Detailed procedures for quantitative determinations of various constituents, and the relevant particulars of the instruments/equipment used for the characterisation and structural assessment of the newly synthesised compounds are described in this Chapter.

ELEMENTAL ANALYSES

Beryllium<sup>1</sup>

<i>(i) Gravimetry<sup>1</sup></i>

An accurately weighed sample (0.1g) was taken in a 250 cm<sup>3</sup> beaker and 100 cm<sup>3</sup> of water was added. To it was added 5 cm<sup>3</sup> of
8 M HNO₃ and heated on a hot plate till dissolution. The solution was cooled and beryllium was precipitated as hydroxide by adding ammonia solution (1:1 v/v) at pH 8-9. The precipitate was filtered and then transferred back to the original beaker. The precipitate was dissolved in dilute mineral acid. The solution was diluted to 100 cm³ and the pH was adjusted to 2. A 5 cm³ of 15% diammonium hydrogen phosphate solution was added (the reagent solution was previously adjusted to a pH of 5.5). To it was added 5 cm³ of ammonium acetate until the pH was 5.5. The solution was digested just below the boiling point for 5-10 min, cooled and filtered the granular precipitate. The precipitate was redissolved in the minimum volume of hot 6M hydrochloric acid and reprecipitated by using only 1 cm³ of the reagent. The precipitate was filtered again, washed with 0.5 M acetate buffer (3.5 g of ammonium acetate and 3.0 cm³ of glacial acetic acid per 100 cm³ of water) and finally ignited at 1000°C and weighed as Be₂P₂O₇ in the usual manner.

(ii) Atomic Absorption Spectrophotometry, (AAS)²,³.

In order to verify the results, beryllium contents were also determined by AAS techniques by following standard procedures.

Oxalate⁴

An accurately weighed amount of the compound was treated with 25 cm³ of 0.1 M Sodium hydroxide solution and then 100 cm³ of water was added to it. The mixture was boiled for ca. 15 min followed by filtration. The precipitate was washed several times with water. The filtrate and washings were collected and from which
the oxalate content of the compound was determined by the following method. The combined filtrate and washings was neutralized with dilute sulphuric acid (0.5 M). An amount of 15 cm$^3$ of concentrated sulphuric acid was added to the solution. The resulting solution was then titrated against standard 0.02M potassium permanganate solution maintaining the temperature of the solution at ca 60°C.

\[ 1 \text{ cm}^3 \text{ of 0.1M KMnO}_4 = 0.22 \text{ g of } C_2O_4^{2-} \]

Fluoride$^5$

An accurately weighed amount of the compound was dissolved in water (for an insoluble compound, 1-2 cm$^3$ of conc. HNO$_3$ was added to assist dissolution). The compound was decomposed with 20-25 cm$^3$ of 30% aqueous NaOH Solution. The mixture was heated over a steam-bath for ca. 10 min to ensure complete decomposition. The precipitate of metal hydroxide (in case of uranium compounds, hydroxide or hydrated oxide) formed due to the addition of aqueous ammonia (1:1 v/v) was separated out by filtration and washed several times with water. The filtrate and washings were collected for fluoride estimation. To the combined washing and filtrate, 2 or 3 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 was added to it until colour changed to just yellow, followed by the addition of 10% sodium hydroxide solution until the colour ultimately just changed to blue. The mixture was then treated with 1 cm$^3$ of concentrated hydrochloric acid and 5.0 g of lead nitrate, and then heated on a steam-bath. After all the lead nitrate had
dissolved, 5.0 g crystalline sodium acetate was added to the solution. 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 precipitated lead chloride fluoride, PbClF, was filtered through a weighed sintered glass crucible (grade 4) and weighed as PbClF after drying at 140 -150 °C to constant weight. In the volumetric estimation, the precipitated PbClF was quantitatively collected by filtration through a Whatman 542 filter paper and washed once with cold water, then 3 or 4 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 on a steam-bath for 4 or 5 min. A known excess of 0.1M silver nitrate solution was then added to it, followed by digestion on a steam-bath for 30 min and then cooled to room temperature in the absence of light. The precipitated silver chloride was filtered through a sintered glass crucible (Grade 4) and washed with cold water. The unreacted silver nitrate in the filtrate and washings was titrated with a 0.1M potassium thiocyanate 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 silver nitrate consumed.

