant stirring. The yellow precipitate is digested on waterbath for 15 min. and then filtered through Whatman filter

paper No. 41. It is washed with about 10 mL of 1:9 HCl solution and then with distilled water till the washings are acid free. The precipitate is dissolved in 25 mL of standard NaOH solution (0.5485 M). The solution and washings are collected in a volumetric flask and diluted to 250 mL with distilled water. An aliquot of 25 mL of this diluted solution is titrated with standard HCl solution (0.05357 M) using phenolphthalein indicator (end point as pink to colourless). This is the reading for back titration.

Blank Titration : An aliquot of 25 mL of NaOH solution (0.5485M) is diluted to 250 mL and 25 mL of this diluted NaOH solution is titrated with standard HCl solution (0.05357 M) using phenolphthalein indicator till the end point pink to colourless is obtained.

Mean titration readings:

Blank titration : 25.6 mL of 0.05357 M HCl

Back titration : 13.1 mL of 0.05357 M HCl

$\therefore$ Difference : 12.5 mL of 0.05357 M HCl.

1 mL of 0.5 M HCl $\equiv$ 1.830 mg of PO_4^{3-}

$\therefore$ 12.5 mL of 0.05357 M HCl $\equiv$ 2.451 mg of PO_4^{3-}

Thus 25 mL from diluted solution contains 2.451 mg of PO_4^{3-}

$\therefore$ 250 mL of diluted solution contains 24.517 mg of PO_4^{3-}.

The results obtained for different volumes of stock solution of PO_4^{3-} are summarized in Table 3.1.

Table 3.1 : Determination of concentration of stock solution of phosphate

mL of stock solution of PO_4^{3-}	(Blank-Back) titration reading (mL)	Amount of PO_4^{3-} (mg)	mg / mL of PO_4^{3-}
25.0	12.5	24.51	0.9804
20.0	10.1	19.77	0.9885
15.0	7.8	15.21	1.0140
			Mean 0.9943

3.3.2 Estimation of Ca^{2+}

3.3.2a Complexometric titrations :

Reagents :

Preparation of Mg-EDTA solution :

It is prepared by mixing equal volumes of 0.2 M solutions of EDTA and $MgSO_4$. The solution is neutralised to pH 8 to 9, by adding NaOH solution (phenolphthalein should just give red colour). The small quantity of above solution is taken, few of drops of buffer solution (pH 10) and few drops of Eriochrome Black T are added. A violet colour should be

produced which turns blue on the addition of a drop of EDTA and red on the addition of a single drop of 0.01 M $MgSO_4$ solution. This confirms equimolarity of Mg and EDTA. If the condition is not satisfied, little EDTA or $MgSO_4$ solution is to be added.

Stock solution of Ca^{2+} ions (1 mg / mL) : 1.25 g of $CaCO_3$ is dissolved in water acidified with little concentrated HCl. The solution is diluted to 500 mL with distilled water.

EDTA solution (0.01 M approx.) : 37.225 g of Na_2-EDTA is dissolved in distilled water. The solution is diluted to 10 litre.

Standard zinc sulphate (0.01 M) solution : 0.718 g of pure $ZnSO_4 \cdot 7H_2O$ is dissolved in distilled water and the solution is diluted to 250 mL.

Buffer solution (pH 10) : 17.5 g of pure NH_4Cl is dissolved in 142 mL of strong ammonia. The solution is diluted to 250 mL.

Erichrome Black T indicator : 0.5gindicator is dissolved in 100 mL alcohol.

Procedures :

Standardization of EDTA solution :

An aliquot of 25 mL of standard zinc sulphate solution (0.01 M) [The exact molarity of the solution we used is 0.009918 M] is taken in the titration flask, neutralised with dilute ammonia and to it ~ 5 mL of buffer solution (pH 10) and 5 drops of Eriochrome Black T indicator are added. The solution is titrated with EDTA solution till the end point wine red to blue colour is obtained.

Mean titration reading = 23.3 mL of EDTA solution

Exact molarity of EDTA = 0.01065

Estimation of calcium by direct titration with EDTA solution :

An aliquot of 5.0 mL of Ca^{2+} ion solution (1 mg/mL) is taken in the titration flask and neutralised with dilute ammonia. To it 5 mL of Mg-EDTA solution and 5 mL of buffer solution (pH 10) are added. The solution is titrated with EDTA solution using Eriochrome Black T.

Mean titration reading :

11.3 mL of 0.01065 M EDTA

1 mL of 1 M EDTA ≡ 40.08 mg of Ca^{2+}

∴ 11.3 mL of 0.01065 M EDTA ≡ 4.82 mg of Ca^{2+}

Thus 5 mL of stock solution contains 4.82 mg of Ca^{2+}

The results obtained for different volumes of stock solution of Ca^{2+} are summarized in Table 3.2.

Table 3.2 : Determination of concentration of stock solution of calcium

mL of stock solution of Ca^{2+}	Mean titration reading (mL)	Amount of Ca^{2+} (mg)	mg / mL of Ca^{2+}
5.0	11.3	4.82	0.9640
10.0	23.4	9.99	0.9986
15.0	35.9	15.32	1.0212
			Mean 0.9946

Estimation of calcium by back titration with standard zinc sulphate solution :

An aliquot of 5 mL of Ca^{2+} ion solution (1 mg / mL) is taken in the titration flask and neutralised with dilute ammonia. To it exactly 25 mL of EDTA solution (0.01065 M) and 5 mL of buffer solution (pH 10) are added. The excess of EDTA is back titrated with standard zinc sulphate solution (0.009918 M) using Eriochrome Black T indicator until the end point, blue to wine red colour, is obtained. Blank titration

is carried out by titrating 25 mL of EDTA solution with zinc sulphate solution using Eriochrome Black T indicator. From the difference in readings (Blank-Back), the amount of calcium is calculated.

Mean titration readings :

Blank titration : 26.8 mL of 0.009918 M $ZnSO_4$ solution

Back titration : 14.4 mL of 0.009918 M $ZnSO_4$ solution

Difference : 12.4 mL of 0.009918 M $ZnSO_4$ solution ≡ 11.6 mL of EDTA solution (0.01065 M)

1 mL of 1 M EDTA ≡ 40.08 mg of Ca^{2+}

∴ 11.6 mL of 0.01065 M EDTA ≡ 4.9519 mg of Ca^{2+}

Thus 5 mL of stock solution contains 4.95 mg of Ca^{2+}

3.3.2b Redox titrations[2] :

Reagents :

Aqueous solution of ammonium acetate (7.2 %)

Aqueous solution of ammonium oxalate (1 %)

Aqueous solution of potassium permanganate (approx. 0.1 N) (3.16 g per litre).

Standard sodium oxalate solution (0.1 N) : 1.225 g of pure A.R. grade sodium oxalate is dissolved in distilled water and the solution is diluted to 250 mL.

Sulphuric acid (2 N).

Procedures :

Standardization of $KMnO_4$ solution

An aliquot of 10 mL of standard sodium oxalate solution (0.1 N) is taken in the titration flask. After adding 25 mL of sulphuric acid (2 N) to it, the solution is warmed and titrated with potassium permanganate solution (approx. 0.1 N) until the permanent pink colour is obtained. From the titration reading exact normality of $KMnO_4$ is calculated.

Mean titration reading = 9.9 mL of $KMnO_4$ solution
Exact normality of $KMnO_4$ solution = 0.1010

Estimation of Ca^{2+} using $KMnO_4$

To an aliquot of 5 mL of stock solution of Ca^{2+} (1 mg/mL), taken in the beaker, 15 mL of ammonium acetate solution (7.2 %) is added. The solution is heated and 15 mL of ammonium oxalate solution (1 %) is added to precipitate calcium oxalate. The precipitate is digested for 15 min. on water bath and then filtered through Whatman filter paper No. 41. The precipitate is washed with small amount of distilled water and then dissolved in 25 mL of hot sulphuric acid solution (2 N). The liberated oxalic acid is titrated with potassium permanganate solution (0.1010 N) until permanent

faint pink colour is obtained.

Mean titration reading = 2.5 mL of 0.1010 N $KMnO_4$ solution

1 mL of 1 N $KMnO_4$ solution ≡ 20.04 mg of Ca^{2+}

∴ 2.5 mL of 0.1010 N $KMnO_4$ solution ≡ 5.0601 mg of Ca^{2+}

Thus 5 mL of stock solution contains 5.06 mg of Ca^{2+}

3.3.3 Estimation of calcium and phosphate together

Analysis of synthetic mixture :

The synthetic mixture for analysis (40 mL) can be prepared by mixing known volumes of stock solutions of Ca^{2+} and PO_4^{3-} (each one ranging in between 5 to 35 mL).

Method I

Estimation of PO_4^{3-} :

From the mixture taken, PO_4^{3-} ions are separated as described in article 3.3.1. The precipitate of quinoline molybdophosphate complex is dissolved in exactly 25 mL of sodium hydroxide (0.5 M) solution and the solution is diluted to 250 mL. This solution is used for the estimation of PO_4^{3-} as described earlier.

Estimation of Ca^{2+} :

The filtrate and washings obtained after removing the precipitate of quinoline molybdophosphate complex are collected

together. The pH of this solution is adjusted to ~ 10 by adding liquor ammonia and the solution is diluted to 250 mL exactly. From an aliquot of 50 mL from this solution, Ca^{2+} ions may be estimated by any of the following two methods. (A) Direct Titration with EDTA and (B) Back Titration with standard zinc sulphate solution (refer article 3.3.2a). From this amount of Ca^{2+} in 50 mL aliquot , the amount in 250 mL of diluted solution (i.e. in the original volume of synthetic mixture) is calculated.

Method II

Estimation of Ca^{2+}:

From the mixture taken, Ca^{2+} ions are separated as described in article 3.3.2b. The precipitate of calcium oxalate is dissolved in ~ 25 mL of hot H_2SO_4 (2 N) and the solution is titrated with previously standardized $KMnO_4$ solution (0.1010 N). From the titration reading the amount of Ca^{2+} in the synthetic mixture is calculated.

Estimation of PO_4^{3-}:

From the filtrate obtained after removing the precipitate of calcium oxalate, PO_4^{3-} ions are precipitated as quinoline molybdophosphate complex (as described earlier). The precipitate is dissolved in 25 mL NaOH solution (0.5 M) and the

solution is diluted to 250 mL. Then aliquot of 25 mL of this solution is used for estimation of PO_4^{3-} (refer article 3.3.1). From this amount of PO_4^{3-} (in 25 mL aliquot), the amount in 250 mL of diluted solution (i.e. in the original volume of synthetic mixture) is calculated.

Analysis of the salt containing Ca^{2+} and PO_4^{3-} :

The exactly weighed amount (about 50 mg) of anhydrous dibasic calcium phosphate (molecular weight 136.05) is used for the present analysis.

[The expected amounts of Ca^{2+} and PO_4^{3-} in it can be calculated as follows :

	$CaHPO_4$	≡ Ca	≡	PO_4
	136.05	≡ 40.08	≡	94.97
∴	50 mg	≡ 14.73 mg	≡	34.90 mg]

The weighed amount of the salt is dissolved in HCl solution (1:9) and it is diluted to ~ 50 mL with distilled water. The solution is used for estimation of Ca^{2+} and PO_4^{3-} by any of the two methods mentioned.

The representative results for analysis of synthetic mixtures and the salt are given in Table 3.3.

Table 3.3 : Estimation of Ca^{2+} and PO_4^{3-} from the synthetic mixtures and salt

Samples[a]	Method I						Method II			
	Ca^{2+}				PO_4^{3-}		Ca^{2+}		PO_4^{3-}	
	Method IA		Method IB							
	Titer mL EDTA (0.01065 M)	Calculated amount (mg)	Titer (mL)[b] $ZnSO_4$ (0.00918 M)	Calculated amount (mg)	Titer (mL)[b] HCl (0.05367 M)	Calculated amount (mg)	Titer mL $KMnO_4$ (0.1010 M)	Calculated amount (mg)	Titer (mL)[b] HCl (0.05357 M)	Calculated amount (mg)
SM_1 Ca^{2+} (4.97mg) PO_4^{3-} (34.80mg)	2.3	4.91	2.5	4.97	18.0	35.19	2.4	4.86	17.9	35.10
SM_2 Ca^{2+} (34.81mg) PO_4^{3-} (4.97 mg)	16.4	35.00	17.1	34.06	2.6	5.00	17.1	34.61	2.6	5.10
Salt: $CaHPO_4$ Ca^{2+} (14.73mg) PO_4^{3-} (34.90mg) in 50 mg salt	7.0	14.94	7.3	14.51	17.9	35.10	7.3	14.77	18.1	35.49

a : The values in the parantheses are expected values
b : Difference between the readings of Blank and Back Titrations.

3.3.4 Estimation of Calcium and Phosphate in Dietary Supplement Tablets

Disintegration of Tablet :

After weighing exactly one tablet (if its weight is ~ 1 g), it is disintegrated in a 250 mL conical flask. [For the tablet having weight less than 0.6 g, two tablets are used instead of one, in order to get the readings in the range suitable for titrimetric analysis] . The disintegration is carried out using 10 mL of nitric acid (1:1), followed by 5 mL of concentrated hydrochloric acid (which is used for the removal of excess of nitric acid, as is indicated by disappearance of brown fumes). After disintegration, the solution is cooled, mixed carefully with ~ 50 mL of distilled water, warmed and filtered. The filter paper is washed with distilled water till it is free from acid. The filtrate and the washings are collected together and diluted to 250 mL. An aliquot of 25 mL of this solution is used for estimation of calcium and phosphate using any one of the two methods suggested earlier.

For the drug samples analysed in the present work, the data given for each drug by the manufacturer is mentioned, which is followed by our observations and results (refer Tables 3.4 to 3.8).

The details for the first trial (out of three trials) of analysis for drug sample D_1 (Cal-D-min) are given as a representative case.

Drug Sample D_1 : Name : Cal-D-min

Name of the manufacturer : Kirti Works, Bombay

Contents : Each tablet contains 0.5 g dibasic calcium phosphate (Dicalcium phosphate I.P.)

Vitamin D_3 USP 200 IU

The amount of Ca^{2+} and PO_4^{3-} (calculated considering anhydrous compound) -

Ca^{2+} : 147.30 mg per tablet

PO_4^{3-} : 349.10 mg per tablet

Average weight of the tablet : 1.2244 g

Weight of the tablet taken for analysis = 1.2298 g

Method I

Estimation of PO_4^{3-}

Mean titration readings :

Blank titration : 25.6 mL of 0.05357 M HCl

Back titration : 8.1 mL of 0.05357 M HCl

(Blank-Back) reading ≡ 17.5 mL.

1 mL of 0.5 M HCl ≡ 1.83 mg of PO_4^{3-}

$\therefore$ 17.5 mL of 0.05357 M HCl ≡ 3.4312 mg of PO_4^{3-}

(in 25 mL of diluted solution)

$\therefore$ Amount of PO_4^{3-} in 250 mL diluted solution = 34.312 mg (in 25 mL original solution).

$\therefore$ Amount of PO_4^{3-} in 250 mL original solution = 343.12 mg (in 1.2298 g of sample)

$\therefore$ Amount of PO_4^{3-} in 1.2244 g (average weight) of tablet = 341.62 mg.

Estimation of Ca^{2+}

Method IA : Direct Titration with EDTA

Mean Titration reading = 6.8 mL of 0.01065 M EDTA

1 mL of 1 M EDTA $\equiv$ 40.08 mg of Ca^{2+}

$\therefore$ 6.8 mL of 0.01065 M EDTA $\equiv$ 2.9025 mg (in 50 mL diluted solution)

$\therefore$ Amount of Ca^{2+} in 250 mL diluted solution $\equiv$ 14.5129 mg (in 25 mL of original solution)

$\therefore$ Amount of Ca^{2+} in 250 mL original solution $\equiv$ 145.129 mg (in 1.2298 g of sample)

$\therefore$ Amount of Ca^{2+} in 1.2244 g (average weight) tablet $\equiv$ 144.50 mg.

Estimation of Ca^{2+}

Method IB : Back Titration of excess EDTA with standard zinc sulphate solution.

Blank Titration reading = 26.8 mL of 0.009918 M $ZnSO_4$ solution.

Back Titration reading = 19.4 mL of 0.009918 M $ZnSO_4$ solution

(Blank-Back) reading = 7.4 mL of 0.009918 M $ZnSO_4$ solution.

Volume of EDTA consumed by Ca^{2+} ≡ 6.8 mL

1 mL of 1 M EDTA ≡ 40.08 mg of Ca^{2+}

∴ 6.8 mL of 0.01065 M EDTA ≡ 2.9357 mg of Ca^{2+} (in 50 mL of diluted solution)

∴ Amount of Ca^{2+} in 250 mL of diluted solution = 14.6786 mg (in 25 mL original solution)

∴ Amount of Ca^{2+} in 250 mL of original solution = 146.786 mg (in 1.2298 g of sample)

Amount of Ca^{2+} in 1.2244g(average weight) of tablet = 146.15 mg.

