

The Extraction of Germanium and Gallium from Germanite.

By Kazuo SAITO.

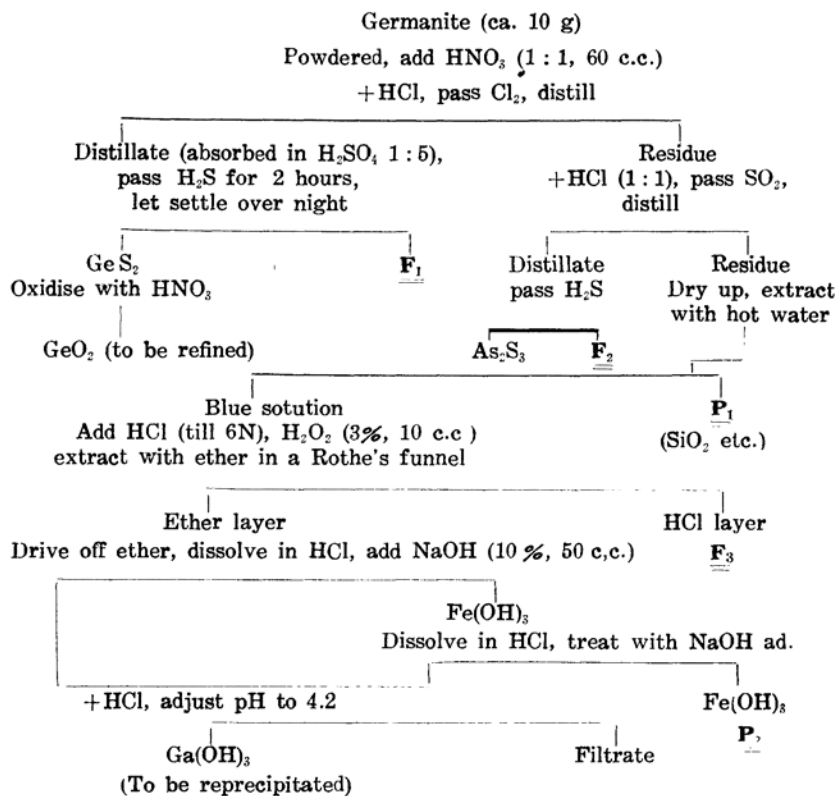
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The author has planned to prepare pure germanium compound, which is available as the standard substance in the studies of the chemistry of germanium, from germanite in small scale. The main constituents of the mineral is as follows:⁽¹⁾

Cu	45.60%
Fe	7.22
Ge	6.20
Zn	2.61
Pb	0.19
S	31.34
As	5.03
SiO ₂	0.75
Total	98.94

The minor elements are Ga, Na, P, Mg, Ca, Ti, Al, Mo, W, Sb, Mn, V, Au, and (Hg); they are detected by spectroscopic method with E-2 spectroscope (Adam Hilger).

Table 1.



(1) The quantitative analysis was carried out at Tsumeb, Africa.

The course of separation is systematised in Table 1.⁽²⁾ Germanium is distilled from hydrochloric acid solution in the current of chlorine; the yield is about 6.1%.

Preparation of pure germanium dioxide. The spectroscopic test of the unrefined germanium dioxide indicates that the main impurities are Si, Fe, Mg, Na, Ca and Ti. They are all common elements and those elements which would be caused by imperfectness of the separation are not found. So it is unnecessary to be too timid of incompleteness of the separation in such a small scaled work in laboratory.⁽³⁾

Several methods⁽⁴⁾ to remove the minor elements had been tried and in consequence it could be understood that too much complicated operations are not desirable for the preparation of a pure compound in this case. Thus the following process is recommended. Germanium dioxide is dissolved in caustic soda solution. To oxidise arsenic that would be accompanied, pass chlorine gas through the alkaline solution; add hydrochloric acid and distill. The distillate is absorbed in distilled hydrochloric acid. Germanium hydroxide produced by the hydrolysis in the flask adheres so tightly to the bottom of the vessel, that the supernatant liquid can be decanted without any loss of the precipitate. Add cold water into the vessel, shake well and decant it out; repeat this washing for several times. (If the distillate be absorbed in water, the yield of the pure hydroxide will be better, but the precipitate does not adhere to the bottom so tightly, therefore various operations are required for its separation.) Dry the vessel at room temperature (application of heat causes contamination of silicon from the glass), scrape off the precipitate and ignite it in a platinum crucible.