$$1 \text{ cm}^3 \text{ of } 1\text{M AgNO}_3 = 0.0190 \text{ g of F}^-$$

29
Phosphate

As beryllium of the dihydrogenphosphato(difluoro)beryllate compound interferes in gravimetric determination of phosphate in the form of ammonium magnesium phosphate hexahydrate, a spectrophotometric method employing ammonium molybdovanadate reagent was used. The reagent, ammonium molybdovanadate solution was prepared by dissolving 1.5 g $\text{NH}_4\text{VO}_3$ in 400 cm$^3$ of dilute $\text{HNO}_3$ (1:1 v/v) (solution A) and 90 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}.4\text{H}_2\text{O}$ in 400 cm$^3$ of $\text{H}_2\text{O}$ (Solution B) and mixing them together and then diluting the volume to 1 litre.

A known quantity of the compound (0.1g) was taken in a 250 cm$^3$ glass beaker and to it was added 5 cm$^3$ of conc. $\text{HNO}_3$ and heated on a hot plate till dryness. The beaker was cooled and 2 cm$^3$ of conc. $\text{HNO}_3$ and 50 cm$^3$ of water were added and again heated till complete dissolution. The solution was cooled and then transferred to a 250 cm$^3$ volumetric flask and the volume was made up to the mark. In a 50 cm$^3$ calibrated volumetric flask, 5 cm$^3$ aliquot of the sample solution was transferred and 15 cm$^3$ of ammonium molybdovanadate reagent was added while swirling the flask. The volume was made up to the mark and the solution was set aside for 15 min. Absorbance of this solution was measured at 430 nm against a reagent blank. The concentration of phosphate was found out from a standard calibration graph made similarly on a series of standard phosphate solution (25 to 250 μg phosphorus per 50 cm$^3$).
Uranium

(i) Gravimetry

Uranium was estimated gravimetrically as U₃O₈. An accurately weighed amount of an uranium compound was dissolved in a minimum volume of dilute (2.0 M) H₂SO₄ in the presence of a few drops of methyl red indicator and the solution was heated to boiling. The hot solution was treated with dilute ammonia solution (1:1 v/v) until the indicator just turned yellow. A yellow precipitate was obtained at this stage. A Whatman accelerator was added and the solution was warmed for 1 or 2 min, precipitate was filtered off on a Whatman 541 filter paper, and washed well (3 or 4 times) with a hot 2% solution of ammonium nitrate. The wet filter paper along with the precipitate was dried in a platinum crucible over a Meker burner at a low temperature until the carbon was destroyed. The crucible was then heated strongly being placed in a slanting position so as to maintain a good oxidising condition. The crucible with its content was cooled in a desiccator and weighed. The ignition process was repeated until constant weight was attained. Uranium was finally weighed as U₃O₈.

(ii) Spectrophotometry by H₂O₂

A 0.3g of the compound was taken in a 100 cm³ glass beaker and 5 cm³ of conc. HNO₃ and 30 cm³ of water were added to it. The beaker was heated on a hot plate and the solution was boiled for 5-10 min. The solution was cooled and transferred to a 50 cm³ volumetric flask and the volume was made up to the mark. In
another 50 cm$^3$ volumetric flask 5 cm$^3$ of the aliquot was transferred and to it were added 1 cm$^3$ of 30% $H_2O_2$ and 5 cm$^3$ of 50% sodium hydroxide. The volume was made up to the mark and the flask was shaken properly. This was set aside for 5 min and absorbance of the yellow solution was measured at 420 nm against a similarly prepared reagent blank. The concentration of uranium was found out from a calibration curve composed of a plot of absorbances vs. a series of known concentration of uranium solutions (1 to 5 mg of U per 50 cm$^3$).

(iii) Fluorimetry

As the fluorimetric method is highly sensitive, uranium determination in compounds was resorted to using very dil. sample solutions.

