CHAPTER II

METHODS OF PREPARATION OF STARTING MATERIALS, ELEMENTAL ANALYSES AND PARTICULARS OF INSTRUMENTS/EQUIPMENT USED FOR CHARACTERIZATION AND STRUCTURAL ASSESSMENT OF THE COMPOUNDS

Detailed procedures adopted for the preparation of different starting materials as well as for quantitative determination of various constituents and the relevant particulars of the instruments/equipment used for the characterization and structural assessment of the newly synthesized compounds are described in this Chapter.
All the chemicals used were of reagent grade quality.

*Preparation of alkali hydrogen fluorides,¹* $\text{AHF}_2$ ($\text{A} = \text{K}, \text{Na} \text{or NH}_4$)

An amount of 36.2 mmol of powdered alkali carbonate $\text{A}_2\text{CO}_3$ was dissolved in 40% hydrofluoric acid maintaining the ratio of M:HF as 1:4. To the clear solution thus obtained, pyridine was added slowly until the precipitation was complete. The white crystalline compound thus obtained was separated by decantation, washed free from hydrofluoric acid by pyridine, and then with acetone and finally dried *in vacuo*.

*Preparation of $\text{MnO(OH)}_2$*

In a typical preparation, a solution of 2.2g (11.84 mmol) of MnSO$_4$.H$_2$O in 350 cm$^3$ of water was treated with 34 cm$^3$ of a 3% H$_2$O$_2$ (30 mmol) solution. An amount of 50 cm$^3$ of a 0.2M ammonia solution (10 mmol) was added under constant stirring. The mixture was boiled for ca. 5 min. and then filtered. The dark brown compound formed in this process was washed with about 1.5 lit. of hot water on the filter and then used for the subsequent reactions.

*Preparation of $\text{UO}_3$.4$\text{H}_2$O*

Uranyl nitrate hexahydrate, $\text{UO}_2(\text{NO}_3)_2$.6$\text{H}_2$O, (5.0g, 9.96 mmol) was dissolved in water (100 cm$^3$), to which was added pyridine (10 cm$^3$) whereupon a yellow precipitate appeared. This was separated
by decantation, washed three or four times with water, twice with acetone and finally dried on a steam-bath to obtain yellow uranium trioxide, $\text{UO}_3\cdot4\text{H}_2\text{O}$ (yield: 2.8g, [78.4%]).

Elemental Analyses

$\text{Manganese}^{3}$

Manganese was determined by complexometric titration with EDTA using Eriochrome Black T as an indicator.

In this procedure, an accurately weighed amount of the compound was decomposed by the addition of 20-25 cm$^3$ of 0.1M NaOH solution and the mixture was heated for ca.10-15 min. on a steam-bath for complete decomposition. The resulting hydrated oxide of manganese was quantitatively separated by filtration and washed three or four times with cold water. The brown-black precipitate was dissolved in dilute hydrochloric acid followed by the addition of 0.5g of hydroxyl ammonium chloride to prevent oxidation. The solution was diluted to 100 cm$^3$, warmed slightly and then neutralised by the addition of 0.1M NaOH solution. 3 cm$^3$ of triethanolamine was added to keep manganese in solution, when it was subsequently made alkaline by the addition of 2 cm$^3$ of a buffer solution (pH = 10) and then several drops of Erio T indicator was added. The resulting mixture was titrated with
standard 0.05M EDTA solution at about 40°C until the colour permanently changed from red to blue.

\[ 1 \text{ cm}^3 \text{ 0.05M EDTA} = 2.747 \text{ mg of Mn} \]

**Uranium**

Uranium was estimated gravimetrically as uranyl oxinate.

An accurately weighed amount of the compound was dissolved in a minimum volume of dilute (6M) nitric acid followed by the addition of dilute ammonia until a yellow precipitate was obtained. The precipitate was filtered off on a Whatman 541 filter paper, washed three or four times with water and finally dissolved in a minimum volume of 1% acetic acid solution. To the resulting solution 5g of ammonium acetate was added, which was then heated to boiling followed by the addition of 4% oxine solution dropwise, until an orange precipitate appeared. The whole was then heated on a water-bath for ca. 15 min. and then filtered through a sintered glass crucible (G-4). The precipitate was washed three or four times with hot water, then by cold water and finally dried to constant weight at 110°C. The precipitate was weighed as uranyl oxinate, \([\text{UO}_2(\text{C}_9\text{H}_6\text{ON})_2\cdot\text{C}_9\text{H}_7\text{ON}].\]