Method II

Estimation of Ca^{2+} (permanganometry)

Mean Titration reading = 7.1 mL of 0.1010 N $KMnO_4$ solution

1 mL of 1 M $KMnO_4$ ≡ 20.44 mg of Ca^{2+}

7.1 mL of 0.1010 N $KMnO_4$ = 14.3706 mg of Ca^{2+} (in 25 mL original solution)

∴ Amount of Ca^{2+} in 250 mL original solution = 143.706 mg (in 1.2298 g of sample)

∴ Amount of Ca^{2+} in 1.2244 g (average weight) of tablet = 143.08 mg.

Estimation of PO_4^{3-}

Blank Titration reading = 25.6 mL of 0.05357 M HCl solution

Back Titration reading = 8.3 mL of 0.05357 M HCl solution

(Blank-Back) reading = 17.3 mL of 0.05357 M HCl solution

1 mL of 0.5 M HCl ≡ 1.83 mg of PO_4^{3-}

∴ 17.8 ml of 0.05357 M HCl = 3.48997 mg of PO_4^{3-}
(in 25 mL diluted solution)

∴ Amount of PO_4^{3-} M 250 mL diluted solution = 34.8997 mg
(in 25 mL of original solution)

∴ Amount of PO_4^{3-} in 250 mL of original solution = 348.997 mg
(in 1.2298 g of sample)

∴ Amount of PO_4^{3-} in 1.2244 g (average weight) of tablet = 347.47 mg.

Drug Sample D_2 : Name : Ossopan

Name of the manufacturer : TTK Pharma Ltd., Old Trunk Road, Madras 600 043.

Contents : Each dragee contains extract of bone of young animals (0.2 g); Tartrazine coloured; calcium 33 mg, Phosphorous 15 mg (i.e. 46 mg PO_4^{3-}). Average weight of the tablet = 0.5216 g.

Weight of the two tablet taken for analysis = 1.0922 g

Drug Sample D_3 : Name : Ostocalcium

Name of the manufacturer : Glaxo, Bombay

Contents : Each tablet contains : Vitamin D_3 (Cholecalciferol IP) 400 IU, Vitamin B_{12} IP 5 mg, Vitamin C,

IP 50 mg, Tribasic calcium phosphate IP 0.33 g (equivalent to 125 mg of Ca^{2+})

Colour sunset yellow FCF.

Expected (calculated) amount of PO_4^{3-} per tablet = 191.1mg.

Average weight of the tablet = 0.9428 g

Weight of the tablet taken for analysis = 0.9541 g.

Drug Sample D_4 : Name : Ossivite

Name of the manufacturer : John Wyth (India) Ltd., Bombay.

Contents : Vitamin A IP (as Palmitate) 2500 I.U., Cholecalciferol U.S.P. (Vitamin D_3) 500 I.W., Dabasic Calcium phosphate I.P. 150 mg., Calcium carbonate I.P. 50 mg (contains Ponceau 4 R and Tartrazine as colorants).

Expected (Calculated) amount of Ca^{2+} per tablet = 64.214 mg.

Expected (Calculated) amount of PO_4^{3-} per tablet = 104.72 mg.

Average weight of the tablet = 0.5750g

Weight of the two tablets taken for analysis = 1.1355 g.

Drug Sample D_5 : Name : Kalzana

Name of the manufacturer : German Remidies Ltd., Bombay 400 092

Contents : Each tablet contains : Calcium Dibasic phosphate I.P. 430 mg, Cholecalciferol (Vitamin D_3) I.P. 200 I.U., Ascorbic acid (Vitamin C) 40 mg, Calcium content 101 mg, Colour sunset yellow,

Expected (Calculated) amount of PO_4^{3-} per tablet = 237.30 mg

Average weight of the tablet = 0.9883 g

The weight of the tablet taken for analysis = 1.0242 g

3.4 RESULTS AND DISCUSSION

All the results for the estimation of Ca^{2+} and PO_4^{3-} have been summarized in Table 3.9. They indicate that the proposed methods are simple, reproducible and accurate within the limits of titrimetric analysis. As the assay of drug samples is available, the reliable evaluation of the students' performance can be done. The samples used here contain calcium and phosphate as inorganic ions.

So far the samples having other additional constituent inorganic ions, the modifications seem to be necessary.

For complexometric estimation of calcium, direct titration method seems to be better than back titration method.

The methods are useful to determine Ca^{2+} and PO_4^{3-} from the same sample. Moreover, they are useful for the students to know about some of the aspects of analytical chemistry such as disintegration of the sample, quantitative precipitation of the desired ion and dissolution of the precipitate followed by volumetric estimation of the desired ion. The methods are also useful to gain experience of different types of volumetric analysis e.g. acid-base titration (estimation of PO_4^{3-}),

Table 3.4 : Analysis of Cal-D-min (Sample D_1)
Expected amount of Ca^{2+} = 147.30 mg / tablet
Expected amount of PO_4^{3-} = 349.10 mg / tablet

	Observed values	Mean $\bar{x}$	Deviation $d_i = \lvert\bar{x} - x_i\rvert$	$\sum d_i^2$	Standard deviation σ	Standard relative deviation S_R	Relative error %
Ca^{2+} (Method IA)	144.50 142.32 145.23	144.02	0.48 1.7 1.21	14.5845	1.0706	0.7433	2.23
Ca^{2+} (Method IB)	146.78 141.98 152.36	147.04	0.26 5.06 5.32	53.9736	3.6733	2.498	0.18
PO_4^{3-} (Method I)	341.62 341.27 345.19	342.69	1.07 1.42 2.50	9.4113	2.1	2.775	1.84
Ca^{2+} (Method II)	143.08 143.29 143.29	143.22	0.14 0.07 0.07	0.0294	0.1212	0.085	2.77
PO_4^{3-} (Method II)	347.47 352.43 342.78	347.56	0.09 4.87 4.77	46.48	4.82	2.45	0.44

deviation $d_i = \bar{x} - x_i$ where $\bar{x}$ = mean of observed values and x_i = observed value

standard deviation $\sigma = \sqrt{\sum d_i^2 / (N-1)}$ where N= number of observations

standard relative deviation $S_R = \sigma / \bar{x} \times 100$

Relative % error = [Expected value - Mean of observed values ($\bar{x}$) / (Expected value)] x 100

Table 3.5 : Analysis of Ossopan (Sample D_2)
Expected amount of Ca^{2+} = 33.00 mg / tablet
Expected amount of PO_4^{3-} = 46.00 mg / tablet

	Observed values	Mean $\bar{x}$	Deviation $d_i = \lvert\bar{x} - x_i\rvert$	$\sum d_i^2$	Standard deviation σ	Standard relative deviation S_R	Relative error ε
Ca^{2+} (Method IA)	34.65 31.95 35.07	33.89	0.76 1.94 1.18	5.7336	1.693	4.99	2.70
Ca^{2+} (Method IB)	31.60 32.40 32.83	32.28	0.68 0.12 0.55	0.7793	0.6242	1.93	2.18
PO_4^{3-} (Method I)	44.94 46.62 46.03	45.87	0.93 0.75 0.16	1.453	0.8523	1.86	0.28
Ca^{2+} (Method II)	32.87 31.38 34.36	32.87	nil 1.49 1.49	4.440	1.49	4.53	0.39
PO_4^{3-} (Method II)	45.88 47.52 44.55	45.98	0.10 1.54 1.43	4.426	1.487	3.24	0.04

Table 3.c : Analysis of Ostocalcium (Sample D_3)
Expected amount of Ca^{2+} = 125 mg/tablet
Expected amount of PO_4^{3-} = 191.1 mg/tablet

	Observed values in mg.	Mean $\bar{x}$	Deviation $d_1 = \lvert\bar{x} - x_1\rvert$	Σd_1^2	Standard deviation σ	Standard relative deviation S_R	Relative error %
Ca^{2+} (Method IA)	122.33 125.25 123.26	123.61	1.28 1.64 0.35	4.4505	1.4900	1.21	1.11
Ca^{2+} (Method IB)	123.74 128.18 124.69	125.54	1.80 2.64 0.85	10.9321	2.3380	1.86	0.[illegible]3
PO_4^{3-} (Method I)	193.75 190.88 192.58	192.40	1.35 1.52 0.18	4.1653	1.4430	0.75	0.[illegible]8
Ca^{2+} (Method II)	124.01 129.58 127.71	127.10	3.09 0.61 2.48	16.0700	2.8300	2.23	1.68
PO_4^{3-} (Method II)	194.72 190.88 190.88	192.16	2.56 1.28 1.28	9.8304	2.2170	1.15	0.55

Table 3.7 : Analysis of Ossivite (Sample D_4)
Expected amount of Ca^{2+} = 64.21 mg / tablet
Expected amount of PO_4^{3-} = 104.72 mg / tablet

	Observed values in mg	Mean $\bar{x}$	Deviation $d_1 = \lvert\bar{x} - x_1\rvert$	Σd_1^2	Standard deviation σ	Standard relative deviation S_R	Relative error %
Ca^{2+} (Method IA)	62.69 66.52 67.52	65.57	2.88 0.95 1.95	12.99	2.55	3.88	2.12
Ca^{2+} (Method IB)	62.44 60.06 65.09	62.53	0.09 2.47 2.56	12.66	2.52	4.03	2.61
PO_4^{3-} (Method I)	99.29 106.80 100.95	102.35	3.06 4.45 1.40	31.126	3.945	3.854	2.26
Ca^{2+} (Method II)	61.50 60.71 64.95	62.39	0.89 1.68 2.56	10.168	3.97	3.61	2.83
PO_4^{3-} (Method II)	101.27 99.17 106.05	102.16	0.89 2.99 3.89	24.8643	3.53	3.45	2.44

Table 3.8 : Analysis of Kalzana (Sample D_5)
Expected amount of Ca^{2+} = 101.00 mg / tablet
Expected amount of PO_4^{3-} = 237.36 mg / tablet

	Observed values in mg	Mean $\bar{x}$	Deviation $d_i = \lvert\bar{x} - x_i\rvert$	Σd_i^2	Standard deviation σ	Standard relative deviation S_R	Relative error %
Ca^{2+} (Method IA)	105.03 97.53 106.91	103.16	1.87 5.63 3.75	49.2563	4.96	4.81	2.14
Ca^{2+} (Method IB)	102.97 104.97 102.99	103.64	0.67 1.33 0.65	2.6403	1.15	1.11	2.61
PO_4^{3-} (Method I)	232.70 236.39 232.25	233.78	1.08 2.61 1.53	10.3194	2.27	0.97	1.51
Ca^{2+} (Method II)	101.51 98.44 102.29	100.75	0.76 2.31 1.54	8.285	2.04	2.02	0.25
PO_4^{3-} (Method II)	240.27 235.82 234.03	236.71	3.56 0.89 2.68	20.048	3.21	1.36	0.27

Table 3.2 : Analysis* of synthetic mixtures, salt, and drug samples for estimation of Ca^{2+} and PO_4^{3-}

Sample with expected results		METHOD I						METHOD II					
		Ca^{2+}			PO_4^{3-}			Ca^{2+}			PO_4^{3-}		
		Observed amount mg	Relative error %	Standard deviation relative %	Observed amount mg	Relative error %	Standard deviation relative %	Observed amount mg	Relative error %	Standard deviation relative %	Observed amount mg	Relative error %	Standard deviation relative %
Synthetic Mixtures SM_1 (4.97 mg Ca^{2+} and 34.80 mg PO_4^{3-})	IA	4.91	-1.21	—	35.19	1.12	—	4.96	2.21	—	35.10	0.86	—
	IB	4.97	Nil										
SM_2 (34.61 mg Ca^{2+} and 4.27 mg PO_4^{3-})	IA	35.00	0.55	—	5.00	0.60	—	34.61	0.87	—	5.10	2.62	—
	IB	34.06	2.14										
Salt $CaHPO_4$ (14.73 mg Ca^{2+} and 34.90 mg PO_4^{3-} in 50.00 mg salt)	IA	14.94	1.43	—	35.10	0.5	—	14.77	0.31	—	35.49	1.66	—
	IB	14.51	1.50										
Drug samples (D_1-D_5)													
D_1 (147.30 mg Ca^{2+} and 349.10 mg PO_4^{3-} per tablet)	IA	144.02	2.23	0.7433	342.69	1.84	2.77	143.22	2.77	0.085	347.58	0.44	2.45
	IB	147.04	0.18	2.498									
D_2 (33.00 mg Ca^{2+} and 46.00 mg PO_4^{3-} per tablet)	IA	33.89	2.70	4.99	45.87	0.28	1.858	32.87	0.39	4.53	45.98	0.04	3.24
	IB	32.28	2.18	1.934									
D_3 (125.00 mg Ca^{2+} and 190.10 mg PO_4^{3-} per tablet)	IA	122.61	1.112	1.207	192.40	0.6809	0.7501	127.10	1.68	2.23	192.16	0.55	1.15
	IB	125.84	0.43	1.862									
D_4 (64.21 mg Ca^{2+} and 104.72 mg PO_4^{3-} per tablet)	IA	66.67	2.124	3.88	102.35	2.263	3.854	63.39	2.83	3.61	102.16	2.44	3.45
	IB	62.53	2.61	4.03									
D_5 (101.00 mg Ca^{2+} and 227.36 mg PO_4^{3-} per tablet)	IA	103.16	2.14	4.81	233.78	1.61	0.9716	100.75	0.25	2.01	236.71	0.27	1.36
	IB	103.64	2.61	1.11									

* The values are mean of three replicates

IA : Method of direct titration with EDTA

IB : Method of Back titration with zinc sulphate.

Complexometry (estimation of Ca^{2+}), redox titration (estimation of Ca^{2+}).

There are two reports[3,4] of similar type of work, but both of them involve use of ion exchange chromatography. Dietz[3] has reported a Freshman laboratory experiment - "The determination of calcium in dietary supplement tablets by ion exchange", where a cation exchanger is used to retain Ca^{2+} and equivalent amount of H^+ ions liberated is estimated using alkalimetry. In this experiment, however, the tablets containing calcium lactate are suitable (The limited solubility of calcium carbonate and phosphate makes the samples containing these compounds unsuitable for the experiment).

A method of estimation of calcium and magnesium in presence of phosphate in oral rehydration formulation has been reported by Barje[4]. Here the separation of phosphate is done by passing aqueous solution of the sample through a column of anion exchange resin before the complexometric estimation of calcium and magnesium. (Estimation of phosphate is not reported).

As compared to both these methods the procedures suggested by us seem to be simpler and less costly.

REFERENCES

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chapter 4

DETERMINATION OF IRON FROM IRON-SUPPLEMENT TABLETS BY REDOX TITRATIONS USING ZINC DUST AS REDUCTANT

The sceptical chemist .... draws conclusions regarding materials ..... chiefly on the basis of quantitative chemical analysis which ..... is the touchstone of all chemical hypothesis.