An amount of 0.1 g of the compound was dissolved in a 5 cm$^3$ of conc. $HNO_3$ in a 100 cm$^3$ beaker and heated on a hot plate till dryness to decompose peroxide. To it, 15 cm$^3$ of water was added and the residue was dissolved by using 1 or 2 cm$^3$ of conc. $HNO_3$ and then by heating. The solution was cooled and transferred to a 100 cm$^3$ volumetric flask and the volume was made up to the mark with distilled water. A 3 cm$^3$ of this solution was taken into a 100 cm$^3$ volumetric flask containing 10 cm$^3$ of conc. $HNO_3$ and the volume was made upto 100 cm$^3$. A 3 cm$^3$ aliquot of this solution was transferred to a shaking vial and 15 cm$^3$ of saturated solution of $Al(NO_3)_3 \cdot 9H_2O$ was added. To this was added 10 cm$^3$ of ethylacetate and the vial was stoppered. It was shaken for 2 min. After 10 min, .5 cm$^3$ of ethylacetate was separated out and filtered through a Whatman no. 1 filter paper into a dry
test tube. Aliquots of 0.1 cm$^3$ each of ethylacetate were pipetted to a series (usually 4 nos.) of platinum blanks (previously washed and cleaned) and the solutions were evaporated under IR lamp. Around 0.4g of dry NaF and Na$_2$CO$_3$ (1:4) flux in the form of pellets were added to each of the platinum blanks and fused at 850°C for 2 min in a muffle furnace. The beads formed in platinum blanks were cooled and fluorescence of these beads was measured after 15 min in a Jarrel-Ash Fluorimeter. The concentration of uranium in the unknown solution was found out from a calibration curve plotted between the fluorescence readings and the known concentrations of uranium.

Active Oxygen (Peroxo Oxygen)

(i) Permanganometry$^{10}$

An accurately weighed amount of a peroxo compound was dissolved in 4.0 M sulphuric acid in the presence of about 4 g of boric acid. Boric acid was used to prevent any loss of active oxygen by forming perboric acid. The resulting solution was then titrated with a standard solution of potassium permanganate.

\[ 1 \text{ cm}^3 \text{ of } 1\text{M KMnO}_4 = 0.08505 \text{ g of } H_2O_2 \]

(ii) Iodometry$^{11}$

To a freshly prepared 1.0 M sulphuric acid solution, containing an appropriate amount of potassium iodide (1 g in 100 cm$^3$) was added an accurately weighed amount of the peroxo compound with continuous stirring. The mixture was allowed to stand for ca. 15 min in the dark under a CO$_2$ atmosphere. The liberated iodine was
then titrated with a standard sodium thiosulphate solution adding 2 cm$^3$ of freshly prepared starch solution when the iodine colour was nearly discharged.

\[1 \text{ cm}^3 \text{ of} \ 1\text{M} \text{Na}_2\text{S}_2\text{O}_3 = 0.01701 \text{ g of H}_2\text{O}_2\]

Sulphate$^{12}$

A known amount of the compound was treated with 25 cm$^3$ of water and was completely dissolved by the addition of a few drops of dilute HNO$_3$ (6M). A concentrated solution of aqueous ammonia (sp.gr. 0.9) was added to the solution slowly with stirring and the mixture was heated on a steam bath for ca. 30 min. The precipitate was separated by filtration, and it was carefully washed 2 or 3 times with cold water. The combined filtrate and washings was retained for the estimation of sulphate. The solution was concentrated by boiling and then neutralized with dilute (6 M) nitric acid (volume of the solution was 230 cm$^3$). The solution so obtained was acidified by the addition of 0.3 - 0.6 cm$^3$ of concentrated HCl solution and heated to boiling. A warm solution (10-12 cm$^3$) of 5% barium chloride (5 g of BaCl$_2$.2H$_2$O in 100 cm$^3$ of water) was added from a burette or a pipette drop by drop with continuous stirring and the resultant precipitate was allowed to settle for ca. 2 min. The supernatant liquid was tested for complete precipitation by adding a few drops of barium chloride solution. The process was repeated until slight excess of barium chloride was present in the mixture to ensure complete precipitation. The mixture was kept covered on a steam-bath for 1 h in order to allow time for complete
precipitation of $\text{BaSO}_4$. The precipitated barium sulphate was filtered through a previously weighed sintered glass crucible (grade 4) using 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. $110 \, ^\circ\text{C}$ and heated for 10-15 min at a higher temperature (ca. $600 \, ^\circ\text{C}$) followed by cooling in a desiccator. The ignition process was continued until constant weight was attained. The sulphate content of the sample was finally weighed as $\text{BaSO}_4$.

