CHAPTER 2
Methods of Elemental Analyses and Particulars of Instruments/Equipment Used for Characterisation and Structural Assessment

The details of the methods used for quantitative determination 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

Vanadium

Vanadium was estimated volumetrically by titration with a standard potassium permanganate solution. A near boiling solution of an accurately weighed amount of the vanadium(V) compound, after removing peroxide, was treated with a stream of sulphur dioxide for ca 10 min, and then with a stream of carbon dioxide to expel any excess of sulphur dioxide. The vanadium(IV) solution thus obtained was cooled at ca 80°C, and finally titrated with a standard potassium permanganate solution.
Active Oxygen (Peroxo Oxygen)\(^{2-4}\)

(i) **Permanganometry\(^2\)**

An accurately weighed amount of a peroxovanadate(V) compound was dissolved in 7N sulphuric acid containing ca 4g of boric acid. Boric acid was used to form perboric acid to prevent any loss of active oxygen. The resulting solution was then titrated with a standard potassium permanganate solution.

\[
1 \text{ cm}^3 \text{ of } 1\text{N KMnO}_4 \equiv 0.01701\text{g of } \text{H}_2\text{O}_2
\]

This method is suitable for determination of peroxide contents in peroxovanadium(V) compounds.

(ii) **Iodometry\(^3\)**

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

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

This method gives the total amount of peroxide plus vanadium present in the compound. On deduction of the contribution of vanadium(V) from the total amount of iodine liberated, the net peroxide content of the compound is evaluated.
(iii) Determination of peroxide ($O_2^{2-}$) content by titrating with a standard $Ce^{4+}$ solution

An accurately weighed amount of a peroxovanadate(V) compound was dissolved in a 2N sulphuric acid solution in the presence of an excess of boric acid. Peroxide was then determined by titrating with a standard $Ce^{4+}$ solution. Vanadium(V) does not interfere in this method.

Sulphate

A known amount of sulphato compound of vanadium was dissolved in about 25 cm$^3$ of water, and 0.6 cm$^3$ of concentrated hydrochloric acid was added to it. The solution was diluted to 200 cm$^3$, and then boiled for nearly 40 min. A warm solution (10-12 cm$^3$) of 5% barium chloride ($5g$ BaCl$_2$.2H$_2$O in 100 cm$^3$ of water) was added from a burette or pippette 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. 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 over a steam-bath for 1h in order to allow time for complete precipitation of BaSO$_4$. The precipitated barium sulphate was filtered through a previously weighed sintered glass crucible (grade 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, and heated for 10-15 min at a higher temperature (ca 600°C)
followed by cooling in a desiccator. The heating process was continued until a constant weight was attained.

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

The estimation of sulphate in fluoro(sulphato)ferrate(III) complexes required decomposition of the compound prior to the estimation of SO$_4^{2-}$. A weighed amount of the compound was treated with 25 cm$^3$ of water, and dissolved completely by the addition of a few drops of dilute nitric acid. The solution was then treated with 30% solution of aqueous ammonia in order to decompose the compound, and to separate iron(III) as iron(III) hydroxide. The solution was filtered, the residue washed thoroughly with water, and the filtrate and washings were collected for the estimation of sulphate.

The solution was concentrated by boiling and then neutralised with dilute nitric acid. An amount of 2 cm$^3$ of concentrated hydrochloric acid was added to the solution and the whole was boiled for nearly 40 min. The sulphate content in the resulting solution was then determined gravimetrically as barium sulphate following the procedure described in the case of sulphate estimation in sulphato compounds of vanadium.

**Fluoride**

An accurately weighed amount of a fluorosulphatovanadate(IV) or a fluoroferrate(III) compound was dissolved in water. While the fluoride estimation in the fluorovanadate compounds could be
made directly from their aqueous solutions, the estimation of fluoride in the fluoroferrates(III) required decomposition of the compound prior to the estimation of fluoride. The fluoroferrate(III) compound was decomposed by treating with 30% aqueous ammonia and the mixture was heated over steam bath for ca 10 min to ensure complete decomposition. The hydrated iron(III) oxide formed due to the addition of aqueous ammonia was separated out by filtration and washed several times with water. The filtrate and washings were collected together for fluoride estimation.

To the above solution 2 to 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 dilute 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 5.0g of lead nitrate, and then heated on a steam bath. After all the lead nitrate had dissolved, 5.0g crystallised sodium acetate was added to the solution and the solution was digested on a steam bath for about half an hour with occassional stirring, and then allowed to stand overnight.