— G.T. Morgan

CHAPTER 4

DETERMINATION OF IRON FROM IRON-SUPPLEMENT TABLETS BY REDOX TITRATIONS USING ZINC DUST AS REDUCTANT

ABSTRACT

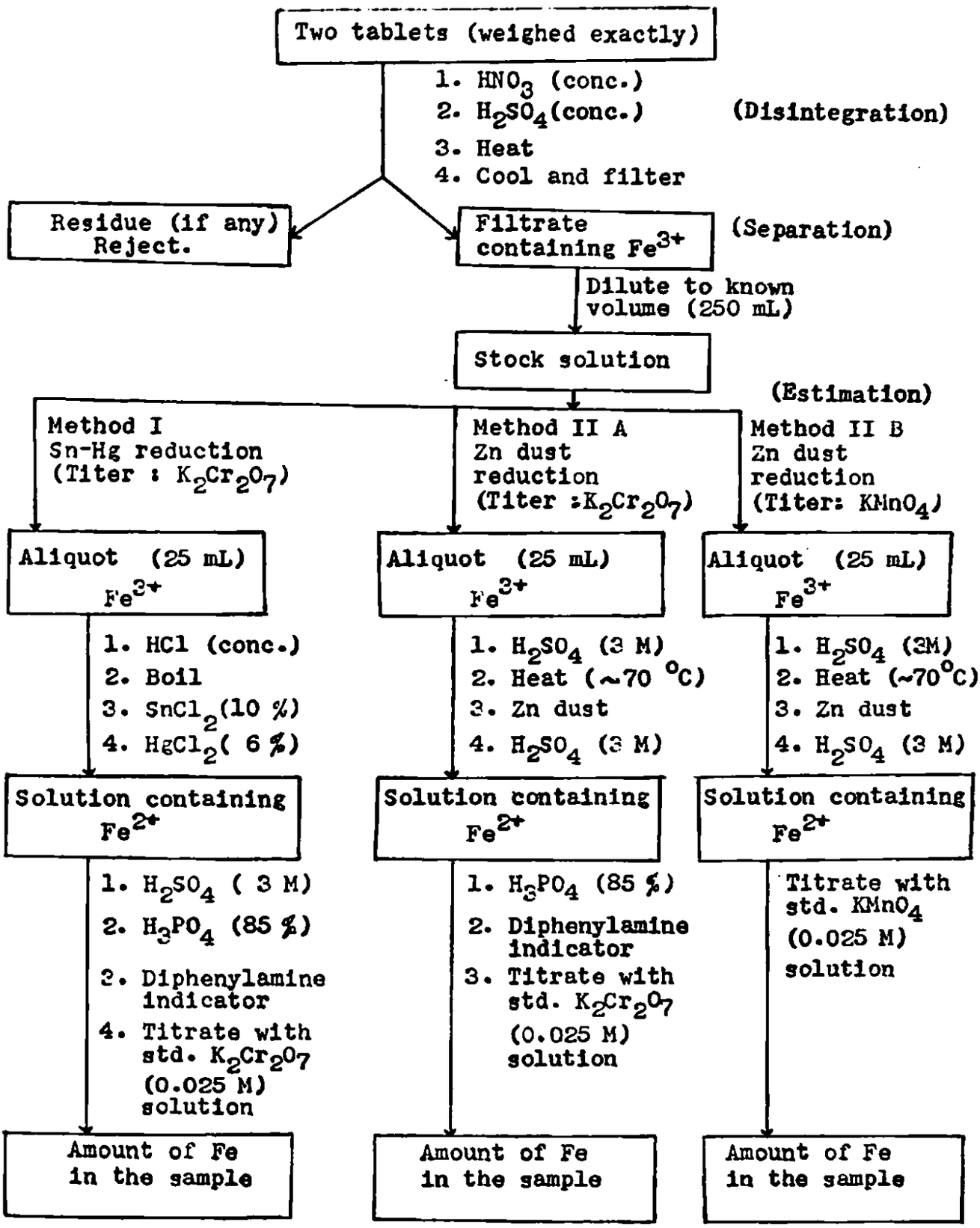
A simple group experiment for determination of iron from haematinic tablets - a familiar consumer product - is given here for execution in two 3-h laboratory periods. Ferric ions obtained after complete disintegration of the sample, are reduced with zinc dust in acid solution and the determination of iron can be done using either potassium dichromate or potassium permanganate solution. The experiment introduces the students to comparative study of both the redox reactions as well as their application to analytical chemistry.

4.1 INTRODUCTION

With the increasing awareness about the pollution problems and environmental safety, it has become necessary to modify the conventional experimental procedures. As an alternative to the conventional Sn-Hg reduction method (which involves use of $HgCl_2$), we have tried the reduction of ferric ions as per some reported procedures using the reductants like zinc dust[1-3], zinc granules, aluminium powder, aluminium wire[4], aluminium foil, magnesium powder and magnesium ribbon. Out of these, reduction with zinc dust in presence of sulphuric acid is found to be suitable for complete reduction of ferric ions within reasonable time. Using this method, therefore, an experiment has been set up for estimation of iron from iron supplement tablets. These samples contain iron in different forms such as ferrous fumarate, ferrous sulphate, ferroglycine sulphate and ferrous calcium citrate complex. The method involves disintegration of tablets, reduction of ferric ions with zinc dust in presence of sulphuric acid and finally the titrimetric estimation. It enables the students to gain experience of redox titrations using potassium permanganate as well as potassium dichromate. The waste solutions obtained can be easily disposed off after removal of metal ions by precipitation[5].

The flow-sheet and reactions for the experiment are given herewith.

Flow sheet


Two tablets (weighed exactly)
1. HNO_3 (conc.)
2. H_2SO_4(conc.)
3. Heat
4. Cool and filter
(Disintegration)
Residue (if any) Reject.
Filtrate containing Fe^{3+}
(Separation)
Dilute to known volume (250 mL)
Stock solution
(Estimation)
Method I
Sn-Hg reduction
(Titer : $K_2Cr_2O_7$)
Method II A
Zn dust reduction
(Titer :$K_2Cr_2O_7$)
Method II B
Zn dust reduction
(Titer: $KMnO_4$)
Aliquot (25 mL) Fe^{3+}
Aliquot (25 mL) Fe^{3+}
Aliquot (25 mL) Fe^{3+}
1. HCl (conc.)
2. Boil
3. $SnCl_2$(10 %)
4. $HgCl_2$(6 %)
1. H_2SO_4 (3 M)
2. Heat (~70 °C)
3. Zn dust
4. H_2SO_4 (3 M)
1. H_2SO_4 (3M)
2. Heat (~70°C)
3. Zn dust
4. H_2SO_4 (3 M)
Solution containing Fe^{2+}
Solution containing Fe^{2+}
Solution containing Fe^{2+}
1. H_2SO_4 (3 M)
2. H_3PO_4 (85 %)
3. Diphenylamine indicator
4. Titrate with std. $K_2Cr_2O_7$ (0.025 M) solution
1. H_3PO_4 (85 %)
2. Diphenylamine indicator
3. Titrate with std. $K_2Cr_2O_7$ (0.025 M) solution
Titrate with std. $KMnO_4$ (0.025 M) solution
Amount of Fe in the sample
Amount of Fe in the sample
Amount of Fe in the sample

Equations

Disintegration of tablets and Estimation of iron :

$$Fe^{2+} \xrightarrow{HNO_3} Fe^{3+}$$

$$\text{Organic matter} \xrightarrow{\substack{1.HNO_3 \\ 2.H_2SO_4}} \text{Volatile products}$$

Method I : Sn-Hg reduction

$$2\ Fe^{3+} + Sn^{2+} \longrightarrow 2\ Fe^{2+} + Sn^{4+} \quad \text{(reduction)}$$

$$Sn^{2+} + 2\ Hg^{2+} \longrightarrow Sn^{4+} + Hg_2^{2+} \quad \text{(elimination of } Sn^{2+}\text{)}$$

(excess)

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \longrightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$$

Method II : Zinc dust reduction

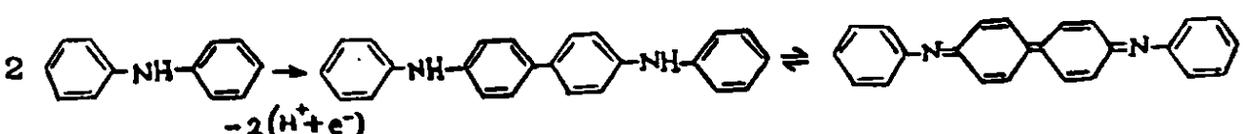
$$2\ Fe^{3+} + Zn \xrightarrow{H_2SO_4} 2\ Fe^{2+} + Zn^{2+} \quad \text{(reduction)}$$

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2(g) \quad \text{(elimination of Zn)}$$

(excess)

Method II A: Titration with $K_2Cr_2O_7$

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \longrightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$$



Diphenylamine (indicator) — Diphenylbenzidine — Diphenylbenzidine violet

Method II B : Titration with $KMnO_4$

$$10\ Fe^{2+} + 2\ MnO_4^- + 16\ H^+ \longrightarrow 10\ Fe^{3+} + 2\ Mn^{2+} + 8\ H_2O$$

(Standardization of $KMnO_4$:

$$(2\ Na^+ + C_2O_4^{2-}) + 2\ H^+ \longrightarrow H_2C_2O_4 + 2\ Na^+$$

$$2\ MnO_4^- + 5\ H_2C_2O_4 + 6\ H^+ \longrightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O\ )$$

4.2 THEORETICAL BACKGROUND

Disintegration of drug sample

As estimation of iron is done by redox titrations, removal of organic matter is necessary. The concentrated nitric acid is useful for removal of organic matter as well as for oxidation of ferrous ions to ferric ions. The concentrated sulphuric acid is useful to remove excess of nitric acid which otherwise may interfere in the analysis.

Estimation of iron

In the conventional method[2], reduction of ferric ions is done using $SnCl_2$ and HCl. The excess of $SnCl_2$ is removed by adding $HgCl_2$ solution. In the method suggested here, reduction of ferric ions is carried out using zinc dust in presence of sulphuric acid. In this method sufficient amount of sulphuric acid is to be added to dissolve zinc dust completely or otherwise the solution is to be filtered to

remove undissolved zinc dust.

The advantage of this method is that after reduction of ferric ions the solution can be titrated against potassium dichromate or also against potassium permanganate solution (use of Zimmermann-Reinhardt's solution[2] is not required). During the titration with potassium permanganate solution diphenylamine indicator may be used to get distinct end point[2].

4.3 EXPERIMENTAL

All the reagents and chemicals used are of Analar or equivalent grade. The procedure is set by using standard solutions prepared from iron salts and then used for the estimation of iron present in some drugs. (Some of the well-known iron-supplement tablets are used for the analysis). The detailed procedures for the three methods used for the analysis are given below.

Reagents

Concentrated acids : nitric acid, sulphuric acid, hydrochloric acid.

Phosphoric acid (85 %),

Zinc dust

Diphenylamine indicator solution (1 %): The solution is prepared in concentrated sulphuric acid.

Sulphuric acid (3 M) : 84 mL of concentrated sulphuric acid is diluted to 500 mL with distilled water.

$SnCl_2$ solution (10 %) : 12 g of pure tin metal (granules) is dissolved in 100 mL of hot concentrated hydrochloric acid and the solution is diluted to 200 mL.

$HgCl_2$ (6 % aqueous solution)

Stock solution of Fe(III) : (concentration 1 mg / mL) using $Fe(NH_4)(SO_4)_2.12\ H_2O$: 4.3168 g of ammonium ferric sulphate (molecular weight 482.19) is dissolved in about 200 mL of distilled water containing ~ 5 mL of 3 M H_2SO_4 solution and the solution is diluted to 500 mL with distilled water.

Potassium permanganate solution (~ 0.025 N) : About 3.95 g of potassium permanganate is dissolved in about 500 mL of distilled water. The solution is warmed and then filtered. The filtrate is diluted to 5 litre with distilled water.

Potassium dichromate solution (~ 0.025 N) : 6.1280 g of potassium dichromate is dissolved in about 500 mL of distilled water and solution is diluted to 5 litre with distilled water.

Standard sodium oxalate solution (0.025 N) : 0.4188 g of anhydrous sodium oxalate (molecular weight 134.00) is dissolved in distilled water, the solution is diluted to 250 mL with distilled water.

Standard solution of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (0.025 N) solution : 2.4509 g of ammonium ferrous sulphate (molecular weight = 392.14) is dissolved in distilled water, the solution is diluted to 250 mL with distilled water.

Procedures :

Standardization of $KMnO_4$ solution (approx. 0.025 N) : An aliquot of 10 mL of standard sodium oxalate solution (0.025 N) is taken in the titration flask. After adding 10 mL of sulphuric acid (3 M) it is warmed and titrated with $KMnO_4$ solution until the permanent pink colour is obtained. From the titration reading exact normality of $KMnO_4$ solution is calculated.

Mean titration reading = 10.1 mL of $KMnO_4$ solution.

Thus exact normality of $KMnO_4$ solution = 0.02475.

Standardization of $K_2Cr_2O_7$ solution (approx. 0.025 N) : An aliquot of 10 mL of standard ammonium ferrous sulphate (0.025 N) solution is taken in the titration flask, 10 mL of H_2SO_4 (3 M) solution, 5 mL of H_3PO_4 solution (85 %) and 4 drops of diphenylamine indicator are added. The solution is titrated with $K_2Cr_2O_7$ solution until persistant blue-violet colour is observed. From the titration reading exact normality of $K_2Cr_2O_7$ solution is calculated. Mean titration reading = 9.8 mL of $K_2Cr_2O_7$ solution. Thus exact normality of $K_2Cr_2O_7$ solution = 0.02551.

Estimation of Iron from salts :

Estimation of Fe from salt No. 1

Ammonium Ferric sulphate $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$

(Molecular weight = 482.19)

Method I : Reduction using of $SnCl_2$ + HCl

Procedure : An aliquot of 25 mL of Fe(III) solution (concentration 1 mg / mL) is taken in the titration flask. To it 3 mL of concentrated HCl solution is added and the solution is boiled. To this hot solution is added $SnCl_2$ solution (10 %) till the disappearance of yellow colour. Then dilute $SnCl_2$ solution is added dropwise until faint green colour is obtained. The solution is cooled and $HgCl_2$ solution (6 %) is added till slight turbidity is obtained. To this solution ~10 mL of H_2SO_4 solution (3 M), 3 mL of H_3PO_4 solution (85 %) and 3 drops of diphenylamine indicator are added. The solution is titrated with standard $K_2Cr_2O_7$ solution (0.025 N) until persistant blue-violet colour is obtained.

Mean titration reading = 18.6 mL of $K_2Cr_2O_7$ solution (0.02551 N).

1 mL of 1 N $K_2Cr_2O_7$ solution ≡ 55.85 mg of Fe

$\therefore$ 18.6 mL of 0.02551 N $K_2Cr_2O_7$ solution ≡ 26.50 mg of Fe.

Method II : Reduction with zinc dust

Part A : Titration with $K_2Cr_2O_7$ solution

Procedure : To the 25 mL of Fe(III) solution (concentration: 1 mg / mL) taken in a conical flask, 10 mL of sulphuric acid (3 M) is added. It is heated to ~ 70 ^{o}C on a hot plate and ~ 0.5 g of zinc dust is added. The conical flask is covered with a watch glass. After 5 min., 5 mL of sulphuric acid (3 M) is added. The flask is shaken until all the zinc dust is consumed and evolution of hydrogen has stopped. To this solution 5 mL of sulphuric acid (3 M), 5 mL of phosphoric acid (85 %) and 3 drops of diphenylamine indicator are added. The solution is titrated with standardized $K_2Cr_2O_7$ solution (0.025 N) until persistant blue-violet colour is obtained.

The blank titration may be carried out using which the necessary correction for the main titration reading can be given. (As the blank titration reading was found to be less than 0.1 mL, to give such correction was not possible).

Mean titration reading = 18.5 mL of $K_2Cr_2O_7$ solution (0.02551 N)

1 mL of 1 N $K_2Cr_2O_7$ solution $\equiv$ 55.85 mg of Fe

$\therefore$ 18.5 ml of 0.02551 N $K_2Cr_2O_7$ solution $\equiv$ 26.36 mg of Fe.

Method II : Titration with $KMnO_4$ solution

Part B

Procedure : An aliquot of 25 mL of Fe(III) solution is taken in a conical flask. The reduction of ferric ions is carried out by following procedure as is used for Part A. Then to this solution, 5 mL of sulphuric acid (3 M), 5 mL of phosphoric acid (85 %) are added. The solution is titrated with standardized $KMnO_4$ solution (0.025 N) until persistant faint pink colour is obtained. Here distinct end point, blue violet colour, may be obtained by adding diphenylamine indicator just before the end point.[2]

The blank titration may be carried out using which the necessary correction for the main titration reading can be given. (As this reading was found to be negligible (< 0.1 mL), such correction was not required).

Mean titration reading = 19.1 mL of $KMnO_4$ solution (0.02475 N)

1 mL of 1 N $KMnO_4$ solution $\equiv$ 55.85 mg of Fe

$\therefore$ 19.1 mL of 0.02475 N $KMnO_4$ solution $\equiv$ 26.40 mg of Fe

The procedure is repeated for all the methods by taking different volumes of Fe(III) solution. Some of the representative results are given in Table 4.1.

Table 4.1 : Observations and results of estimation of Fe from $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ [Salt No. 1]

mL of stock solution of Fe(III) (concentration 1mg Fe/mL	Method I: Sn-Hg reduction		Method II : Zinc reduction method			
	Titer: $K_2Cr_2O_7$ (0.02551N)		Titer: $K_2Cr_2O_7$ (0.02551 N) A		Titer: $KMnO_4$ (0.02475M) B	
	Titration reading (mL)	Calculated amount of Fe (mg)	Titration reading (mL)	Calculated amount of Fe (mg)	Titration reading (mL)	Calculated amount of Fe (mg)
25	18.6	26.50	18.5	26.36	19.1	26.40
20	14.8	21.08	14.8	21.08	15.3	21.15
10	7.4	10.54	7.3	10.40	7.2	9.95

Estimation of Fe from salt No. 2

Ammonium ferrous sulphate $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$
(Molecular weight = 392.11)

Procedure : After weighing exactly (0.70060 g), the salt is put into a 250 mL beaker. It is then treated with a mixture prepared by taking 2 mL of concentrated nitric acid and 5 mL of concentrated sulphuric acid (nitric acid oxidises Fe(II) to Fe(III) ions)[3]. The solution is heated until the brown fumes due to nitric acid are stopped. After cooling it is diluted with ~ 50 mL of distilled water and again heated to dissolve the iron salt. The solution is cooled and diluted exactly to 250 mL with distilled water. An aliquot of 25 mL of this solution is used for titrimetric estimation of Fe. The procedures for estimation by Method I (Sn-Hg reduction method), Method II (Zn dust reduction method with $K_2Cr_2O_7$ as titrant) and Method IIB (Zn dust reduction method, with $KMnO_4$ as titrant) are already discussed for salt No. 1.

