

cm.<sup>-1</sup> The intensity distribution in these heads suggests the probability of  $\nu$  20340 as the (0, 0) head. The two systems may be designated as  $\gamma$  and  $\alpha$  respectively, on the analogy of the  $ZrO^1$  and the  $TiO^2$  bands which the present bands resemble closely.

Analysis of the bands is in progress and details will be published shortly.

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1. F. Lowater, *Proc. Phy. Soc.*, 1932, **44**, 51.
2. *Ibid.*, 1928, **41**, 557.

#### GYPSIFICATION OF APATITES IN THE KODURITES

DURING the course of detailed chemical and optical studies of the Kodurites from the manganese mines of the Garividi area in the Vizagapatam district, a rather unusual case of the alteration of apatite to gypsum along the peripheral zones was noticed. The apatite is a manganese fluor variety with the formula  $3(Ca.Mn)_3.P_2O_8.Ca(F_2.Cl_2)$ . During the optical examination, it was noted that the periphery of the apatite showed different optical features from those normal to the apatite. The central grain shows uniaxial negative characters with straight extinction, whereas the peripheral zone is biaxial negative with inclined extinction which polarizes with second order blues and pinks, characteristic of gypsum. The analysis of the apatite and its modal composition indicated 92.93% of apatite and 7.07% of gypsum.

Chertification and kaolinisation are universal in the Kodurites. The problem of the origin of the cherts and kaolin in this area as elsewhere is a debatable point, i.e., whether it is due to hydrothermal or meteoric alteration.

Vogt<sup>1</sup> in common with several other investigators attributed kaolinisation of the felspars to carbonated waters. Lindgren<sup>2</sup> controverted this view on the ground that the pure aluminic silicate cannot be formed in the presence of carbonated waters alone and that the presence of  $H_2SO_4$  is essential to bring about kaolinisation. Fermor<sup>3</sup> ruled out this possibility on the ground that there was no evidence of the presence of the influence and action of  $H_2SO_4$  in the Kodurites. The gypsification of the apatites in the

Kodurites of the Garividi area is fairly frequent and this points clearly to the action of sulphuretted waters. Therefore, it appears that the view put forward by Lindgren regarding the importance of  $H_2SO_4$  in kaolinisation of felspars really finds a support here since there is a replacement of apatite by gypsum ( $CaSO_4 \cdot 2H_2O$ ). The authors do not, however, claim that this alteration is brought about exclusively by hydrothermal agencies.

We are not aware of any reported occurrence of the gypsification of apatites in literature.

A detailed paper embodying the results of chemical and optical study of the Kodurites and associated formations by one of us (G.P.R.) is under publication elsewhere.

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March 16, 1949.

1. Vogt, *Trans. Amer. Inst. Ming. Eng.*, **31**, 150.
2. Lindgren, Waldemer, *Ibid.*, **30**, 658.
3. Fermor, L.L., "Manganese-Ore Deposits of India," *Mem. G. S. I.*, **37**, 274-75.

#### VANADAMETRY—PART III

##### Volumetric Estimation of Ferrous Salt in the Presence of Phenols

IN Parts I and II of this series the advantages of sodium vanadate as a volumetric reagent in place of permanganate or dichromate have been emphasized. Viswanadham and Gopala Rao<sup>3</sup> have shown that citric acid in ferrisubchloridum citratum B.P. interferes in the estimation of ferrous iron, by potassium dichromate. They have proposed the use of sodium vanadate. Lyons and Appleyard<sup>1</sup> who found a similar interference by citric acid and sugars proposed ceric sulphate for the estimation. Ferrey<sup>5</sup> showed that ceric sulphate does not give satisfactory results in the estimation of ferrous iron in the presence of phenol. As several phenolic compounds are used in pharmaceutical preparations as preservatives, it was considered necessary to investigate the problem in detail.

We have now found that dichromate oxidizes phenol, ortho-cresol, paracresol, *m*-cresol, and resorcinol, in the presence of ferrous salts by an induced mechanism. Ceric sulphate is capable of oxidizing the phenolic compounds even in the absence of ferrous salts to dirty coloured compounds

insoluble in dilute sulphuric acid, so that this reagent is not suitable for the estimation of ferrous salts in the presence of phenolic compounds. Sodium vanadate has, however, been found to give excellent results as shown in the following table.

