Chapter II

Materials & Experimental Methods
2.1 Materials

All chemicals and reagents used were of analytical reagent grade BDH (AR) or E. Merck (AR). Double distilled water, freshly boiled, was used throughout.

2.1.1 Preparation of barium bromate

Barium bromate was synthesized by the method already reported\textsuperscript{26,135} using potassium bromate and barium chloride. The stoichiometric amount of potassium bromate was added to a solution prepared by dissolving 100g of BaCl\textsubscript{2}.2H\textsubscript{2}O in water and the precipitated Ba(BrO\textsubscript{3})\textsubscript{2} was washed several times to eliminate any potassium chloride. The product was dried and recrystallised. It was analyzed for bromate purity iodometrically\textsuperscript{134}. 99.1 percent pure barium bromate monohydrate was obtained.

2.1.2 Preparation of nickel bromate

Nickel bromate was synthesized by the method already known\textsuperscript{26} using barium bromate (prepared by the above method) and nickel sulphate. Stoichiometric amount of NiSO\textsubscript{4}.7H\textsubscript{2}O was added to a solution containing 10g of barium bromate dissolved in 500ml hot water. The precipitated barium sulphate was filtered off. The filtrate was carefully evaporated to 25ml. The excess barium bromate precipitated was filtered. The filtrate was now evaporated at 50\degree C under vacuum. The product was recrystallised from water and analyzed for bromate purity iodometrically\textsuperscript{134}. Nearly 10g of pure sample of composition Ni(BrO\textsubscript{3}).6H\textsubscript{2}O was obtained with 99% purity.

2.1.3 Preparation of yttrium bromate

For preparing yttrium bromate\textsuperscript{57-59}, first yttrium sulfate was made by the following procedure. Stoichiometric amount of yttrium oxide was weighed and soaked in water and sulphuric acid solution was added slowly. The mixture was warmed and the temperature was gradually raised to 500\degree C to convert it to anhydrous yttrium sulphate. It was now dissolved in ice cold water and the resulting solution was poured into a slight excess of barium bromate solution. The precipitated barium sulphate was filtered off. The resulting solution was warmed on a hot plate overnight and then evaporated using a rotatory evaporator. The solution was concentrated to obtain crystals of yttrium bromate. The crystals were filtered, air dried at
room temperature and then recrystallised. 99% pure yttrium bromate of composition Y(BrO₃)₉H₂O was obtained.

2.1.4. Preparation of neodymium bromate

Neodymium bromate was synthesized by the method similar to the one used for yttrium bromate. The crystals were grown by solid evaporation of the aqueous solution of neodymium bromate prepared by double decomposition of neodymium sulphate and barium bromate in a hot aqueous solution. The recrystallised sample was analyzed for purity. Nearly 99% Neodymium bromate of composition (NdBrO₃)₉H₂O was obtained.

2.1.5. Preparation of magnesium bromate, cadmium bromate, zinc bromate and strontium bromate

The stoichiometric amount of MSO₄ (M = Mg, Cd, Zn) was added to a solution containing 4g of Ba(BrO₃)₂. H₂O dissolved in 200ml hot water. The precipitated barium sulphate was filtered off and the filtrate was evaporated to about 10ml. Any excess barium bromate precipitated was also filtered off. The solution was then evaporated at 80°C under vacuum and about 4g of each bromate was obtained. The samples were recrystallised, dried and analysed for bromate purity iodometrically. Nearly 99% pure samples were obtained.

Strontium bromate was prepared from strontium carbonate and bromic acid (obtained by reaction of barium bromate solution with sulphuric acid).