The procedure is repeated by taking different quantities of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$. Some of the representative results are given in Table 4.2.

Determination of iron from iron-supplement tablets

Using Sn-Hg reduction method and zinc reduction method, estimation of iron from iron-supplement tablets has been carried

Table 4.2 : Observations and results of estimation of Fe from $FeSO_4(NH_4)_2SO_4{\cdot}6H_2O$ [Salt No. 2]

Quantity of $FeSO_4(NH_4)_2SO_4{\cdot}6H_2O$ taken for analysis	Expected amount of Fe in 250 mL of the solution	Method I: Sn-Hg reduction		Method II : Zinc reduction			
				A		B	
		Titer : $K_2Cr_2O_7$ (0.02551 N)		Titer: $K_2Cr_2O_7$ (0.02551 N)		Titer : $KMnO_4$ (0.02475 N)	
		Titer for 25 mL aliquot	Fe content found in 250 mL solution	Titer for 25 mL aliquot	Fe content found in 250 mL solution	Titer for 25 mL aliquot	Fe content found in 250 mL solution
(g)	(mg)	(mL)	(mg)	(mL)	(mg)	(mL)	(mg)
0.70060	99.77	7.0	99.73	7.1	101.16	7.2	99.52
0.52000	74.05	5.2	74.09	5.3	75.51	5.4	74.64
0.25000	49.84	3.4	48.44	3.5	49.87	3.5	48.38

out. The experimental procedure involves disintegration of the tablets, reduction of ferric ions and finally the titrimetric estimation. Two tablets are disintegrated to get the readings in the range suitable for titrimetric analysis.

Disintegration of the tablets[3]

After weighing exactly, two tablets are disintegrated carefully in a 250 mL beaker by successive treatments of small portions (5 mL and 2 mL) of concentrated nitric acid till there is no darkening of the solution (indication of the complete removal of organic matter). It is then treated with a mixture prepared by taking 2 mL of concentrated nitric acid and 5 mL of concentrated sulphuric acid. The solution is heated until the brown fumes due to nitric acid are stopped. After cooling, it is diluted with ~ 50 mL of distilled water and again heated to dissolve the iron salt. The solution is cooled, filtered through Whatman filter paper No. 41 and washed with distilled water till free from acid. The filtrate and washings are diluted exactly to 250 mL with distilled water. An aliquot of 25 mL of this solution is used for estimation of iron. The estimation is done by Method I (Sn-Hg reduction), Method IIA and Method IIB (Zinc dust reduction) as described earlier.

For the drug samples analysed in the present work, the data given for each drug by the manufacturer is mentioned. Iron content per tablet is claculated from the composition of

iron-containing compound present in the drug. This is followed by our observations and results (refer Tables 4.3 to 4.8).

The details for the first trial (out of three trials) of analysis for drug sample D_1 (Dumex) are given as a representative case.

Drug sample D_1 : Name : Dumex

Name of the manufacturer : Pfizer Ltd., Thane

Contents : Each tablet contains : Ferrous fumarate 300 mg, Thiamine mononitrate 5 mg, Ascorbic acid 75 mg, Niacenamide 50 mg, pyridoxene hydrochloride 1.5 mg, Folic acid IP 0.75 mg, Vit. B_{12} IP 7.5 mg.

Average weight of the tablet = 0.76239 g.

Iron content per tablet = 98.65 mg.

Weight of two tablets taken for analysis = 1.65270 g.

Method I : (Sn-Hg reduction method)

Mean titration reading = 15.4 mL of $K_2Cr_2O_7$ solution (0.02551 N)

1 mL of 1 N $K_2Cr_2O_7$ solution ≡ 55.85 mg of Fe

∴ 15.4 mL of 0.02551 N $K_2Cr_2O_7$ solution ≡ 21.9409 mg of Fe

Thus 25 mL of diluted solution contains 21.9405 mg of Fe

∴ 250 mL of diluted solution contains 219.409 mg of Fe (in 1.65270 g of sample)

∴ 0.76239 g (average weight) of tablet contains 101.21 mg of Fe.

iron-containing compound present in the drug. This is followed by our observations and results (refer Tables 4.3 to 4.8).

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Weight of two tablets taken for analysis = 1.65270 g.

Method I : (Sn-Hg reduction method)

Mean titration reading = 15.4 mL of $K_2Cr_2O_7$ solution (0.02551 N)

1 mL of 1 N $K_2Cr_2O_7$ solution ≡ 55.85 mg of Fe

∴ 15.4 mL of 0.02551 N $K_2Cr_2O_7$ solution ≡ 21.9409 mg of Fe

Thus 25 mL of diluted solution contains 21.9405 mg of Fe

∴ 250 mL of diluted solution contains 219.409 mg of Fe (in 1.65270 g of sample)

∴ 0.76239 g (average weight) of tablet contains 101.21 mg of Fe.

Method II : Reduction with zinc dust

Method IIA : Titration with $K_2Cr_2O_7$ solution

Mean titration reading = 14.6 mL of $K_2Cr_2O_7$ solution (0.02551 N).

1 mL of 1 N $K_2Cr_2O_7$ solution ≡ 55.85 mg of Fe.

∴ 14.6 mL of 0.02551 N $K_2Cr_2O_7$ solution ≡ 20.8011 mg of Fe.

Thus 25 mL of diluted solution contains 20.8011 mg of Fe

∴ 250 mL of diluted solution (1.65270 g of sample) contains 208.011 mg of Fe

∴ 0.76239 g (average weight) of tablet contains 95.96 mg of Fe.

Method IIB : Titration with $KMnO_4$ solution

Mean titration reading = 15.6 mL of $KMnO_4$ solution (0.02475 N).

1 mL of 1 N $KMnO_4$ solution ≡ 55.85 mg of Fe.

∴ 15.6 ml of 0.02475 N $KMnO_4$ solution ≡ 21.5634 mg of Fe.

Thus 25 mL of diluted solution contains 21.5634 mg of Fe.

∴ 250 mL of diluted solution contains 215.634 mg of Fe (in 1.65270g of sample).

∴ 0.76239 g (average weight) of tablet contains 99.47 mg of Fe.

Drug Sample D_2 : Name : Macrofolin

Name of the manufacturer : Glaxo, Bombay

Contents : Each tablet contains : Folic acid 750 mg, Vitamin B_{12} 7.2 mg, Ferrous Fumarate 200 mg.

Average weight of the tablet ≡ 0.41010 g

Iron content per tablet = 65.76 mg

Drug Sample D_3 : Name : Fefol

Name of the manufacturer : Eskayef Ltd., Bangalore

Contents : Each tablet contains : Dried Ferrous sulphate IP : 150 mg, Folic acid IP 0.5 mg colour : Amarnath.

Average weight of the tablet = 0.47466 g

Iron content per tablet = 55.17 mg

Drug Sample D_4 : Name : Fessovite

Name of the manufacturer : Eskayef Ltd., Bangalore

Contents : Each capsule contains : Dried ferrous sulphate IP 150 mg, Ascorbic acid IP 50 mg, Riboflavine IP 2 mg, Thiaminemononitrate IP 2 mg, Nicotinamide IP 15 mg, Pyridoxine hydrochloride IP 1 mg, Pantonthonic acid 2.5 mg.

Average weight of the tablet = 0.47836 g

Iron content per tablet = 55.17 mg

Drug Sample D_5 : Name : Zenfer

Name of the manufacturer : Noel Chemicals, Bombay

Contents : Each capsule contains Ferroglycine sulphate equivalent to elemental iron : 50 mg, Vitamin B_{12} IP 10 mcg., Folic acid IP 1 mg, Calcium Levulinate USP 75 mg, Zinc sulphate IP 5 mg.

Average weight of the capsule = 0.49989 g

Iron content per capsule = 50.0mg.

Drug Sample D_6 : Name : Raricap HT

Name of the manufacturer : NR Jet Pharmaceuticals Ltd., Bombay.

Contents : Each tablet contains : Ferrous calcium citrate complex 500 mg equivalent to Iron 25 mg and calcium 85 mg, Vitamin B_2 IP 2 mg, Vitamin B_6 IP 1 mg, Vitamin C IP 35 mg, Vitamin B_{12} IP 1 mcg, Folic acid IP 0.3 mg.

Average weight of the tablet = 1.05185 g

Iron content of the tablet = 25.0mg.

4.4 RESULTS AND DISCUSSION

The results obtained for the amount of iron per tablet using zinc dust reduction method (refer Table 4.9) seem to be in good agreement with the iron content as mentioned on the manufacturer's label and also with those obtained using conventional method i.e. Sn-Hg reduction method. The method has advantages like simple experimental procedure and use of

Table 4.3 : Analysis of Dumex (Sample D_1)
Expected amount of Fe= 98.65 mg/tablet

D_1 (Dumex)	Weight of two tablets taken for analysis	Titer reading	Fe content per tablet	Mean	Deviation	Standard deviation	Standard relative deviation S_R	Relative error
	g	mL	mg	$\bar{x}$	$d_i=\lvert\bar{x}-x\rvert$	σ	%	%
Method I (Sn-Hg reduction)	1.65270	15.4	101.21		0.60			
	1.70900	16.4	104.24	100.61	3.63	3.9640	3.94	1.98
Titer: $K_2Cr_2O_7$ (0.02551N)	1.66792	14.8	96.28		4.23			
Method IIA (Zn reduction)	1.65270	14.6	95.96		1.45			
	1.70900	15.1	95.97	97.41	1.44	2.4970	2.56	1.26
Titer : $K_2Cr_2O_7$ (0.02551N)	1.66792	15.4	100.29		2.86			
Method IIB (Zn reduction)	1.65270	15.6	99.47		1.09			
	1.70900	16.4	101.13	100.58	0.57	0.6697	0.67	1.94
Titer : $KMnO_4$ (0.02475N)	1.66792	16.0	101.09		0.53			

Contd...

Table 4.3 (contd.)

Deviation d_i = Mean value - observed value = $|\bar{x} - x_i|$

Standard deviation $\sigma = \sqrt{\frac{\sum d_i^2}{N - 1}}$ where N = number of observations.

Relative % error = $\frac{\text{Expected value - Mean of observed values } (\bar{x})}{\text{Expected value}} \times 100$

where expected value is Fe content per tablet according to Manufacturer's Label

Standard relative deviation $S_R = \frac{\text{Standard deviation } (\sigma)}{\text{Mean } (\bar{x})} \times 100$

Table 4.4 : Analysis of Microfolin (Sample D_2)
Expected amount of Fe = 65.76 mg/tablet

D_2 (Macrofolin)	Weight of two tablets taken for analysis	Titer reading	Fe content per tablet	Mean	Deviation	Standard deviation	Standard relative deviation S_R	Relative error
	g	mL	mg	$\bar{x}$	$d_1=\lvert\bar{x}-x\rvert$	σ	%	%
Method I (Sn-Hg reduction)	0.80195	9.8	71.40		3.13			
	0.83000	9.5	66.88	68.27	1.39	2.7160	2.72	3.82
Titer : $K_2Cr_2O_7$ (0.02551N)	0.83435	9.5	66.53		1.74			
Method IIA (Zn reduction)	0.80195	9.7	70.67		2.41			
	0.83000	9.7	68.28	68.26	0.02	2.42	3.55	3.80
Titer : $K_2Cr_2O_7$ (0.02551N)	0.83435	9.4	65.83		2.43			
Method IIB (Zn reduction)	0.80195	10.0	70.69		2.85			
	0.83000	9.6	65.57	67.84	2.27	2.61	3.85	3.16
Titer : $KNnO_4$ (0.02475N)	0.83435	9.9	67.26		0.58			

Table 4.5 : Analysis of Fefol (Sample D_3)
Expected amount of Fe = 55.17 mg/tablet

D_3 (Fefol)	Weight of two tablets taken for analysis	Titer reading	Fe content per tablet	Mean	Deviation	Standard deviation	Standard relative deviation	Relative error
	g	mL	mg	$\bar{x}$	$d_1=\lvert\bar{x}-x\rvert$	σ	S_R %	%
Method I (Sn-Hg reduction) Titer : $K_2Cr_2O_7$ (0.02551N)	0.93610	7.4	53.46		0.26			
	0.94180	7.6	54.57	53.72	0.85	0.75	1.40	2.63
	0.92900	7.3	53.14		0.58			
Method IIA (Zn reduction) Titer : $K_2Cr_2O_7$ (0.02551N)	0.93610	7.7	55.63		2.16			
	0.94180	7.3	52.42	53.47	1.05	1.86	3.48	3.08
	0.92900	7.2	52.41		1.06			
Method IIB (Zn reduction) Titer : $KMnO_4$ (0.02475N)	0.93610	7.8	54.67		0.57			
	0.94180	8.0	55.73	55.24	0.49	0.53	0.96	0.13
	0.92900	7.6	55.32		0.08			

Table 4.6 : Analysis of Fessovite (Sample D_4)

Expected amount of Fe = 56.17 mg/tablet

D_4 (Fessovite)	Weight of two tablets taken for analysis g	Titer reading mL	Fe content per tablet mg	Mean $\bar{x}$	Deviation $d_1 = \lvert\bar{x}-x\rvert$	Standard deviation σ	Standard relative deviation S_R %	Relative error %
Method I (Sn-Hg reduction)	0.96135	7.8	55.30		0.31			
	0.95672	7.4	52.72	54.99	2.27	2.14	3.89	0.33
Titer : $K_2Cr_2O_7$ (0.02551N)	0.95720	8.0	56.96		1.97			
Method IIA (Zn reduction)	0.96135	7.7	54.59		0.07			
	0.95672	7.2	52.00	54.52	2.52	2.48	4.55	1.18
Titer : $K_2Cr_2O_7$ (0.02551N)	0.95720	8.0	56.96		2.44			
Method IIB (Zn reduction)	0.96135	8.6	59.15		2.59			
	0.95672	8.2	56.67	56.56	0.11	2.64	4.67	2.52
Titer : $KMnO_4$ (0.02475N)	0.95720	7.8	53.88		2.68			

Table 4.7 : Analysis of Zenfer (Sample D_5)

Expected amount of Fe = 50.00 mg/tablet

D_5 (Zenfer)	Weight of two tablets taken for analysis	Titer reading	Fe content per tablet	Mean	Deviation	Standard deviation	Standard relative deviation S_R	Relative error
	g	mL	mg	$\bar{x}$	$d_1 = \lvert\bar{x}-x\rvert$	σ	%	%
Method I (Sn-Hg reduction) Titer : $K_2Cr_2O_7$ (0.02551N)	1.00780	7.0	49.47		0.76			
	1.00569	7.2	50.99	50.23	0.76	0.76	1.51	0.46
	1.00674	7.1	50.23		0.00			
Method IIA (Zn reduction) Titer : $K_2Cr_2O_7$ (0.02551N)	1.00780	7.0	49.47		0.28			
	1.00569	6.9	48.86	49.75	0.89	1.06	2.13	0.50
	1.00674	7.2	50.93		1.18			
Method IIB (Zn reduction) Titer : $KMnO_4$ (0.02475N)	1.00780	7.2	49.37		0.74			
	1.00569	7.3	50.16	50.11	0.05	0.71	0.22	1.42
	1.00674	7.4	50.79		0.68			

Table 4.8 : Analysis of Raricap (Sample D_6)
Expected amount of Fe = 25.00 mg/tablet

D_6 (Raricap)	Weight of two tablets taken for analysis	Titer reading	Fe content per tablet	Mean	Deviation	Standard deviation	Standard relative deviation	Relative error
	g	mL	mg	$\bar{x}$	$d_i = \lvert\bar{x} - x\rvert$	σ	S_R %	%
Method I (Sn-Hg reduction)	2.13912	3.5	24.53		1.09			
	2.18810	3.9	26.71	25.62	1.09	1.09	4.25	2.48
Titer : $K_2Cr_2O_7$ (0.02551N)	2.16360	3.7	25.63		0.01			
Method IIA (Zn reduction)	2.13912	3.5	24.53		1.1			
	2.18810	3.8	26.03	25.63	0.40	0.96	3.75	2.52
Titer : $K_2Cr_2O_7$ (0.02551N)	2.16360	3.8	26.32		0.69			
Method IIB (Zn reduction)	2.13912	3.8	25.83		0.07			
	2.18810	4.0	26.58	25.76	0.82	0.86	3.34	3.04
Titer : $KMnO_4$ (0.02475N)	2.16360	3.7	24.86		0.90			

Table 4.9 : Estimation of iron* from iron supplement tablets

Drug sample with Fe content per tablet (indicated on label)	Method I : Sn-Hg reduction			Method II : Zn dust reduction					
				A			B		
	Titer : $K_2Cr_2O_7$			Titer : $K_2Cr_2O_7$			Titer : $KMnO_4$		
	Fe content found	Relative error	Standard deviation (Relative)	Fe content found	Relative error	Standard deviation (Relative)	Fe content found	Relative error	Standard deviation (Relative)
mg	mg	(%)	(%)	mg	mg	(%)	mg	(%)	(%)
D_1 (98.65)	100.61	1.98	3.94	97.41	1.26	2.56	100.58	1.94	0.67
D_2 (65.76)	68.27	3.82	2.72	68.26	3.80	3.55	67.84	3.16	3.85
D_3 (55.17)	53.72	2.63	1.40	53.47	3.08	3.48	55.24	0.13	0.96
D_4 (55.17)	54.99	0.33	3.89	54.52	1.18	4.55	56.56	2.52	4.67
D_5 (50.00)	50.23	0.46	1.51	49.75	0.50	2.13	50.11	1.42	0.22
D_6 (25.00)	25.62	2.48	4.25	25.63	2.52	3.75	25.76	3.04	3.34

* The values are mean of three replicates.

dilute titer solutions.