For the gravimetric estimation, the precipitated lead chloride fluoride, PbClF, was filtered through a weighed Gooch crucible (grade 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 and washed once with cold water, then 3 to 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 over steam bath for 4-5 min. A known excess of saturated 0.1N silver nitrate solution was then added to it, followed by digestion on a steam bath for 30 min, and then cooled at room temperature in the absence of light. The precipitated silver chloride was filtered through a sintered glass crucible and washed with cold water. The unreacted silver nitrate in the filtrate and washings was titrated with a standard 0.1N potassium thiocyanate solution using 1 cm$^3$ of ferric ion indicator 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.

$1 \text{ cm}^3$ of 1N AgNO$_3 \equiv 0.0190$g of F.

**Carbon, Hydrogen, and Nitrogen**

Carbon, hydrogen and nitrogen were estimated by micro analytical methods. The results of analyses were obtained from Micro Analytical Laboratories, Regional Sophisticated Instrumentation Centre (RSIC), Central Drug Research Institute, Lucknow, and also from Micro Analytical Laboratories, RSIC, NEHU, Shillong.
A weighed amount of the iron(III) compound was dissolved in 30 cm$^3$ of 5N hydrochloric acid solution and heated in a steam bath. To the hot solution a concentrated solution of tin(II) chloride (solution was made as per standard procedure) was added dropwise from a burette, with stirring, until the yellow colour of the solution has nearly disappeared. The reduction of iron(III) to iron(II) was then completed by diluting the concentrated solution of tin(II) chloride with 2 volumes of dilute hydrochloric acid, and adding the dilute solution dropwise, with stirring after each addition, until the liquid attained a faint green colour, quite free from any tinge of yellow. The solution was then rapidly cooled under the tap, with protection from the air, and the slight excess of tin(II) chloride present removed by adding 10 cm$^3$ of a saturated solution (5% at 25°C) of mercury(II) chloride rapidly in one portion and with thorough mixing; a slight silky white precipitate of mercury(I) chloride was obtained.

After the addition of mercury(II) chloride solution, the whole was allowed to stand for 5 min. Dilute (1M) sulphuric acid (200 cm$^3$) was added to it and then titrated with standard potassium dichromate solution using N-phenyl-anthranilic acid as internal indicator, until the colour changed from green to violet-red.

\[1 \text{ cm}^3 \text{ of } 1\text{N } \text{K}_2\text{Cr}_2\text{O}_7 \equiv 0.05585 \text{g of Fe}\]
Sodium and Potassium

Sodium and potassium contents were determined by flame photometry. A solution containing sodium or potassium ions was acidified with hydrochloric acid. The acidified solution thus obtained was used for flame photometry.

Particulars of Instruments/Equipment used

pH Measurement

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

Molar Conductance

Molar conductance measurements were made using Philips PR 9500 conductivity bridge. Conductivity grade water was used for the purpose.

Magnetic Susceptibility

The Gouy method was used to measure magnetic susceptibilities of the complexes. The compound Hg[Co(NCS)_4] was used as the standard for calibration.

Electronic Spectra

Electronic spectral measurements of solutions were made on Beckman model UV-26 and Cary model 2300 Spectrophotometers.
Infrared Spectra

Infrared spectra were recorded in KBr on the following spectrophotometers:

(1) Perkin-Elmer model 297
(2) Perkin-Elmer model 983

Laser Raman Spectra

Laser Raman (LR) spectra were recorded on a SPEX Ramalog model 1403 Raman spectrometer. The 4880Å laser line from spectra-physics model 165-09 Argon laser and 6471Å laser line from coherent model Innova 90K Krypton ion laser was used as the excitation source. 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 a quartz capillary or in the form of a pressed pellet. The solution LR spectra were recorded by taking the sample solution in quartz capillary. The recording was done at ambient temperatures.

ESR Spectra

ESR spectra of polycrystalline solids as well as those of aqueous solutions of the compounds were recorded using a Varian E109, X-band ESR spectrometer with 100 Kc field modulator.
REFERENCES


4. A.I. Vogel, Ref. 2, p 325.

5. A.I. Vogel, Ref. 2, p 463.

6. (a) A.I. Vogel, Ref. 2, p 569.
   (b) A.I. Vogel, Ref. 2, p 269.

7. A.I. Vogel, Ref. 2, p 309.