**Fluoride**

An accurately weighed amount of a fluoromanganate(III) or a fluorouranate(VI) compound was dissolved in water. The
fluoromanganate(III) compound was decomposed with 20-25 cm$^3$ of 0.1M NaOH solution, and the fluorouranate(VI) compound was decomposed by the addition of 20-25 cm$^3$ of 25% aqueous ammonia. The mixture was heated over steam-bath for ca. 15 min. to ensure complete decomposition. The hydrated manganese oxide and ammonium diuranate formed due to the addition of NaOH and aqueous ammonia, respectively, was separated out by filtration and washed several times with water. The filtrate and washings were collected for fluoride estimation. To the combined washings and filtrate, two or three drops of bromophenol blue indicator and 3 cm$^3$ of 10% sodium chloride solution were added and the whole was diluted to ca. 250 cm$^3$. Dilute nitric acid (6M) was added to it until the colour just changed to yellow followed by the addition of 0.1M NaOH solution until the colour just changed to blue. The mixture was then treated with 1 cm$^3$ of conc. HCl and 5g of Pb(NO$_3$)$_2$ and then heated on a steam-bath. After all the lead nitrate had dissolved, 5g crystallised sodium acetate was added to the solution and the solution was digested on a steam-bath for about half an hour with occasional stirring and then allowed to stand overnight.

For the gravimetric estimation, the precipitate lead chloride fluoride, PbClF, was filtered through a sintered glass crucible (G-4) and weighed as PbClF after drying at 140-150°C to constant weight. In the volumetric estimation, the precipitate PbClF was quantitatively collected by filtration through a Whatman 542
filter paper, washed once with cold water, then three or four times with saturated solution of lead chloride fluoride, and finally once more with cold water. The precipitate was then dissolved in 100 cm$^3$ of 5% (v/v) nitric acid by heating over a steam-bath for 5 min. A known excess of 0.1M AgNO$_3$ solution was added to it followed by digestion on a steam-bath for ca. 30 min. and then cooled to room temperature in the absence of light. The precipitated silver chloride was filtered through a sintered glass crucible (G-4) and washed thoroughly with cold water. The unreacted silver nitrate in the filtrate and washings was titrated with 0.1M KSCN solution using 1 cm$^3$ of ferric ion indicator solution until one drop of thiocyanate solution produced a permanent faint brown colour. The amount of silver nitrate in the filtrate, thus found, was subtracted from that originally added, and the content of fluoride was then calculated from the amount of AgNO$_3$ consumed.

\[ 1 \text{ cm}^3 \times 1\text{M AgNO}_3 = 0.019\text{g of F} \]

**Sulphate**

A known amount of trifluoromonosulphatomanganate(III) was decomposed by the addition of 20-25 cm$^3$ of 0.1M NaOH solution. The mixture was heated over a steam-bath for ca. 15 min. to ensure complete decomposition. The hydrated manganese oxide thus formed
was separated out by filtration and washed several times with water. The filtrate and washings were retained for sulphate estimation. The solution was concentrated by boiling and neutralised with 6M nitric acid. The solution so obtained was acidified by the addition of 0.5 cm$^3$ of conc. HCl and heated to boiling. A warm solution (10 cm$^3$) of 5% Barium chloride in water was added dropwise with stirring and the resultant precipitate was allowed to settle for ca. 5 min. The supernatant liquid was tested for complete precipitation by adding a few drops of barium chloride solution. The process was repeated until a slight excess of barium chloride was present in the mixture to ensure complete precipitation. The mixture was kept covered on a steam-bath for 1h in order to achieve complete precipitation of BaSO$_4$.

The precipitated barium sulphate was filtered through a previously weighed sintered glass crucible (G-4) using a gentle suction. The precipitate was washed with warm water until the filtrate gave no precipitate with a few drops of silver nitrate solution. The crucible with its content was dried at ca. 110°C followed by cooling in a dessicator. The heating process was continued until a constant weight was attained.

The sulphate content of the compound was finally weighed as BaSO$_4$. 

44
An accurately weighed amount of fluorophosphatouranate(VI) was treated with 25 cm³ of water and was then dissolved completely by the addition of ca. 1 cm³ of 6M nitric acid. A 25% solution of aqueous ammonia (sp.gr. 0.91) was added to the solution slowly with stirring, and the mixture heated over a steam-bath for ca. 30 min. The precipitated ammonium diuranate was separated by filtration and washed three or four times with cold water. The combined filtrate and washings was neutralised by the addition of 6M HNO₃ followed by the addition 3 cm³ of conc.HCl and a few drops of methyl red indicator. An amount of 25 cm³ of magnesia mixture was added to the solution followed by a slow addition of concentrated aqueous ammonia (sp.gr. 0.91) with vigorous stirring, until the indicator turned yellow. Stirring was continued for a further period of 5 min. and finally an excess of 5 cm³ of concentrated aqueous ammonia (sp.gr. 0.91) was added slowly. The resulting mixture was allowed to stand in cold for 4h, whereupon the white precipitate of ammonium magnesium phosphate hexahydrate settled down. The precipitate was separated quantitatively by filtration, using a sintered glass crucible (G-4) and washed with distilled ethanol three or four times and finally with small portions of ether. The precipitate was dried under vacuo. for ca. 20 min. and finally weighed as MgNH₄PO₄·6H₂O.
Carbon, Hydrogen and Nitrogen

The carbon, hydrogen and nitrogen contents were estimated by micro-analytical methods. The results of the analyses were obtained from the Micro Analytical Laboratory, Department of Chemistry, North-Eastern Hill University, Shillong.