**Carbon, Hydrogen and Nitrogen**

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

**Preparation of deoxygenated water for reactivity studies**

The water used for reactivity studies was deoxygenated by first boiling the water sample for ca. 30 min under $\text{N}_2$ atmosphere and cooling to room temperature followed by bubbling $\text{N}_2$ gas through it for a period of ca. 15 min. The deoxygenated water was stored in an airtight container. The water thus obtained has been used in the reactivity studies throughout.
PARTICULARS OF INSTRUMENTS/EQUIPMENT USED

pH Measurement

The pH values of the reaction solutions were measured by using a Systronics type 335 digital pH meter.

Conductance

The conductance values were measured in conductivity grade water using a Wayne Kerr Automatic Precision Bridge B 905 Conductometer and a Systronics type 304 digital Direct Reading conductivity meter.

Infrared Spectra

The infra-red (IR) spectra were recorded in KBr as well as in nujol mull on the following spectrophotometers.

(i) Perkin-Elmer Model-297

(ii) Perkin-Elmer Model-983

Laser Raman Spectra

Laser Raman (LR) spectra were recorded on a SPEX Ramalog model 1403 Raman Spectrometer. The 4880 A Laser line from spectra-Physics model 165-09 Argon Laser and 5145 A Laser line from spectra physics model 165 Argon 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 quartz capillary or in the form of a pressed pellet. The recording was done at ambient temperatures.
Atomic Absorption Spectrophotometry

A Varian AA-1475 Atomic Absorption Spectrophotometer was used for the determination of beryllium, potassium, uranium, etc.

Colorimetry or Spectrophotometry

Absorbance measurements for the coloured complexes of uranium and phosphorus were made on a Varian 634-S double beam digital and on a Hitachi-2000 microprocessor based spectrophotometers. Electronic spectra were recorded using the later instrument.

Flame Photometry

Sodium and potassium were determined using a Fotoflame (Sr.No. 90957) model Flame photometer.

Fluorimetry

Fluorescence measurements for $\text{UO}_2^{2+}$ determination was made on a Zarell Ash (Division of Fischer Scientific Company) fluorimeter.

Scanning Electron Microscopy (SEM)

All the SEM studies were made on a JEOL SEM JSM - 35CF model Scanning Electron Microscope equipped with an EDAX Model LINKS AN 10000 Data station. When a sample is subjected to electron beam excitation, several signals are generated which include secondary electrons, back scattered electrons, Auger electrons and characteristic x-rays. To analyse a compound visually i.e. to observe the picture of the compound, secondary electrons, back scattered electrons, and transmitted electrons are collected and
displayed. To determine the composition of the sample it is required to record characteristic X-rays or auger electron spectra. The equipment available in our University uses secondary electrons and X-rays for studying the morphology and composition of the specimen respectively. Following are the two types of detectors used for the present investigations:

(i) Secondary electron detector (for morphology)
(ii) X-ray detector (for energy dispersive spectrometry)

Preparation of a sample for such studies was made by spreading the microcrystalline powder of the compound on a graphite plate and then metallising it with either gold or graphite. In SEM experiments, samples were coated with gold by ion sputter coater.

Radiometry

Uranium was determined radiometrically by $\beta$ minus $\gamma$ technique $^{13}$. The ECIL (Sr.No.2162) instrument was used for the determination. While a pancake type $\beta$ tube was used for $\beta$ detection, a thallium activated NaI crystal coupled with photomultiplier tube was used for $\gamma$ detection. Brief description of the instrument is given below:

**Specification of the Detectors**

For $\beta$ counting -

$\beta$ tube model No. 731

Window-1.5-2.0 mg/cm$^3$

Gass filled — Net halogen

Operative voltage - 1000 V
For γ Counting - NaI (Tl) Crystal Size - 2"x13/4"
P.M. Tube - 9514 B

Specification for Radiation Counting System

For β counting - model RCS 4027
For γ counting - (i) Preamplifier
   (ii) Linear amplifier — PA-531
   (iii) Single Channel Analyser — SC-604B
   (iv) High voltage unit — HV — 216 D
References

4. Ref. 1, p. 284.
5. Ref. 1, p. 269.
7. Ref. 1, p. 539.
9. Ref. 6, p. 475.
12. Ref. 1, p. 462.