The conventional method (Sn-Hg method) involves the use of $HgCl_2$ (which is not desirable due to pollution problem). It requires critical addition of reagents viz. $SnCl_2$ and $HgCl_2$, which otherwise may lead to error in analysis. In the method suggested here (zinc-dust method), as the reduction of ferric ions is carried out by using zinc dust in presence of sulphuric acid (instead of hydrochloric acid[1]), the method is applicable for the use of potassium dichromate as well as potassium permanganate (without using Zimmermann-Reinhardt's solution[2]). Thus, the zinc dust method seems to be better than the conventional method. For the samples used, the interference of of other metal ions (present in them) is found to be negligible. The experimental results show that the accuracy and precision are fair.

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chapter 5

PAPER MODELS OF SOME SPECIES CONTAINING OCTAHEDRAL BASIC UNITS

Indeed, to be useful, a model must be wrong in some respects - else it would be the thing itself. The trick is to see - with the help of a teacher - where it's right.

- H.A. Bent

CHAPTER 5

PAPER MODELS OF SOME SPECIES CONTAINING OCTAHEDRAL BASIC UNITS

ABSTRACT

The methods described here, for the construction of octahedra without faces are very useful to get the paper models of octahedral complexes as well as of species having octahedral basic units. The methods are simple and quick. The models obtained are inexpensive, sturdy and portable. By xeroxing standard plans given here, on papers of different colours, various octahedral basic units can be obtained. Using shades of contrast colours we can show different atoms and bonds. We can also indicate on the models the bond angles, bond length, symbols etc. With the help of such units, we can construct the models that are useful for teaching structural inorganic chemistry.

5.1 INTRODUCTION

In teaching structural inorganic chemistry, especially for species such as metal complexes, polyanions etc., the models are very much useful. There are some earlier reports about the preparation of models. The models can be prepared using wooden cocktail picks[1], plastic hair pins[2], drinking straws[3] or cotton swabs[4,5]. But these models are expensive and rather difficult to prepare. The paper models, however, are better in this respect.

A paper model showing the shape of an octahedron, a Platonic solid form, can be built from a piece of card paper as per the master plan given[6,7], from a sealed empty envelope[8,9] or from a constant-width continuous strip of paper[10,11]. A model of twin octahedra having a common line (edge)[12] or a long chain of such octahedra[10] can also be built from the paper. There is an earlier report about the use of a model of an octahedron without faces for teaching stereoisomerism in coordination compounds[13].

Here are given two modified simple methods of constructing models of octahedra without faces. These models, with some additions in the procedure, can show the exact placement of metal atoms, ligating centres and bonds.

Using first method, we can get twin octahedra without faces (each with edge of 5 cm) and a common line, from a squarish card paper (with edge of 20 cm). Using this method one can get either two single octahedra (by cutting along the common line) or a chain of octahedra having common edges (by joining such units using their proper sides). The three dimensional models for species containing chains[14] and layers[15] of octahedra can also be constructed by joining properly the units of twin octahedra.

In the second method, a master plan is slightly modified to get an octahedron without faces (edge of 10 cm) from a card paper of size 40 cm x 20 cm. This octahedron looks as if having made up of six octahedral units. Using such octahedra, we can construct the models of polyoxyanions more easily.

The detailed procedures for preparing some representative models as well as the photographs of these models are given (Refer plates 5.1 to 5.10).

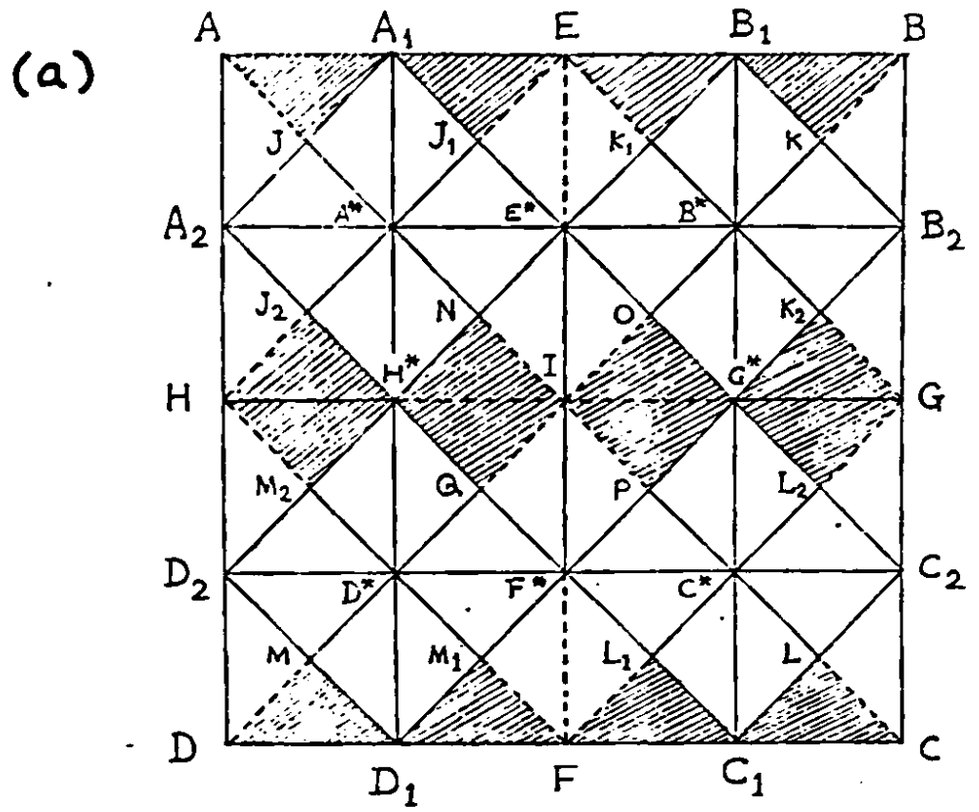
5.2 PREPARATION OF TWIN OCTAHEDRA

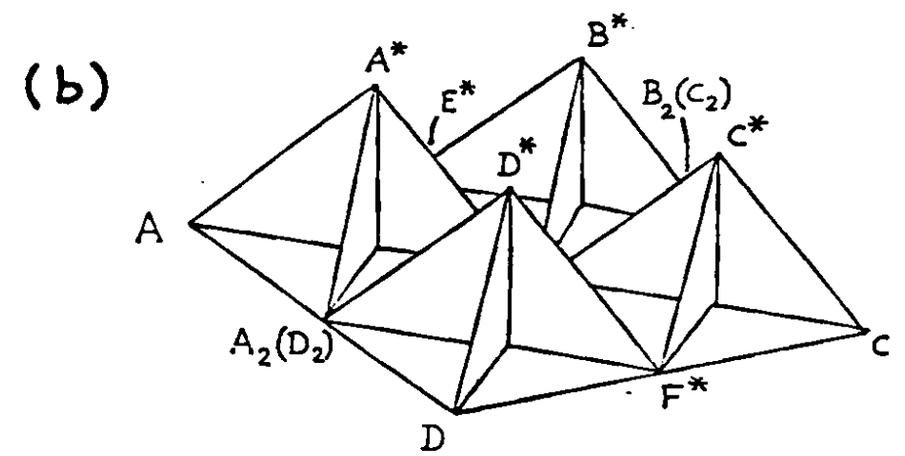
For the model of twin octahedra without faces and having a common line, refer Figure 5.1 and Plate 5.1(a).

(1) The square, ABCD, having side of 20.0 cm is cut from a card paper. It is folded forward lengthwise and diagonalwise to get distinct lines EF, GH, AC and BD as well as the centre I. It is folded forward along the lines EG, GF, FH and EH. The four points obtained due to intersection of the diagonals and these folds form a square $A^*B^*C^*D^*$. Then it is folded backward such that the folds A_1D_1 and B_1C_1 are obtained after folding AD and BC to be overlaid by EF. Similarly folds A_2B_2 and C_2D_2 are obtained. Finally the paper is folded along A_1A_2, B_1B_2, C_1C_2, D_1D_2, A_1C_2, A_2C_1, B_1D_2 and B_2D_1. The additional points of intersection which are formed outside $A^*B^*C^*D^*$ are marked as J, J_1, J_2, K, K_1, K_2, L, L_1, L_2, M, M_1, M_2 and those obtained inside $A^*B^*C^*D^*$ are marked as E^*, F^*, G^*, H^*, N, O, P and Q.

(2) The areas which will be overlaid by the near-by areas are shaded by oblique lines. They are the triangles - AA_1J, EA_1J_1, EB_1K_1, BB_1K, CC_1L, FC_1L_1, FD_1M_1 and DD_1M as well as the squares - $HJ_2H^*M_2$, INH^*Q, IOG^*P and $GL_2G^*K_2$.

(3) The standard plan i.e. ABCD square is cut on the lines - AJ, BK, CL, DM, EJ_1, EK_1, GK_2, GL_2, FL_1, FM_1, HM_2, HJ_2, EE^*, FF^*, NP, OQ and G^*H^* which are indicated in Figure 5.1(a) by dotted lines.





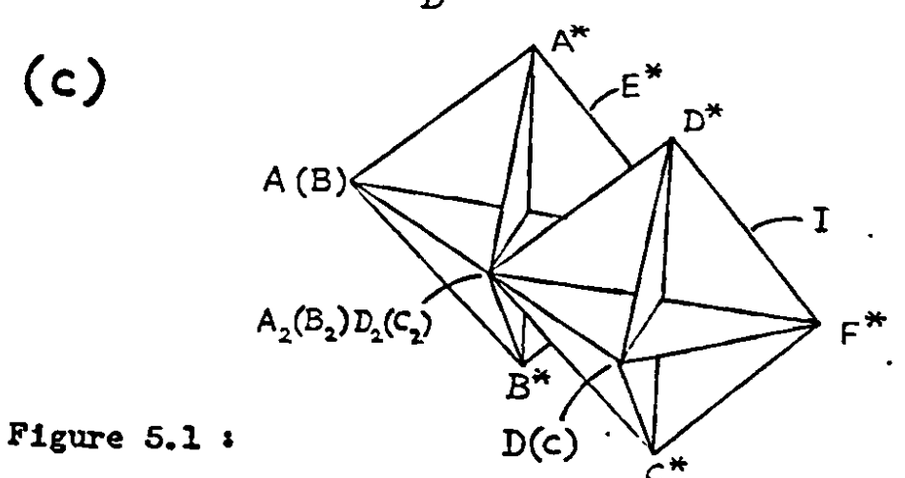


Figure 5.1 :

Standard plan for a paper model of twin octahedra with a common line (a) and the steps to obtain the model (b and c)

(4) The square is now folded carefully as instructed below and the overlaid parts are fixed immediately using a suitable fixing device (A stapler or cellophane tape is recommended for getting a permanent model or the use of paper clips for building a temporary model). In the notations given below the overlaying portion is mentioned first. It is followed by the bracket having the name of the portion which will be overlaid (shown in Figure 5.1(a) by oblique lines) -

$AA_2J(AA_1J)$, $EE^*J_1(EA_1J_1)$, $EE^*K_1(EB_1K_1)$, $BB_2K(BB_1K)$, $GB_2K_2(GG^*K_2)$, $GC_2L_2(GG^*L_2)$, $CC_2L(CC_1L)$, $FF^*L_1(FC_1L_1)$, $FF^*M_1(FD_1M_1)$, $DD_2M(DD_1M)$, $HD_2M_2(HH^*M_2)$, $HA_2J_2(HH^*J_2)$, $NE^*I(NH^*I)$, $OE^*I(OG^*I)$, $PF^*I(PG^*I)$ and $QF^*I(QH^*I)$.

After fixing such forms we get two twin square pyramids having A^*, B^*, C^* and D^* as their apices and I as the corner shared by all of them. Each pyramid has two near-by edges at its base which are shared with its neighbouring pyramids. Folding along E^*F^* brings together the backsides of the rectangles E^*ADF^* and E^*BCF^* (refer figure 5.1(b) and (c)) to superimpose over each other, where they can be fixed to get the desired model.

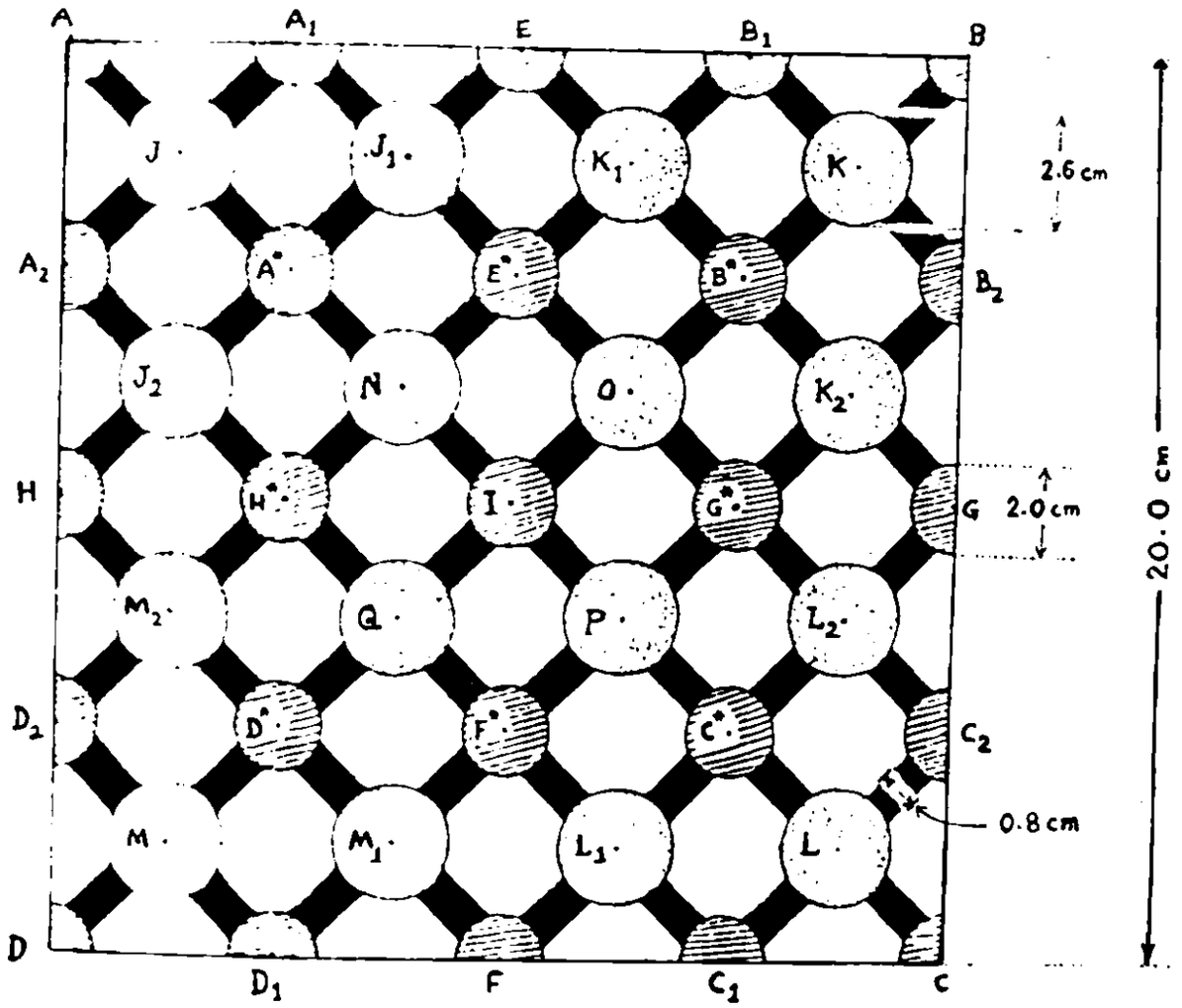
5.3 MODEL SHOWING ATOMS AND BONDS

For preparation of such model refer Figure 5.2(a) and Plate 5.1(b).