Sodium

The sodium content was determined by flame photometry. A solution containing sodium ions was acidified with hydrochloric acid. The acidified solution thus obtained was used for flame photometry.

Rubidium and Caesium

The rubidium and caesium contents in the respective salts of tetrafluoromanganates(III) were estimated gravimetrically as their perchlorates. The precipitate was obtained by following the standard procedure and weighed as $A\text{ClO}_4$ ($A = \text{Rb or Cs}$).

Determination of Elements by Atomic Absorption Spectrophotometry

The Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer (AAS) was used for the quantitative determination of potassium, manganese and uranium. In each estimation, a solution of a known amount of the compound
containing the element under determination was used for the AAS experiment.

*Chemical Determination of Oxidation State of Manganese*

The oxidation state of manganese was determined iodometrically by treating a freshly prepared ice-cold potassium iodide solution, acidified with dilute sulphuric acid, with the compound, followed by titration of the liberated iodine against a standard sodium thiosulphate solution. The iodometry experiment was done under an ice-cold condition.

**Particulars of Instruments/Equipment Used**

*pH Measurement*

pH values of the reaction solutions were measured, whenever required, by using a Systronics Type 335 digital pH meter and also by using BDH indicator paper.

*Solute Electrical Conductance*

Solution Electrical conductance measurements were made by using a Systronics Type 304 digital direct reading conductivity meter and also a Wayne Kerr Automatic Precision Bridge B 905 conductometer.
Magnetic Susceptibility

Magnetic susceptibilities of the complexes were measured by the Gouy method using Hg[Co(NCS)₄] as the standard for calibration.

Infrared Spectra

Infrared spectra were recorded in KBr on Perkin-Elmer models 297 and 983 spectrophotometers.

Laser Raman Spectra

Laser Raman (LR) Spectra were obtained on a SPEX Ramalog Model 1403 spectrometer. The 4880 Å laser line from Spectra Physics Model 165-09 Argon laser and the 6471 Å laser line from coherent mode Innova 90K Krypton ion laser were used as the excitation sources. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube followed by photon-count processing system. The sample was held either in the form of a pellet in KBr or in solution. The recording was done at ambient temperature.

Electron Absorption Spectra

Electron Absorption Spectral measurements of freshly prepared solutions were made on a Cary Model 2390 and Hitachi Model 330.
UV-Vis-NIR Spectrophotometers fitted with a thermostated cell holder.

Reflectance Spectra

Reflectance Spectra were recorded against MgO using a Carl Zeiss Jena VSU 2-P instrument.

ESR Spectra

The ESR Spectra of the reaction solutions were recorded as a function of pH using a Varian E 109 X-Band ESR Spectrometer fitted with 100 K field modulator.

Mass Spectra

The mass spectra were recorded on a Varian MAT CH-5 spectrometer. A direct insertion probe was used to introduce the sample directly into the ion source without any prior heating. The sample was held under vacuo. (inside the mass spectrometer) for ca. 1h in the direct inlet probe before electron impact was initiated. The operating conditions were: electron energy, 70 eV (1 eV = 1.6 x 10^{-19} J); source temperature, 100°C; resolution, 10,000; accelerating voltage, 8 KV. The mass spectrometric observations were made with the ionising beam held constant to obtain reproducible ion intensities.
Scanning Electron Microscopy (SEM)

All the SEM experiments were carried out on a JEOL SEM, JSM-35 CF Model Scanning Electron Microscope. A suspension of the sample in about half a test tube of the solvent in which it was either insoluble or sparingly soluble was ultrasonicated in an ECONO-CLEAN Ultrasonicator for ca. 30 min. Then a drop of the resultant solution was added onto the surface of the brass stub (30 mm dia. x 20 mm high) and allowed to evaporate at room temperature. This was then coated with gold in a fine coat ion sputter JFC-1100. Observations were made on the Scanning Electron Microscope JSM 35 CF operated at 15 KV. Tilt control was fixed at 0° for setting the specimen stage in a horizontal position. WD selector was turned fully clockwise to set the working distance (WD) to 39 mm.
References


5. Ref.3, p.488.


