

## ON THE ESTIMATION OF BERYLLIUM. PART II. A NEW RAPID GRAVIMETRIC METHOD FOR ITS ESTIMATION IN BERYL

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A rapid gravimetric method for the determination of beryllium in beryl, based on a new extraction process using sodium tetrafluoroborate as flux, has been described. In the present method silica is driven away during fusion and beryllium is separated as tetrafluoberyllate from the sparingly soluble complex fluorides of iron and aluminium and then it is estimated as barium fluoberyllate. The method has been compared to several other ones and advantages over others have been discussed.

Several gravimetric methods for the estimation of beryllium in beryl have been described in the literature. In one of these methods (Copaux, *Compt. rend.*, 1919, 168, 610) beryl was decomposed by  $\text{Na}_2\text{SiF}_6$ . In other methods the disintegration of the mineral has always been done with the help of alkaline fluxes. After removal of silica and separation of beryllium from others, it has been estimated as  $\text{BeO}$  (Schoeller and Powell, "The Analysis of Minerals and Ores of the Rarer Elements", 1955, p. 66, Hafner Publishing Company, New York; Hillebrand and Lundell, "Applied Inorganic Analysis", 1953, p. 518, John Wiley and Sons Inc., New York; Quadrat and Svejda, *Chem. Obzor.*, 1950, 25, 85). In the recent methods, after masking iron, aluminium etc. by EDTA, beryllium has been separated as beryllium hydroxide (Brewer, *Analyst*, 1952, 77, 539), beryllium ammonium phosphate (Hurè *et al.*, *Anal. Chim. Acta*, 1952, 7, 37), or extracted as basic butyrate (Banerjee *et al.*, *ibid.*, 1954, 10, 256).

In the present communication a new method, utilising sodium tetrafluoroborate as flux for the decomposition of beryl, has been described (Sen Gupta, *Science & Culture*, 1956, 21, 687). Potassium tetrafluoroborate has not been utilised due to its lower solubility and its coprecipitation with  $\text{BaBeF}_4$  (Dutta and Sen Gupta, this *Journal*, 1956, 33, 146).

### EXPERIMENTAL

Sodium tetrafluoroborate was prepared from molar proportions of boric acid, sodium fluoride and excess of hydrofluoric acid. It was then recrystallised from water, washed with alcohol and dried. All the other reagents used were of reagent quality.

The following three methods were tried for standardisation of a sample of beryl (ground to 200 mesh and properly sampled), which was utilised throughout the work: (i) Estimation of beryllium after separation of iron and aluminium by 8-hydroxyquinoline (Schoeller and Powell, *loc. cit.*) was followed except that double precipitations of aluminium and iron oxinates were done and at the last a fusion of the  $\text{BeO}$  with sodium carbonate was made and after separation of the soluble salts by leaching with hot water  $\text{BeO}$  was estimated. (ii) Estimation as  $\text{BeO}$  according to Brewer (*loc. cit.*). (iii) Determination as  $\text{Be}_2\text{P}_2\text{O}_7$  (Hurè *et al.*, *loc. cit.*).

*Procedure.*—For determining the complete disintegration temperature, beryl was mixed with different proportions of sodium fluoroborate and heated at different temperatures. It was found that the ratio beryl :  $\text{NaBF}_4$  should at least be 1:1 and the tem.

perature for complete decomposition of the mineral should be above  $540^{\circ}$  (ascertained by spectrographic analysis of the residue when silicon was found to be absent); but by the single fusion process (Method B, *vide infra*), only about 98.5% of total beryllium was found to be recovered. That the first residue (containing aluminium, iron fluorides etc.) left after separation of beryllium contained beryllium was ascertained firstly by comparing the % Be recovered as  $\text{BaBeF}_4$  with that found by other methods, which were utilised for the standardisation, and secondly, by analysing the residue spectrographically in which the ultimate lines of beryllium were detected. Hence, it was necessary to resort to refusion of the first residue with  $\text{NaBF}_4$  and it was found that the second residue obtained after refusion and extraction contained no beryllium.