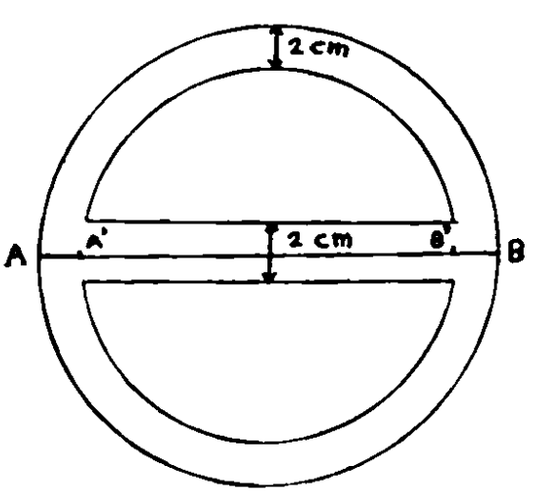
Figure 5.2 : (a) Standard plan for paper model of twin octahedra showing atoms and bonds

(b) Standard plan for a circle giving semicircular segments which indicate ligands

(a)



(b)



AB = 10 cm

A'B' = 8 cm

(1) A 20.0 cm square showing all the points is prepared as described in article 5.2.

(2) Taking points J, J_1, J_2, K, K_1, K_2, L, L_1, L_2, M, M_1, M_2, N, O, P and Q as the centres, circles having diameter of 2.6 cm are drawn. Taking the remaining points as the centres, the circles having diameter of 2.0 cm are drawn. The circlesof 2.6 cm and 2.0 cm diameters represent metal atoms and ligating atoms respectively (The diameters selected do not show the relative sizes of these atoms but just differentiate them). They are shown in the figure by dotted regions and oblique lines. They can be shown by two different colours. The 0.8 cm thick axes joining the circles (shown by dark shading in the figure) represent metal-ligand bonds. They can be shown by third colour.

The cutting, folding and joining of the square ABCD is done as indicated in steps (3) and (4) of article 5.2. It can give finally the twin octahedra indicating the binuclear metal complex with two bridging ligands.

5.4 MODELS OF SOME SIMPLE SPECIES

Using the method given in article 5.3, the models of simple octahedral species can be prepared. The metal atoms and ligating atoms can be distinguished by pasting the circles

of coloured tinted papers with different shades instead of painting.

In case of chelates, the chelating groups can be shown with the help of semicircular segments of coloured card papers. These semicircular segments can be prepared from an annular card paper ring (refer Figure 5.2(b)) with outer and inner diameters of 10 and 8 cm respectively. The ring should have a central segment of 2 cm thickness passing through its centre and along its diameter. The ring is cut into two halves along its diameter AB to get two segments. Such segments are fixed in the slots prepared along the proper edges of an octahedron.

Thus we can prepare the models of simple complexes and of metal chelates (containing bi, tri, ... hexadentate ligands). We have prepared models of some of the species involved in reactions given in earlier chapters, e.g. models of bis and tris metallo-oxalates (Chapter 2) and metal-EDTA complex ion (Chapter 2 and 3) (Refer Plate 5.2 and 5.3).

5.5 MODELS OF SOME POLYANIONS

With some addition in the procedure given in article 5.3 for preparing models of octahedra without faces, we can construct the models of polyanions containing octahedral basic units. Such models are very much useful to understand the complex structure of these polyanions. There is an earlier

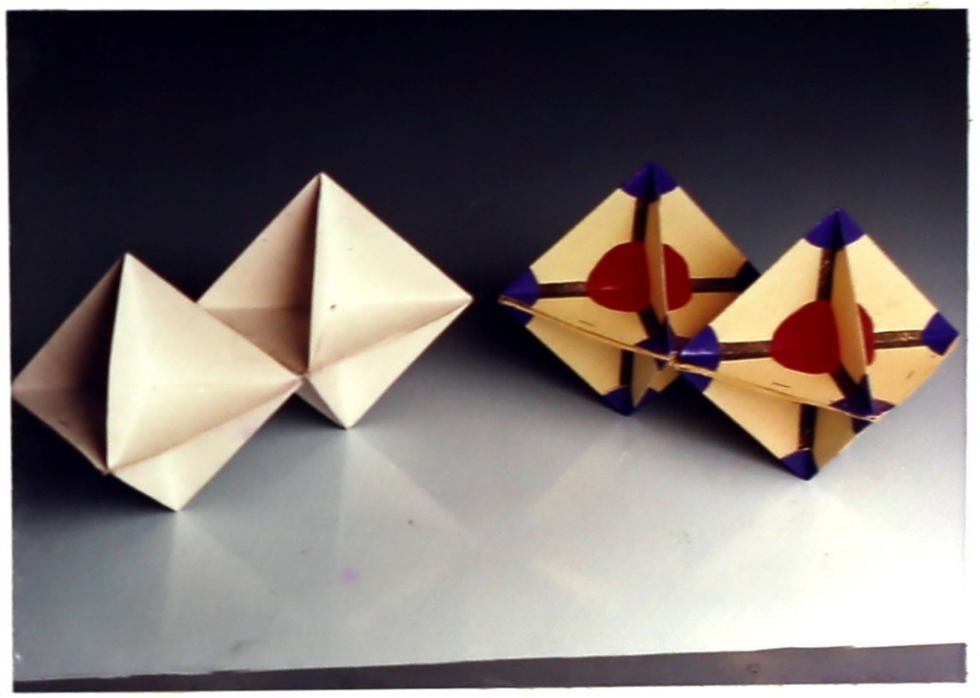


Plate 5.1 : Paper models of (a) twin octahedra without faces and with a common edge; (b) dimeric structure of solid $NbCl_5$

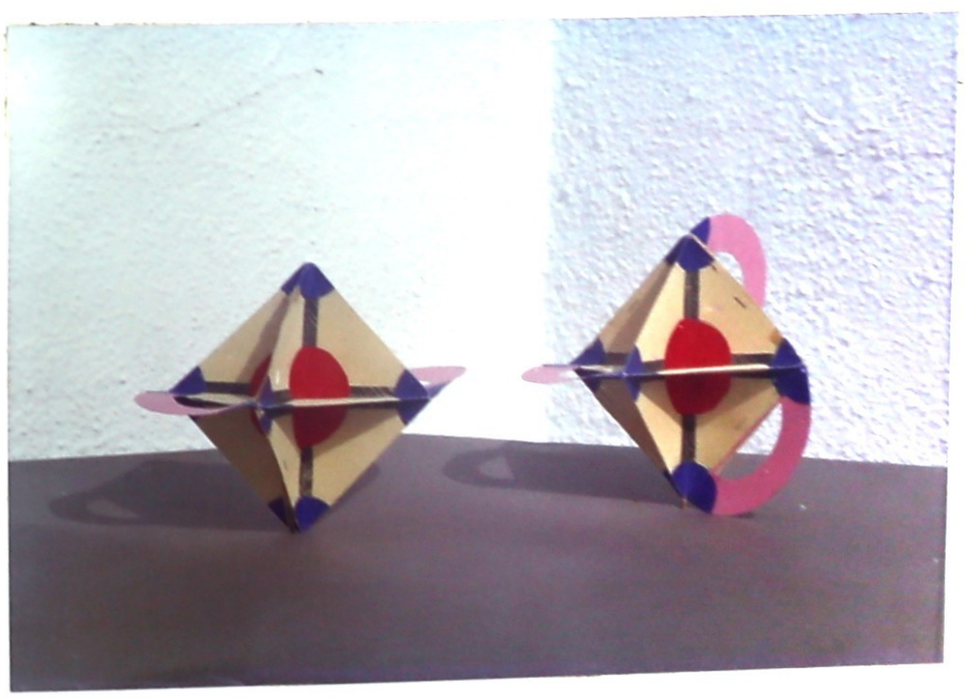


Plate 5.2 : Models of octahedral chelates as
(a)$[M^{II}(C_2O_4)_2].2H_2O$ species
(b)$[M^{III}(C_2O_4)_3]$ species

Plate 5.3 : Model of Metal - EDTA complex

Plate 5.4 : Model of $\left[Nb_6O_{19}\right]^{8-}$ ion

report[15] about the preparation of paper models of polyoxyanions containing MO_6 basic units. However, models prepared by the reported method, seem to be less sturdy and hence cannot be handled easily. Also these octahedral units are with faces. Therefore, it is difficult to show clearly all the atoms and bonds.

We have prepared the models of some of the polyanions in which there are six, seven, eight and ten octahedral MO_6 units. As the octahedral units are without faces, we can show all the atoms, bonds, bondangles, bond lengths, symbols etc. easily. In such polyanions oxygen atoms differ from each other as some of them are shared between varying number of octahedral units while some of them are unshared. In Table 5.1 some of the polyanions with their different types of octahedral units and different types of oxygen atoms are mentioned[15].

To differentiate the various types of octahedral units the card papers of different colours are used. To show oxygen and the metal atoms in each unit the circles of proper size cut out from tinted papers of different shades are used.

The octahedral units are properly attached using stapler and / or cellophane tape. For keeping the units in sturdy position use of small squarish pieces (edge 3 cm) is done. Each piece is inserted to half of its area into the

Table 5.1 : Structural Features in the Union of MO_6 Octahedra in Polyanions

Sr. No.	Polyanion and formula	No. of Octahedra in each set of similarly positioned Octahedra	Oxygen atom sharing scheme for each set of Octahedra						Plate Number
			Number of unshared corners	Number of corners shared by					
				two	three	four	five	six	
1.	Hexaniobate ion, $(Nb_6O_{19})^{8-}$	6*	1	4	0	0	0	1	5.4
2.	Hepta-molybdate ion, $(Mo_7O_{24})^{6-}$	1*	0	2	2	2	0	0	5.5
		2**	2	3	0	1	0	0	
		4***	2	2	1	1	0	0	
3.	Octa-molybdate $(Mo_8O_{26})^{4-}$	2*	1	1	2	0	2	0	5.6
		2**	2	3	0	0	1	0	
		4***	2	1	2	0	1	0	
4.	Decavanadate ion $(V_{10}O_{28})^{6-}$	4*	1	2	2	0	0	1	5.7
		4**	1	4	0	0	0	1	
		2***	0	2	2	0	0	2	

The octahedra belonging to each set of similarly positioned octahedra in each type of polyanion are made of coloured papers like yellow (*), blue (**) and pink (***).

For showing the oxygen atoms (occupying the corners of octahedral units) in the polyoxyanions the colour-code used is as follows: The unshared corners are shown blue while the corners shared by two, three, four, five and six octahedra are shown by green, pink, orange, violet and brown colours respectively.

The metal ion M in each octahedral unit is indicated by deep red colour.

slots prepared along those edges of two octahedral units which are to be joined and then cellophane tape is fixed. This procedure is similar to that used for preparing polyanions containing tetrahedral basic units[16]. With the help of these models it is easy to visualise the arrangement of different octahedral units, metal atoms and oxygen atoms in complicated structure of polyanions (Refer Plate 5.4 to 5.7).

Using similar procedure we have prepared the model for Keggin's structure of $[PMo_{12}O_{40}]^{3-}$ (Refer Plate 5.8) i.e. of molybdophosphate ion (as it is involved in the estimation of PO_4^{3-}, the experiment given in Chapter 3). The model is prepared by joining four sets (each containing three octahedral MoO_6 units) of octahedra to four corners of a regular tetrahedron (which represents PO_4^{3-} ion). The tetrahedral PO_4^{3-} unit is prepared from blue card paper as per the steps[17] given in Figure 5.3. The phosphorus atom at its centre is shown by golden yellow colour.

5.6 MODEL OF AN OCTAHEDRON SHOWING SIX OCTAHEDRAL UNITS

Another method used to get an octahedron without faces has slightly modified master plan (Fig. 5.4). The plan is xeroxed on 40 cm x 20 cm card paper. By folding the paper as mentioned in the first method, we can get an octahedron, made up of six small octahedral units which can be distinguished

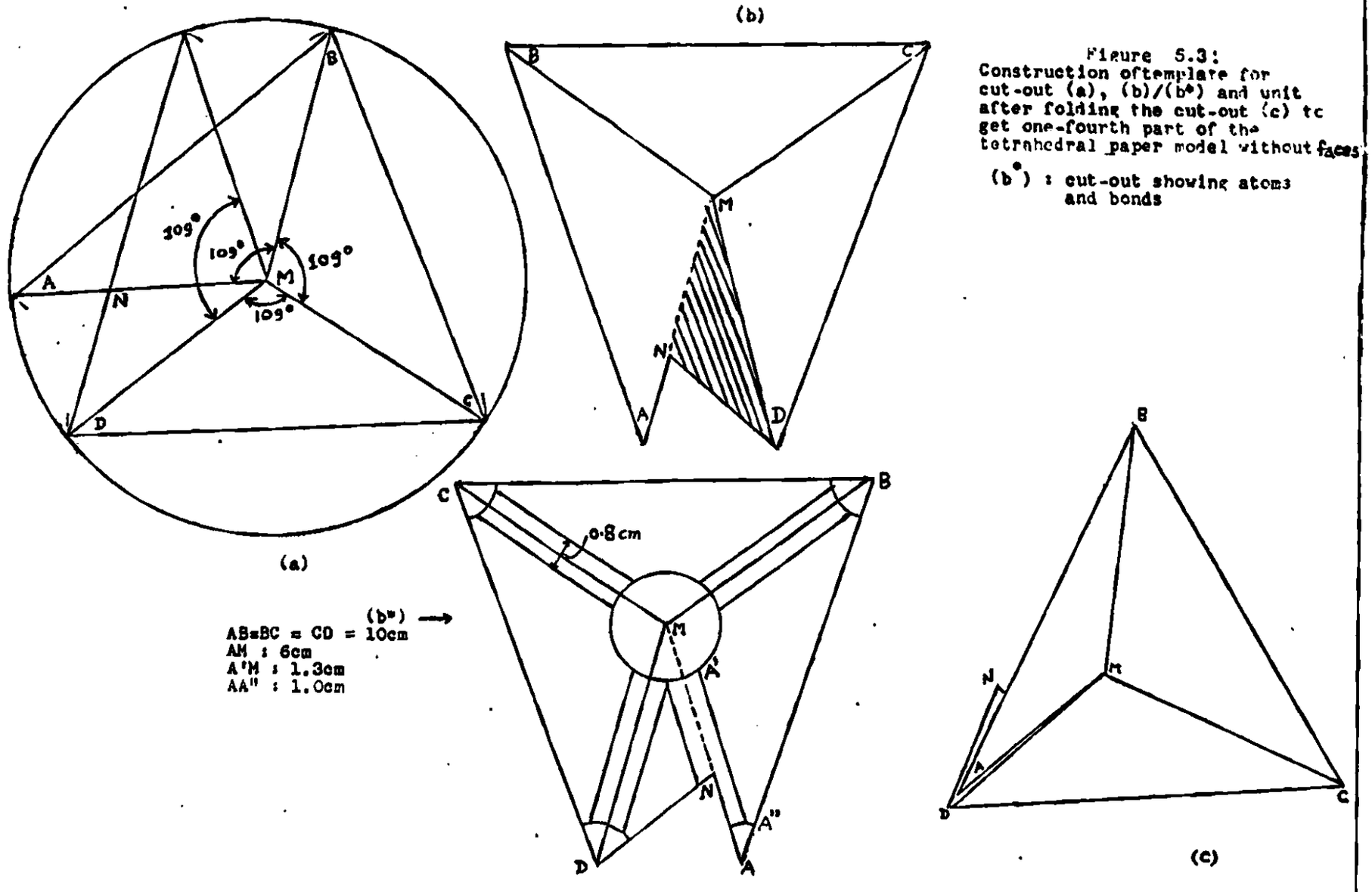


Figure 5.3:
Construction oftemplate for cut-out (a), (b)/(b*) and unit after folding the cut-out (c) tc get one-fourth part of the tetrahedral paper model without faces