Germanium dioxide thus obtained is snow white. The spectroscopic examination of it does not indicate any contamination. (However, as germanium oxide is relatively volatile in the arc, the temperature should be kept comparatively low; therefore it is afraid that the line of several elements might not appear.)⁽⁵⁾ The apparent atomic weight of germanium in this oxide is found between 72 and 73, and it can be applied as the standard substance.

Extraction of gallium and its examination. For the extraction of gallium, Rothe's extraction by ether was carried out.⁽⁶⁾ As arsenic is

(2) R. Berg & W. Keil; *Z. anorg. allg. Chem.* **209** (1932) 383.

L. Dedé & W. Russ; *Ber.* **61** (1928) 2451.

(3) H. J. Abrahams & J. H. Millers; *J. Am. Chem. Soc.* **54** (1932) 86.

(4) E. B. Johnson & L. M. Dennis; *J. Am. Chem. Soc.* **47** (1925) 790.
W. Keil; *Z. anorg. allg. Chem.* **152** (1926) 101.

(5) J. Papish; *J. Am. Chem. Soc.* **49** (1927) 3028.

(6) R. Berg & W. Keil; 1. c.

W. F. Hillebrand & G. E. F. Lundell, "Applied Inorganic Analysis", p. 106.

also extracted with ether from hydrochloric acid solution, the removal of it is required. For this purpose the distillation of arsenic trichloride in the current of sulphur dioxide is recommended. In order to extract gallium completely from the acidic solution with ether, it is desirable to extract it together with large amount of trivalent iron, which can be removed afterwards simply. After the separation of iron, add hydrochloric acid and adjust the pH to 4.2 with aqueous ammonia using methyl red as indicator. Excess of alkali should be avoided. The yield of gallium is about 0.63% of the ore.⁽⁷⁾

In order to examine the accuracy of the extraction, the author has tried to test each fraction, where the loss of gallium would be found, with spectroscopic method (underlined fractions of Table 1). Aluminium alum, in which the absence of gallium has been confirmed, is applied as the carrier. To F_1 , F_2 and F_3 or the Table 1 add 20 cc of 1% alum solution and precipitate hydrated oxide of aluminium as usual.

The arc-spectra were observed with E-2 spectroscope, with the aid of carbon electrode. The conditions were as fellows:

Voltage: 100V D.C. Current: 4-5A Exposure: 2 minutes
Slit: 0.01 mm Plate: Fuji Process $4'' \times 10''$.

The lines found on the plate are as follows:

Table 2.

	F_1	F_2	F_3	P_1	P_2
2500.2 Å	—	—	+	—	—
2944.2	—	—	+	—	—
2943.6	—	—	++	—	+

The appearance of these lines indicates that on the carbon electrode only little gallium is present⁽⁸⁾ (F_3 , 0.00n mg Ga, P_2 , 0.00 on mg Ga). Taking the amounts of the precipitates into consideration, the gallium contents of these fractions must be below one milligram. Thus the above method is recommended for the extration of gallium from germanite. The gallium oxide thus obtained is very pure.

Summary. The author has succeeded to extract germanium and gallium of satisfactory quality almost quantitatively in small scale. Germanium oxide can be refined by redistillation and hydrolysis, and the product is applicable as the standard substance for the chemical study. It is confirmed that Rothe's extraction is a suitable method for

(7) The gallium content of germanite is reported to correspond 0.71, 0.57 and 0.74% (Gmerins Handbuch).

(8) J. Papish & A. Holt; *J. Phys. Chem.* **32** (1928) 142.

the preparation of gallium from germanite.

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*Chemical Institute, Faculty of Science,
Tokyo University.*
