

CHAPTER III

EXPERIMENTS



Materials

Potassium chromate, analytical grade.

Potassium sulphate, analytical grade.

The Preparation of Samples.

1. Crystals of potassium chromate, potassium sulphate.

Potassium chromate and potassium sulphate were recrystallized from saturated aqueous solutions, giving pure polycrystalline potassium chromate and potassium sulphate.

2. Mixed crystals (potassium chromate/potassium sulphate)

Mixed crystals were prepared by dissolving weighed amounts of recrystallized potassium chromate and potassium sulphate in distilled water. The saturated solution was allowed to evaporate slowly at room temperature. After a period of days, the mixed crystals occurred. They were filtered, washed with alcohol, dried up in the oven at 120°C for a day and stored in a desiccator.

3. Mixtures of potassium chromate and potassium sulphate.

Mixtures of potassium chromate and potassium sulphate in various proportions were prepared by weighing the exact amounts of potassium chromate and potassium sulphate and mixed thoroughly together.

The Investigation of Samples.

1. Polarizing microscope investigation.

The samples were examined through the polarizing microscope to observe the external form, the appearance in polarized light and the homogeneity of the samples crystallized in each concentration. The samples, well-formed and no twinning, were chosen for the investigation in other methods.

2. Vibrational spectra investigation.

2.1 Infrared spectra.

The samples were prepared as potassium bromide pressed disk. The dried mixture of potassium bromide and sample was mixed well and ground thoroughly to achieve homogeneous mixture which was transferred into a 13 mm. diameter die. The Shimadzu press was used in making pellet of the mixture under a pressure of 8 tons.

Infrared spectra were recorded at room temperature with Infrared Spectrophotometer Shimadzu IR-440, wavelength range $5000-300 \text{ cm}^{-1}$ at a resolution of 7 peaks in the spectrum of polystyrene film and accuracy of $\pm 2 \text{ cm}^{-1}$.

2.2 Raman spectra.

The samples were ground and packed in glass capillary tubes for Raman measurements.

Raman spectra were recorded at room temperature with a Spex 1401 double beam monochromator with photon counting and

argon ion/ krypton laser excitation. The resolution was better than 3 cm^{-1} and accuracy $\pm 2 \text{ cm}^{-1}$. Incident laser power was 25 mW at the sample.

Raman spectra were obtained by the courtesy of Professor Dr. S.F.A. Kettle, School of Chemical Sciences, University of East Anglia.

3. X-ray powder diffraction investigation.

3.1 X-ray powder photograph method.

The samples were ground, mixed with a little silicon as the internal standard and packed into a hole in a brass holder backed by adhesive tape.

The X-ray powder diffraction photographs were recorded at 26° C with the Guinier-Hagg XDC-700 focusing powder camera using copper K_{α_1} -radiation ($\lambda = 1.5405 \text{ \AA}$), 34 kv, 21 ma. exposed for two hours.

3.2 X-ray diffractometer method.

The samples were ground to a powder size, packed into a window in an aluminium holder backed by adhesive tape, placed in the goniometer, then radiated with copper K_{α_1} -radiation.

X-ray powder diffraction patterns (diffractograms) were obtained with a Philips Powder Diffractometer PW 1050170, copper K_{α_1} at 40 kv and 30 ma conditions. The positions and intensities of diffracted beams were measured by gas proportional counter and recorded on the chart simultaneously.

Determination of the Composition of Mixed Crystals.

1. Analysis of chromate ion in the mixed crystals.

1.1 By iodometric titration.

0.05 g. of mixed crystal was accurately weighed and dissolved in distilled water and added 10 ml. of 1:3 sulphuric acid, 2 g. of potassium iodide crystals. The solution was stoppered and allowed to stand in cool place for 10 min. The liberated iodine was titrated with 0.05 M. sodium thiosulphate solution, which was standardized by primary standard potassium dichromate solution. When the iodine colour was nearly discharged, 5 ml. of starch indicator solution was added and the titration was continued until the blue colour just disappeared. The correction for any thiosulphate consumed by reagent was made by performing a blank titration.

1.2 Titration with ferrous sulphate and permanganate.

0.05 g. of mixed crystal was accurately weighed, dissolved in distilled water, acidified with 10 ml. of 1 M. sulphuric acid solution and added 25 ml. of 0.1 M. solution of Mohr's salt (ferrous ammonium sulphate) and then the excess Mohr's salt solution was back-titrated with permanganate solution that was standardized against sodium oxalate solution. The end point was greyish colour (combination of the green colour of chromium(III) ions with the pink colour of permanganate ions).

1.3 By spectrophotometric method.

The mixed crystal was dissolved in distilled water and measured the absorbance at 360 $m\mu$ with UV-VIS Spectrophotometer Varian Techtron, Model 635.

The concentration of chromate ion in the mixed crystal was determined by comparing with standard calibration curve using standard potassium chromate solution.

2. Analysis of sulphate ion in the mixed crystals.

0.2 g. of mixed crystal was accurately weighed, dissolved in 100 ml. distilled water, added 5 ml. methanol and 5 ml. hydrochloric acid to reduce Cr(VI) to Cr(III). Boiled and concentrated to 50 ml. . Added distilled water to obtain a volume of 200 ml., heated to boiling and added 10 ml. of 10% barium chloride solution. Boiled for 5 min. and allowed to stand overnight. Filtered through the weighed sintered glass crucible No. 4. Washed with hot distilled water, dried at 130 C for 30 min., cooled in a desiccator and weighed.