DETERMINATION OF CHROMIUM IN RUBY[1]

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A search of the literature for data on the chromium content of the natural ruby revealed that none of the recorded analyses of ruby include this element; on the contrary, it has long been taken for granted that an attempt at such a determination is futile. Fremy,[2] in writing about the ruby states that an analysis cannot show the real composition of the mineral; synthesis, however, serves to distinguish between essential and accessory constituents. This statement is a conclusion drawn from extensive experimentation, and forms the basis for the assertion that the color of naturally occurring ruby is due to chromium. Wöhler and Kraatz-Koschlau[3] found that chromium in natural ruby is present in amounts too small to be determined by analytical methods. Doelter[4] also states that the chromium content of ruby is so small that it cannot be quantitatively determined. Doelter and Leitmeier[5] say that only traces of chromium can be detected in ruby. It was, therefore, deemed expedient to find out whether an analytical method could be adapted to the determination of chromium in ruby.

A number of gravimetric methods were tried to determine chromium in known mixtures of the oxides of aluminum and chromium, but they were found unreliable; results obtained with duplicate samples were not concordant, and were always low. It was next decided to test the applicability of a standard volumetric method, in which the chromium is oxidized to chromate, and is titrated with a standard solution of ferrous ammonium sulfate. In order to duplicate the conditions under which the rubies were later to be analyzed after fusion with large amounts of potassium hydrogen sulfate, the following mixtures were prepared which contained

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[2] Fremy, *Synthèse du Rubis*, p. 1, Paris (**1891**).

[3] Wöhler and Kraatz-Koschlau, *Tschermak's miner. petrog. Mitt.*, **18**, 456 (1899).

[4] Doelter, *Sitzb. Wissen. Akad. Wien. Abt.* **I**, **117**, 819 (1908); *Die Farben der Mineralien*, p. 28, Braunschweig (**915**).

[5] Doelter u. Leitmeier, *Handbuch der Mineralchemie*, Vol. 3, Part II, p. 443, Leipzig (**1926**).

known amounts of chromium added from a previously analyzed solution of chromic acid:

A. 15 gm. of potassium hydrogen sulfate, 1 gm. of aluminum oxide, and 0.00128 gm. of chromium;
B. 15 gm. of potassium hydrogen sulfate, 1 gm. of aluminum oxide, and 0.00051 gm. of chromium;
C. 15 gm. of potassium hydrogen sulfate, 0.5 gm. of aluminum oxide, and 0.00025 gm. of chromium.

Each of these mixtures was fused in a platinum crucible. A and B were taken up in 150 c.c. of nitric acid (1:2), while C was taken up in 75 c.c. They were then oxidized with sodium bismuthate in the usual way,[6] and were titrated with one-hundredth normal $KMnO_4$ and $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. The results, listed in Table I, show that the discrepancies are negligible and within the limits of experimental error.

TABLE I

TEST DETERMINATIONS ON KNOWN AMOUNTS OF CHROMIUM IN THE PRESENCE OF SALTS OF ALUMINUM AND POTASSIUM

Mixture	Gm. of chromium used	Gm. of chromium determined by titration
A	0.00128	0.00124
B	0.00051	0.00048
C	0.00025	0.00021

As this method proved to be satisfactory, rubies from several different localities were analyzed for their chromium content in a similar way. All these rubies were chosen particularly for their color, with the object of securing typical specimens. They were first crushed in a "diamond steel" mortar so as to pass a 200 mesh sieve, and were carefully gone over with a magnet to remove particles of steel. It was noticed that the sieve invariably retained the occasional chips that were broken off of the mortar during the process of crushing. Samples of the pulverized material were then fused in a platinum crucible with fifteen times their weight of potassium hydrogen sulfate, and were taken up in water. The fusions in nearly all cases were complete the first time, but occasionally a small insoluble residue had to be re-fused with potassium

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[6] Mahin, *Quantitative Analysis*, p. 467, New York (**1924**).

hydrogen sulfate before proceeding with the determination. The results of these analyses are given in Table II.

Table II

Chromium Content of Rubies

Ruby No.	Place of origin	Weight of sample, gm.	Percent Cr	Percent Cr_2O_3
1	Mysore, India	0.8000 0.2000	0.167 0.171	0.244 0.250
2	Ural Mountains	0.4500 1.0004	0.121 0.119	0.174 0.177
3	Mysore, India	1.0000 1.0000	0.162 0.156	0.237 0.228
4	Zoutpansberg, Transvaal	1.0000 1.1000	0.130 0.131	0.190 0.191
5	Macon County, North Carolina	0.5000 0.4000	0.068 0.070	0.099 0.102

No. 1. Several small, deep red crystals, uniform in color, translucent, containing inclusions (probably zircon).

No. 2. Several deep red crystals, uniform in color, translucent to subtransparent.

No. 3. Several deep red crystals, uniform in color, translucent.

No. 4. Deep red crystal, opaque.

No. 5. Deep red crystal, translucent; basal and a prismatic face completely covered with a heavy layer of fuchsite.

Summary

The chromium content of naturally occurring ruby has been determined by a standard analytical method.

The rubies that were analyzed were found to contain between 0.10 and 0.25 percent chromic oxide.