*Method (A).*—Beryl (0.25–0.35 g.) was mixed intimately with  $\text{NaBF}_4$  (4 g.) in a platinum crucible (30 c.c. capacity). It was then heated with a Bunsen burner first for 4-5 minutes intermittently and then continuously for 10-12 minutes (continuous heating over 15 mins. resulted in a difficultly extractible mass). The crucible was taken in about 100 c.c. of hot water, boiled for several minutes and digested on a water-bath for 20-30 minutes. After removal of the melt, the solution was boiled for 2-3 minutes and cooled to  $40-50^{\circ}$ . Solid sodium bicarbonate was added to raise the  $p_H \sim 7.2-7.4$  (tested with  $p_H$ -paper). The solution was then boiled for a minute or two and after cooling filtered through a fine filter paper. The transference and washings (about 8-10 times) were done by 1%  $\text{NaHCO}_3$  solution. (It was observed that if  $p_H$  of the solution was not raised and filtered as such and the residue washed with water, iron and aluminium found their way into the filtrate and subsequently into  $\text{BaBeF}_4$  precipitate). To the filtrate boric acid (3 g.) was added and its volume was reduced to 100 c.c.

The residue was again fused with  $\text{NaBF}_4$  (1.5 g.) for 5 minutes; the melt was taken in solution and sodium bicarbonate (0.5 g.) and sodium chloride (0.25 g.) were added. The solution after boiling and subsequent cooling was filtered through fine filter paper; the residue was washed as before with 1%  $\text{NaHCO}_3$  solution till free from chloride. The combined filtrates were reduced to 250 c.c., cooled and  $\text{HCl}$  (5*N*) was added to the violet colour of Wesselow's indicator. The solution was heated to boiling and  $\text{BaBeF}_4$  precipitated by dropwise addition of hot 5%  $\text{BaCl}_2$  solution. After heating on a water-bath for an hour, the solution was filtered through a tared sintered glass crucible, washed with hot water, then with alcohol, and dried at  $110-120^{\circ}$ .

*Method (B).*—This method was similar to the previous one except that the refusion of the residue was omitted. The method (A) was followed up to the adjustment of  $p_H$  by  $\text{NaHCO}_3$ . The solution was boiled for 2-3 minutes,  $\text{NaCl}$  (0.25 g.) was added and after cooling it was filtered. The residue was washed with 1%  $\text{NaHCO}_3$  solution till free from chloride. Boric acid (3 g.) and Wesselow's indicator were added, and  $\text{BaBeF}_4$  precipitated and estimated as before.

TABLE I

| Method (i) | ... | ... | % BeO found in a sample of beryl. |
|------------|-----|-----|-----------------------------------|
| (H)        | ... | ... | 12.84, 12.92                      |
| (A)        | ... | ... | 12.78, 12.78, 12.83               |
| (B)        | ... | ... | 12.93, 12.94, 12.82               |
|            | ... | ... | 12.67, 12.66, 12.71               |

## DISCUSSION

The results given above show the relative accuracies of the methods. As low results were obtained each time by method (iii), the results were not submitted; low results were also obtained even with pure beryllium solution, probably under the conditions laid down in that method for the precipitation of beryllium ammonium phosphate, the precipitate did not attain the formula  $\text{BeNH}_4\text{PO}_4$ .

It was found that the beryllium oxide obtained by methods (i) and (ii) and barium fluoberyllate obtained by method (A) contained traces of aluminium as revealed by the appearance of its very faint ultimate lines during their spectrographic examination. It was found; however, that the barium fluoberyllate obtained according to the method (B) contained no aluminium, but this method gave slightly low results as discussed earlier.

It was found that amongst the three methods utilised for standardisation, method (ii) was found to be very convenient requiring less time. But the methods suggested in the present paper require least time in comparison with the others and so may be utilised with advantage.

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