2.1.6 Preparation of samples of barium bromate, nickel bromate, neodymium bromate and yttrium bromate containing intentional impurities

Crystals of barium bromate containing NaBrO₃, KBrO₃, Mg(BrO₃)₂, Sr(BrO₃)₂, Zn(BrO₃)₂, Cd(BrO₃)₂, Ni(BrO₃)₂, Nd(BrO₃)₃, Y(BrO₃)₃, KBr and SrBr₂ respectively as intentional impurities in the mole fraction range 10⁻³ to 10⁻¹ were prepared by very slow evaporation of solutions containing calculated amounts of barium bromate and the other salt. The crystals were separated under suction, washed with small amounts of cold water and dried over P₂O₅.
Similarly samples of nickel bromate containing neodymium bromate, yttrium bromate and zinc bromate, yttrium bromate containing barium bromate and zinc bromate and neodymium bromate containing nickel bromate and barium bromate were also prepared by similar methods.

2.2. Analysis of Bromate – Iodometric Method

To a measured volume (20ml) of an approximately 0.1N standard solution of the bromate 2ml concentrated hydrochloric acid and 10ml of a 5 percent solution of KI were added and the liberated iodine was immediately titrated against standard sodium thiosulphate using starch as indicator\textsuperscript{134}.

2.3. Thermogravimetric Studies

Barium bromate (Sample 1) and samples of barium bromate containing intentional impurities (Samples 2-33) nickel bromate (Sample 34) and samples of nickel bromate containing intentional impurities (Samples 35-43), neodymium bromate (Sample 44) and neodymium bromate containing intentional impurities (Samples 45-48), and yttrium bromate (Sample 49) and yttrium bromate containing intentional impurities (Samples 50-52) in the form of fine powder (200-240 mesh) were used for TG studies.

In the first phase thermograms of Sample 1(i)-24 were recorded in air using Ulvac Sinku-Rio (Japan) TA 1500. In the second phase thermograms of Samples (25-27, 30, 34-52) were recorded in nitrogen using TAQ20 Thermogravimetric Analyser. In the third phase thermograms of samples (28, 29, 31-33) were recorded in nitrogen using Perkin Elmer Thermal Analyser. The heating rate was 5°C min\textsuperscript{-1} in all the TG studies. In all experiments less than 10 mg of the sample was used and the data have all been normalized to a mass of 100 mg. The recorded total mass loss in samples (1-43) agreed almost satisfactorily with the theoretical mass loss confirming nearly complete conversion of the bromate to the bromide. In the case of neodymium and yttrium bromate there was no such agreement showing that the decomposition is not to the bromide alone but oxide formation is also possible. Earlier studies\textsuperscript{45-48} had revealed that replacement of air by nitrogen had no effect on the thermal
decomposition of barium bromate and so in the present studies for samples (1-24), air was used as atmosphere and the remaining samples were analysed in nitrogen atmosphere.

2.4. XRD Studies
With a view to investigate whether any possible change occurs in the crystal structure of the samples during the addition of intentional impurities some of the samples were subjected to X-ray diffraction studies.

Pure barium bromate, nickel bromate, zinc bromate, neodymium bromate and yttrium bromate and samples of barium bromate containing 0.1 mole % of neodymium bromate, nickel bromate containing 0.1 mole % of zinc bromate, neodymium bromate containing 0.1 mole % of nickel bromate, yttrium bromate containing 0.1 mole % nickel bromate and barium bromate containing 0.1 mole % yttrium bromate were subjected to XRD studies.

Wide angle X-ray diffractions of the finely powdered samples were recorded by Philips Analytical diffractometer using CuK-alpha emission. The spectra were recorded in the range of $2\theta = 0$-50 and analyzed using X’ Pert software.

2.5. FTIR Studies
Fourier Transform Infrared Spectroscopy has been widely used in the study of inorganic compounds especially metal complexes. Hydrated salts of transition and inner transition metals have structures similar to coordination compounds with the water molecules of hydration functioning as ligands or coordinated to the metal ion. With a view to get any information relating to this and to explore the possible changes due to the addition of other metal ions as intentional impurities, some of the samples viz. nickel bromate, neodymium bromate, zinc bromate, nickel bromate containing 0.1 M neodymium bromate, nickel bromate containing 0.01M neodymium bromate, nickel bromate containing 0.001 M zinc bromate and nickel bromate containing 0.1 M yttrium bromate were subjected to FTIR studies. The samples were used in the powdered form in a Nicolet-380 FTIR spectrometer.