(b*) : cut-out showing atoms and bonds

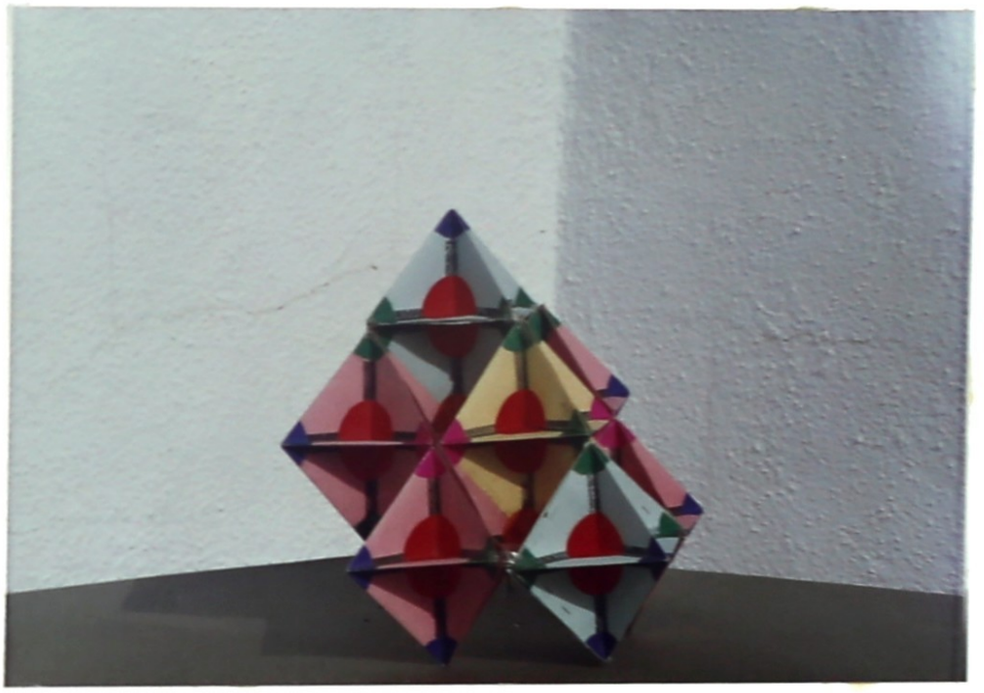


Plate 5.5 : Model of $\left[Mo_7O_{24}\right]^{6-}$ ion

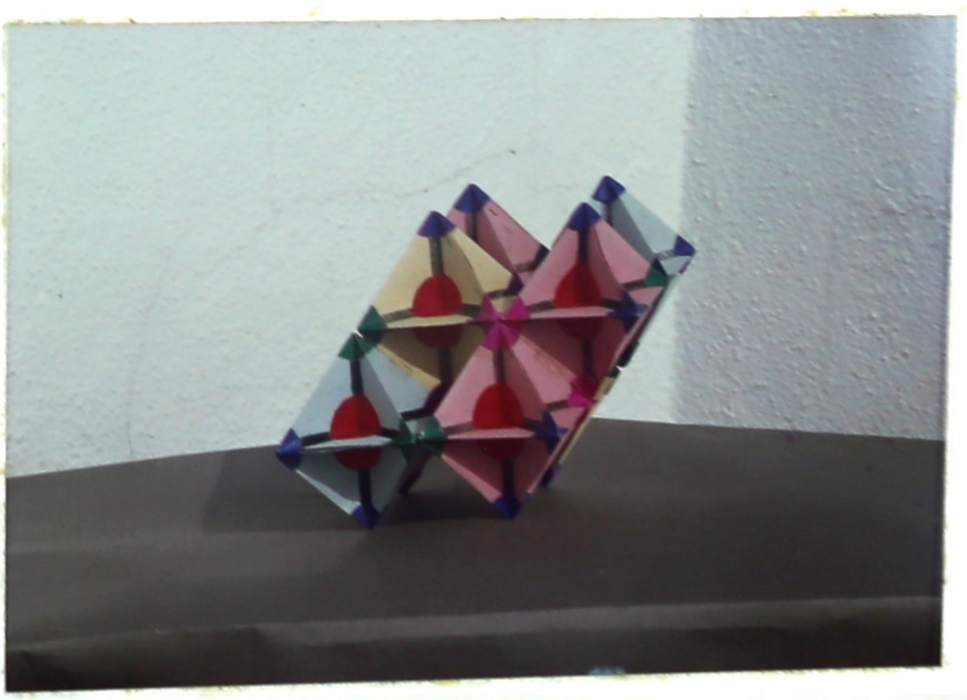


Plate 5.6 : Model of $\left[Mo_8O_{26}\right]^{4-}$ ion

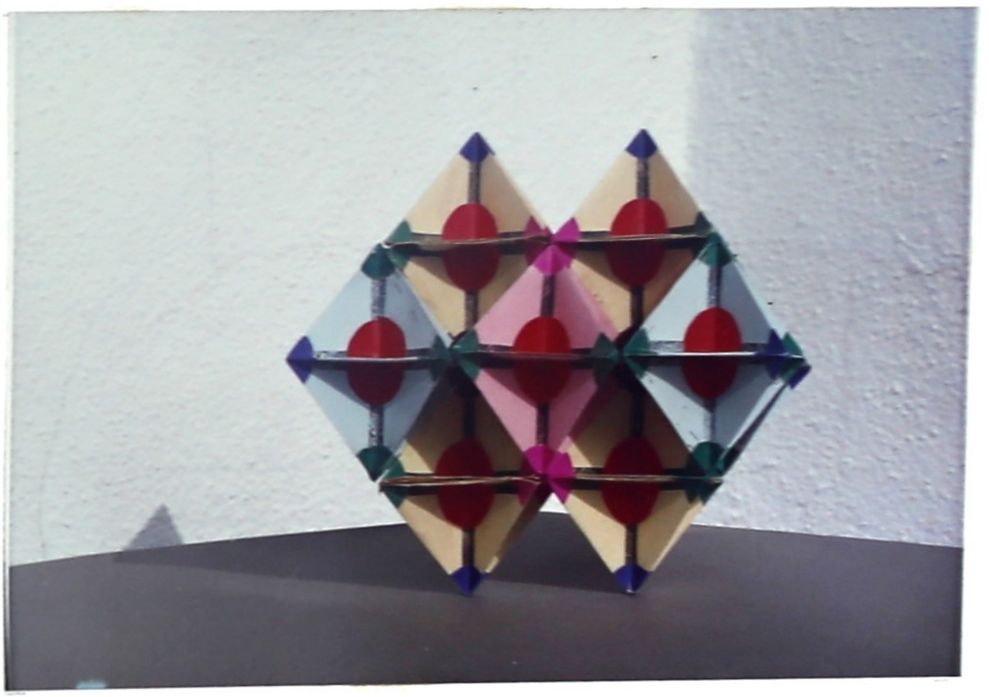


Plate 5.7 : Model of $\left[V_{10}O_{28}\right]^{6-}$ ion

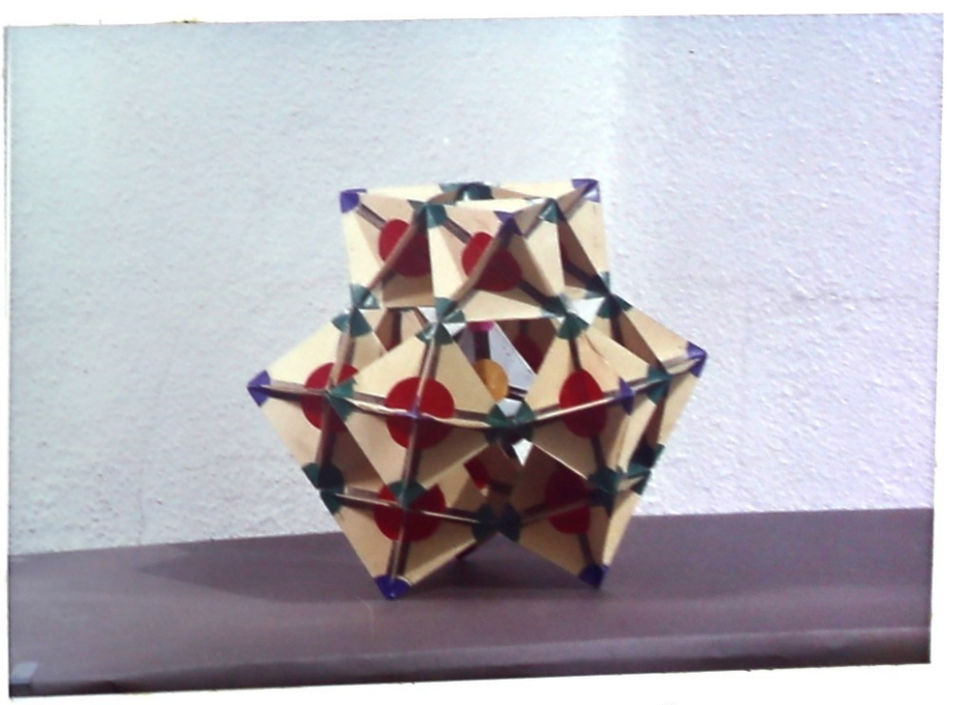


Plate 5.8 : Model of Keggin's structure molybdophosphate ion $\left[PMo_{12}O_{40}\right]^{3-}$

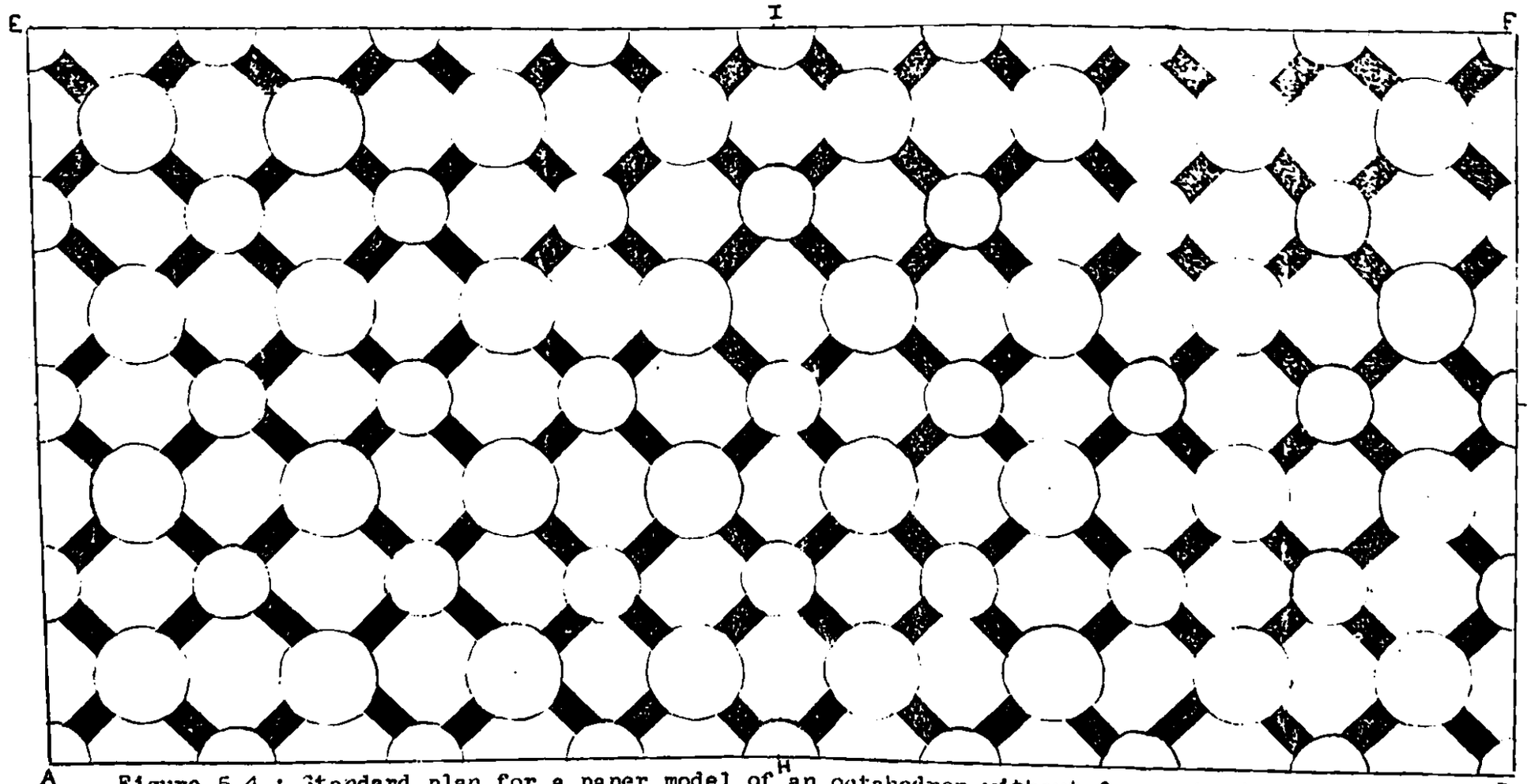


Figure 5.4 : Standard plan for a paper model of an octahedron without faces showing six octahedral units (AEFD = half part of ABCD in Fig. 5.2)
AE = 10 cm , EF = 20 cm.

from each other by painting them with different colours (Refer Plate 5.9).

This method is convenient than the first method for the preparation of model of a species containing six octahedral units. For the models of the species containing less than six octahedral units, some small octahedral units are to be cut from octahedron prepared here. For the models of the species containing more than six octahedral units, additional small octahedral units are to be attached properly to the octahedron prepared. Some representative structures such as $(V_{10}O_{28})^{6-}$ and Anderson's structure of $(TeMo_6O_{24})^{3-}$ are given in Plate 5.10(a) and 5.10(b) respectively. For the model of $(V_{10}O_{28})^{6-}$ three different types of octahedral units are shown by white, orange and blue colours. For the model of $(TeMo_6O_{24})^{3-}$, the six MoO_6 octahedra are arranged in a hexagonal annulus. The resulting cavity is found to be just large enough to accomodate an octahedron corresponding with that of the heteroatom (Te). Six MoO_6 octahedra are white (with molybdenum atoms shown by red colour) while the central octahedron is yellow with the tellurium atom shown by violet colour.

5.7 CONCLUSIVE REMARKS

The proposed methods for preparation of paper models

Plate 5.9 : Models of $\left[Nb_6O_{19}\right]^{8-}$ as (a) octahedron having six $\left[NbO_6\right]$ units; and (b) octahedron containing octahedral arrangement of six Nb^{5+} ions along with basic $\left[NbO_6\right]$ unit (at the extreme lower left hand corner)

Plate 5.10 : Models of (a) $\left[V_{10}O_{28}\right]^{6-}$ and (b) Anderson's structure of $\left[TeMo_6O_{24}\right]^{3-}$

are simple and quick. The models are sturdy and inexpensive (The cost for each model may be ~ Rs. 3-5). The models of simple octahedral species are detachable and they can be unfolded to the squarish sheets (if necessary). Thus, they are portable and can be easily handled. As the models of octahedra are without faces, using coloured papers of different shades we can show metal atoms, ligating atoms, bonds, bond angles, bond length, lone pairs of electrons (if any) and sharing of particular atoms between different octahedral units.

Using these methods we can construct the models of simple octahedral complexes (ML_6) and chelates (like metallo--oxalates, M-EDTA complex). These types of models are useful to teach coordination chemistry (to explain structure of the complexes as well as geometrical and optical isomerism).

We can prepare the models of the species with complex structure e.g. $NbCl_5$ solid, $[Re(CO)_4I]_2$ (dimer with halogen bridges); $[Ti(OC_2H_5)_4]_4$ solid, $Fe_2(CO)_9$, $Co(acac)_2$ (tetramer)[18]; NbI_4 solid (chain with metal-metal interactions); and $ZrCl_4$ solid (zigzag chain of $ZrCl_6$ octahedra).

Also we can build three dimensional models of polyanions such as $[Nb_6O_{19}]^{8-}$, $[Mo_7O_{24}]^{6-}$, $[Mo_8O_{26}]^{4-}$. In such polyanions ligating atoms which vary from each other

depending upon their extent of sharing between octahedral units can be easily distinguished.

In the proposed plan which shows atoms and bonds, suitable modifications can be done to prepare the models of molecules having octahedral geometry and containing lone pairs of electrons e.g. The models of xenon fluorides like XeF_4 (pseudostructure : octahedral with two lone pairs in trans position) and XeF_6 (pseudostructure : ψ -octahedral or capped octahedral with one lone pair). These modifications are based on the procedure that is used for showing tetrahedral placement of ligands with reference to cubic geometry[19].

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appendix

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Titrimetric Estimation of Calcium and Phosphate in Dietary Supplement Tablets-An Inorganic Analytical Undergraduate Experiment

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ABSTRACT:

An experiment involving estimation of calcium and phosphate, is suggested which enables the student to gain experience in three different types of standard titrimetric estimations, namely, neutralization method (alkalimetry), redox method (permanganometry) and complexometry (EDTA titrations). It also gives two methods for separating and estimating one of these constituents in presence of the other, which otherwise is erroneous. The results show accuracy and reproducibility.

Introduction:

The teaching of titrimetric analysis has now introduced purposeful exercises involving analysis of consumer products such as drugs. This necessitates the setting of experiments which familiarize the students with as wide a range of titrimetric reactions as possible. The experiment suggested here is profitable in that it adds variety to the laboratory programme, enables the students to gain experience in analysis of a familiar sample of known composition and increases their awareness about the importance of chemistry of consumer products.

Any of the two methods suggested here for the titrimetric estimation of calcium and phosphate simultaneously, involve combined use of different types of titrimetry namely acid-base, redox and complexometry. This, otherwise, is not possible due to the precipitation of their salt. The analysis of a sample using both the methods will require three 3-h laboratory periods. So another approach is to give the experiment as a group experiment. The students may be devided into pairs, each student being responsible for the use of single method and the data from two methods may ultimately be shared by both. In the proposed methods, phosphate is estimated by 'Quinoline molybdophosphate method' which is better than the conventional 'Ammonium molybdophosphate method'.

In method I, phosphate is separated as quinoline molybdophosphate precipitate and estimated using alkalimetry, while filtrate is used for estimation of calcium using EDTA (either directly[1] or by back titration with standard zinc sulphate[2]). In method II, calcium is separated as calcium oxalate precipitate and then estimated by permanganometry and from the filtrate phosphate is precipitated as quinoline molybdophosphate and estimated by alkalimetry.