Composition of solution		Amount of ferrous iron found by ceric sulphate titration	Amount of ferrous iron found by sodium vanadate titration
Amount of ferrous iron taken	Amount of phenolic compound		
millimols.		millimols.	millimols.
0.7191	nil	0.7200	0.7201
0.7191	0.5008 phenol	0.8230	0.7201
0.7191	0.5090 paracresol	0.8245	0.7201
0.7101	0.4634 ortho cresol	0.8212	0.7086
0.7101	0.4666 meta cresol	0.8194	0.7086
0.7139	0.4562 resorcinol	0.8945	0.7139

Sodium vanadate will thus be found to have some advantages even over ceric sulphate. Detailed results will be published elsewhere.

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1. Gopala Rao and Ramanjaneyulu, *Curr. Sci.*, 1949, 18, 72. 2. Gopala Rao and Brahmaji Rao, *Ibid.*, 1949, 18, 3. Viswanadham and Gopala Rao, *Ibid.*, 1943, 12, 327. 4. Lyons and Appleyard, *Quart. J. Pharm. Pharmacol.*, 1937, 10, 348. 5. Ferrey, *Ibid.*, 1937, 10, 351.

#### THORIUM PERIODATE AND ITS USE IN THORIUM ESTIMATIONS

RAY CHAUDHURY<sup>1</sup> reports that thorium nitrate in dilute nitric acid solution yields on prolonged heating over a water-bath with excess of sodium paraperiodate a gelatinous precipitate of the composition  $\text{ThHIO}_6 \cdot 5\text{H}_2\text{O}$ . This substance is further reported to be stable upto  $600^\circ\text{C}$ . The strength of the acid solution has not been specifically mentioned, but our experiments with 2N acid using potassium periodate in place of the sodium salt have not been successful. We have therefore undertaken a more systematic investigation and our experiments show that precipitation occurs only at 1N or lower acid concentration. Even under these conditions significant quantities of thorium remain in solution though a ten-

fold excess of periodate is used. If, however, hot neutral potassium periodate is added in slight excess to a hot neutral solution of thorium nitrate, there results immediately a white gelatinous precipitate, which may conveniently be filtered and washed through a sintered glass crucible. This, on drying at  $105$  to  $110^\circ\text{C}$ . for 3 to 4 hours, changes to a semi-transparent mass of constant weight, and composition as reported by Ray Chaudhury.<sup>1</sup> The time of drying is not critical, but the temperature should not rise much above  $120^\circ$  (even at  $180^\circ$  iodine vapours are observed). When the above procedure is followed, the precipitation of thorium is quantitative as can be gathered from the following typical results.

Wt. in g. of $\text{ThHIO}_6 \cdot 5\text{H}_2\text{O}$ obtd.	Wt. in g. of thorium calculated	Wt. in g. of thorium taken
0.2471	0.1051	0.1055
0.2479	0.1054	0.1055
0.2368	0.1007	0.1008
0.2357	0.1002	0.1008

Thorium periodate precipitate is soluble in dilute mineral acids and can accurately be estimated volumetrically in the following way:—the washed precipitate is dissolved in dilute hydrochloric acid and a slight excess of potassium iodide is added. The iodine liberated is titrated against standard thiosulphate. One atom of thorium corresponds to one periodate group or eight equivalents of thiosulphate. The following example will illustrate the accuracy of the volumetric estimation 0.1055g. of thorium was taken. The estimated values were 0.1047, 0.1048, 0.1050 and 0.1052.

An interesting property of the periodate precipitate is that while it ordinarily retains five molecules of water of hydration, on prolonged desiccation (3 weeks) in vacuum over caustic potash, a part of this water is lost and its final composition corresponds to  $\text{ThHIO}_6 \cdot 4\text{H}_2\text{O}$ .

Work on the use of periodates in the separation of thorium from cerium earths is in progress.

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1. Ray Chaudhury, *J.I.C.S.*, 1941, 18, 335.