Experimental

The setting of the procedure is done by using standard solutions of Ca^{2+} and $PO^{3}_{4}-$, their synthetic mixtures and a salt of known composition. The detailed procedure is given below and the results are given in Table 1. Some of the well-known dietary supplement tablets containing calcium and phosphate are used for the analysis. After weighing exactly the tablet(∽ 1 g) is disintegrated using 10 mL. of nitric acid (1:1) followed by 5 mL of concentrated hydrochloric acid. (For the tablet having weight less than 0.6 g. two tablets are used instead of one, inorder to get the readings in the range suitable for titrimetric analysis). The solution is

cooled, filtered and then diluted exactly to 250 mL, which can be used for estimation of calcium and phosphate using either of the following methods.

Method I : Estimation of phosphate – To the 25 mL aliquot, 8 mL of concentrated hydrochloric acid and 18 mL of sodium molybdate (15%) are added. The solution is heated and ~ 35 mL of quinoline hydrochloride reagent is slowly added when a yellow precipitate of quinoline molybdophosphate is obtained. After digestion for 15 min, it is filtered through Whatman filter paper No. 41. The precipitate is first washed with hydrochloric acid (1:9), and then by water till it is acid free. The filtrate is diluted exactly to 250 ml and used for calcium estimation. The precipitate is dissolved in exactly 25ml of sodium hydroxide (0.5 M) and the solution is diluted to 250 mL. From this 25mL of the solution is back-titrated with standard hydrochloric acid solution (0.05 M) using phenolphthalein indicator. The blank titration is carried out by diluting 25 mL of sodium hydroxide (0.5 M) to 250mL and then titrating 25mL of this solution against standard hydrochloric acid (0.05 M). From the difference in volume, the amount of phosphate is calculated.

Estimation of calcium : (A) Direct titration with EDTA - To the 50mL of diluted filtrate, ~ 5mL of liquor ammonia is added to make the solution alkaline. Then 1mL of ammonia–ammonium chloride buffer (pH 10), and 5 mL of Magnesium–EDTA solution are added and solution is titrated using Eriochrome Black T indicator against EDTA solution (0.01 M) which is previously standardized using standard Zn^{2+} solution.

B) Back titration with standard zinc sulphate solution.

To the 50 mL diluted filtrate, 5 mL of liquor ammonia, exactly 25 mL of EDTA (0 01 M) and ~ 10 mL of ammonia-ammonium chloride buffer solution are added and excess of EDTA is back titrated with standard zinc sulphate solution (0.01 M) using Eriochrome Black T indicator. Blank titration is carried out by titrating 25 mL of EDTA with zinc sulphate solution. From the difference in readings the amount of calcium is calculated.

Method II : Estimation of calcium - To the 25 mL aliquot, 15 mL of ammonium acetate (7.2 %) solution is added. The solution is heated and 15 mL of ammonium oxalate (1%) solution is added to precipitate calcium oxalate. The precipitate is digested for 15 min and then filtered through Whatman filter paper No. 41. The filtrate is collected and used for estimating phosphate. The precipitate of calcium oxalate is dissolved in ~ 25 mL of hot sulphuric acid (2 N) and the solution is titrated against standard potassium permanganate solution (0.1 N).

Estimation of phosphate – From the filtrate, phosphate is estimated by using the same procedure as described in Method I.

The students may be asked to calculate the results for the average weight of the tablet. Such results are summarized in Table 1.

TABLE-1: ANALYSIS* OF SYNTHETIC MIXTURES, SALT, AND DRUG SAMPLES FOR ESTIMATION OF Ca^{2+} and PO_4^{3-}

Sample with expected results		Method I				Method II			
		Ca^{2+}		PO_4^{3-}		Ca^{2+}		PO_4^{3-}	
		Observed amount in mg	Relative error %	Observed amount in mg	Relative error %	Observed amount in mg	Relative error %	Observed amount in mg	Relative error %
Synthetic Mixtures (SM_1, SM_2)									
SM_1 (4.97 mg Ca^{2+} and 34.80mg. PO_4^{3-} in 25mL)	IA	4.91	−1.21	35.19	+1.12	4.85	−2.21	35.10	+0.86
	IB	4.97	Nil						
SM_2 (34.81mg Ca^{2+} and 4.27mg PO_4^{3-} in 25mL)	IA	35.00	+0 55	5.00	+0.60	34.61	-0.57	5.10	+2.62
	IB	34.06	−2.14						
Salt $CaHPO_4$(anhydrous) (147.30mg Ca^{2+} and 349.10mg PO_4^{3-} in 500.1mg salt)	IA	149.40	+1.43	350.96	+0.53	147.76	+0.31	354.88	+1.66
	IB	145.09	−1.50						
Drug Samples (D_1-D_5)									
D_1 (147.30mg Ca^{2+} and 349.10mg PO_4^{3-} per tablet)	IA	144.02	−2.23	349.36	+0.07	143.22	−2.77	347.65	−0.42
	IB	147 04	−0.18						
D_2 (33.00mg Ca^{2+} and 46.00mg PO_4^{3-} per tablet)	IA	33.23	+0.69	45.87	−0.28	32.87	−0.39	45.98	−0.04
	IB	32.40	−1.82						
D_3 (125.00mg Ca^{2+} and 191.10mg PO_4^{3-} per tablet)	IA	123.58	−1.14	192.25	+0.60	127.00	+1.60	192.01	+0.48
	IB	125.54	+0.43						
D_4 (64.21mg Ca^{2+} and 104.72mg PO_4^{3-} per tablet)	IA	62.39	−2.83	102.90	−1.74	63.60	−1.11	102.16	−2.44
	IB	62.58	−2.54						
D_5 (101.00mg Ca^{2+} and 237.36mg PO_4^{3-} per tablet)	IA	103.16	+2.14	234.78	−1.09	103.75	+2.72	236.71	−0.27
	IB	102.78	+1.76						

*Tho values are mean of three replicates

IA Method of direct titration with EDTA

IB Method of Back titration with Zinc sulphate

CONCLUSIONS: The proposed methods are simple, reproducible and accurate within the limits of titrimetric analysis. As the assay of drug samples is available, reliable evaluation of the students, performance can be done. The samples used here contain calcium and phosphate as inorganic ions. So for the samples having other additional constituent inorganic ions, modifications seem to be necessary. For complexometric estimation of calcium, direct titration method seems to be better than back titration method.

TABLE - 2 : SOME REPRESENTATIVE OBSERVATIONS AND RESULTS OF THE ESTIMATION OF Ca^{2+} and PO_4^{3-}

Sample [a]	Method I						Method II			
	Ca^{2+}				PO_4^{3-}		Ca^{2+}		PO_4^{3-}	
	Method IA		Method IB							
	Titer (mL) EDTA (0.01065M)	Calculated amount (mg)	Titer (mL)[b] $ZnSO_4$ (0.009918M)	Calculated amount (mg)	Titer (mL)[b] HCl (0.06357 M)	Calculated amount (mg)	Titer (mL) $KMnO_4$ (0.1010M)	Calculated amount (mg)	Titer (mL)[b] HCl (0.06357M)	Calculated amount (mg)
Synthetic mixtures SM_1 (4.97 mg Ca, $^{2+}$; 34.80 mg PO_4^{3-})	2.3	4.91	2.5	4.97	16.0	35.19	2.4	4.86	17.9	35.10
SM_2 (34.81 mg Ca, $^{2+}$ 4.97 mg PO_4^{3-})	16.4	35.00	17.1	34.08	2.6	5.00	17.1	34.81	2.6	5.10
Drug D_3 (125.00 mg Ca, $^{2+}$ 191.10 mg PO_4^{3-})	5.8	122.33	6.3	123.74	10.0	193.78	6.2	124.01	10.1	194.72

a : The values in the parentheses are expected values.

b : Difference between the readings of blank and back titration.

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Determination of Iron from Iron-supplement Tablets by Redox Titrations using Zinc Dust as Reductant-A General Chemistry Experiment

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ABSTRACT:

A simple group experiment for the determination of iron from heamatinic tablets-a familiar consumer product - is suggested for execution in two 3–h laboratory periods. Ferric ions obtained after complete disintegration of the sample, are reduced with zinc dust in acid solution and the determination of iron can be done using either potassium dichromate or potassium permanganate solution. The experiment introduces the students to comparative study of both the redox reactions as well as their appiication to analytical chemistry.

INTRODUCTION:

With the increasing awareness about the pollution problems and environmental safety, it has become necessary to modify the conventional experimental procedures As an alternative to conventional Sn-Hg reduction method (which involves use of $HgCl_2$), we have tried the reduction of ferric ions as per some reported procedures using the reductants like zinc dust[1–3], zinc granules, aluminium powder, aluminium wire[4], aluminium foil, magnesium powder and magnesium ribbon. Out of these, reduction with zinc dust in presence of sulphuric acid is found to be suitable for the complete reduction of ferric ions within reasonable time. Using this method, therefore, an experiment has been set up for estimation of iron from iron-supplement tablets. These samples contain iron in different forms such as ferrous fumarate, ferrous sulphate, ferroglycine sulphate, and ferrouscalcium citrate complex. The method involves disintegration of tablets, reduction of ferric ion with zinc dust in presence of sulphuric acid and finally the titrimet ic estimation. It enables the students to gain the experience of redox titrations using potassium permanganate. The waste solutions obtained can be easily disposed off after removal of metal ions by precipitation[5].

EXPERIMENTAL

All the reagents and chemicals used are of Analar or equivalent grade. The procedure is set by using standard solutions prepared from iron salts and then used for the analysis of drugs.

Disintegration of drug sample[3]:- After weighing exactly, two tablets are disintegrated carefully in a 250 mL beaker by successive treatments of small portions (5 mL and 2 mL) of concentrated nitric acid till no darkening of the solution(indication of the complete removal of organic matter). It is then treated with a mixure prepared by taking 2 mL of concentrated nitric acid and 5 mL of concentrated sulphuric acid. The solution is heated until the brown fumes due to nitric acid are stopped After cooling, it is diluted with ~50 mL of distilled water and again heated to dissolve the iron salt. The solution is cooled and filtered through Whatmann filter paper No. 41 and diluted exactly to 250 mL.

Titrimetric Procedures : To the 25mL aliquot in a 250 mL conical flask, 10mL of sulphuric acid (3 M) is added It is heated to ~70°C on a hot plate and ~0.5g of zinc dust is added. The conical flask is covered with a watch glass. After

5min, 5mL of sulphuric acid (3M) is added. The flask is shaken until all the zinc dust is consumed and evolution of hydrogen has stopped. To this solution, 5mL of sulphuric acid (3M) and 5 mL of phosphoric acid (85%) are added.

The solution can be titrated against standard potassium dichromate solution (~0.025 N) after adding 4 drops of diphenylamine indicator (1% in concentrated sulphuric acid) until persistant blue-violet colour is observed.

Alternatively the titrations can also be carried out by using standard potassium permanganate solution (~0.025 N). Here, the distinct end point may be obtained by adding diphenylamine indicator just before the end point[2].

It is suggested to carry out blank titration using which the necessary correction for the main titration reading can be given.

For comparison of our results, conventional Sn-Hg reduction method has also been used. The results obtained for the three methods are summarised in Table 1.

CONCLUSION:

The results obtained (Table 2) for the amount of iron per tablet using zinc dust reduction method are in good agreement with the iron content as mentioned on the manufacturer's label as with those obtained using Sn-Hg reduction method. The method has advantages like simple experimental procedure, use of dilute titer solutions and safe disposal of waste solutions. As the reduction of ferric ions is carried out by using zinc dust in presence of sulphuric acid (instead of hydrochloric acid[1]), the method is applicable for the use of potassium dichromate as well as of potassium permanganate (without using Zimmermann-Reinhardt's solution[2]). For the samples used, the interference of other metal ions present in them, seems to be negligible. The experimental results show that the accuracy and precision are fair.

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We thank the Head, University Department of Chemistry, Pune and the Principal, Modern College, Pune for providing facilities, as well as R.G. Limaye for the valuable suggestions.

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TABLE 1 : ESTIMATION OF IRON* FROM IRON SUPPLEMENT TABLETS

Drug sample with Fe content per tablet (indicated on label) (mg)	Sn–Hg reduction method Titer : $K_2Cr_2O_7$			Zn reduction method Titer : $K_2Cr_2O_7$			Zn reduction method Titer : $KMnO_4$		
	Fe content found (mg)	Relative error (%)	Std. deviation (Relative) (%)	Fe content found (mg)	Relative error (%)	Std. deviation (Relative) (%)	Fe content found (mg)	Relative error (%)	Std. deviation (Relative) (%)
D_1 (98.65)	100.61	+1.98	3.94	97.41	−1.26	2.56	100.56	+1.94	0.67
D_2 (65.76)	68.96	+4.86	2.34	69.07	+5.03	1.42	68.06	+3.50	2.66
D_3 (55.17)	53.56	−2.92	0.88	53.48	−3.06	3 50	55.25	+0.15	0.88
D_4 (55.17)	55.06	−0.20	3.70	54.88	−0.53	5.22	56.33	+2.10	5 63
D_5 (50.00)	50.01	+0.02	1.71	49.78	−0.44	1.69	50.30	+ 0.60	1.83
D_6 (25.00)	25.85	+3.40	3.07	25.51	+2.04	3.07	25.82	+3.28	2.23

*The values are mean of three replicates.

TABLE 2 : SOME REPRESENTATIVE OBSERVATIONS AND RESULTS OF THE ESTIMATION OF IRON

Sample with expected amount of iron (mg) in 250 mL of the solution	Sn Hg reduction method		Zn reduction method			
	Titer: $K_2Cr_2O_7$ (0.02551 N) Titer for 25 mL aliquot (mL)	Fe content found in 250 mL (mg)	Titer : $K_2Cr_2O_7$ (0.02551 N) Titer for 25 mL aliquot (mL)[a]	Fe content found in 250 mL (mg)	Titer: $KMnO_4$ (0.02475 N) Titer for 25 mL (mL)[a]	Fe content found in 250 mL (mg)
Salts						
$Fe(NH_4)(SO_4)_2 12H_2O$ (263.98)	18.6	265.00	18.5	263.57	19.1	264.02
$Fe(NH_4)_2SO_4\ 6H_2O$ (99.77)[b]	7.0	99.73	7.1	101.16	7.2	99.62
Drug samples						
D_5(100.00)[c]	7.1	101.16	7.0	99.72	7.3	100.90
D_6 (50.00)[c]	3.6	51.29	3.5	49.86	3.7	51.14

a : Difference between main titration reading and blank titration reading

b : The disintegration procedure (used for drug samples) converts Fe^{2+} to Fe^{3+}

c : Amount of iron in two tablets (as two tablets are used)

Advance Abstracts

PROCEEDINGS
OF THE
SEVENTY SEVENTH SESSION OF THE
INDIAN SCIENCE CONGRESS
COCHIN, 1990

SECTION : CHEMISTRY

President : Prof. Amiya Kumar Banerjee

INDIAN SCIENCE CONGRESS ASSOCIATION
14, DR. BIRESH GUHA STREET
CALCUTTA-700 017

47. Preparation and Thermogravimetry of Ammonium Metallo -Oxalates of Al (III), Fe (III) and Cu (II)

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and
S. R. Pokharkar
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Key words : *Ammonium metallo-oxalates, TGA*

The preparation characterisation, and thermogravimetric study of ammonium salts of metallo-oxalates - $(NH_4)_3$ Al $(C_2O_4)_3 \cdot 3H_2O$, (NH_4) Fe $(C_2O_4)_3 \cdot 3H_2O$, and $(NH_4)_2$ Cu $(C_2O4)_2 \cdot 2H_2O$ is reported. The TGA curves are studied to get the degree of decomposition and hence the energy of activation for each step of the decomposition. This exercise, is much useful to familiarise the postgraduate students with the preparation of pure complex, standard titrimetric estimations of various constituents and use of thermogravimetric analysis, all of which are involved in a purposeful investigation.

48. Synthesis and Structural Investigation of some Mixed-Ligand Cyanonitrosyl $\{CrNO\}^5$ Complexes of Chromium with some Tertiary Alkylanlines.

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Six novel mixed-ligand cyanonitrosyl complexes of chromium (I) of composition, $[Cr (NO) (CN)_2 (L)_2 (H_2O)]$ (where L = N, N-dimethylaniline, N, N-diethylaniline, N-ethyl-N-methylaniline, N, N-dimethyl-p-toluidine, N, N-dimethyl-m-toluidine or N, N-dimethyl-m-anisidine) have been prepared by the interaction of potassium pentacyanonitrosylchromate (I) monohydrate, $K_3 [Cr (NO) (CN)_5] \cdot H_2O$ with the said tertiary amines. The complexes, which have been characterized by elemental analyses, magnetic measurements, conductance studies, electron spin resonance and infrared spectral studies, contain chromium (I) in a low-spin $\{CrNo\}^5$ electron configuration.