⁸R. G. Treuting: Private communication.

⁴R. D. Heidenreich and W. Shockley: *Report on Strength of Solids*. (1948) p. 57. London. Physical Society.

⁵D. M. Evans, D. N. Layton, and H. Wilman: *Proceedings Royal Society* (1951) **A205**, p. 17.

⁶D. C. Jillson: *Trans. AIME* (1950) **188**, p. 1009;

JOURNAL OF METALS (August 1950).

⁷F. L. Vogel, W. G. Pfann, H. F. Corey, and E. E. Thomas: *Physical Review* (1953) **90**, p. 489.

⁸C. J. Gallagher: *Bulletin American Physical Society* (1953) **28**, No. 4, p. 10.

⁹G. L. Pearson, W. T. Read, Jr., and F. J. Morin: *Physical Review* (1954) **93**, p. 666.

Technical Note

Purification of Gallium by Zone-Refining

by D. P. Detwiler and W. M. Fox

IN the course of research on semiconducting inter-metallic compounds, it became necessary to obtain gallium metal of greater purity than that available commercially. Several methods were considered for further purification, including acid leaching,¹ fractional crystallization,² and zone-refining.³⁻⁵ The method of fractional crystallization was discarded as being equivalent to zone-refining in purification but inefficient in material and time. Both acid leaching and zone-refining were tried, and the method finally adopted is a combination of the two.

The acid leaching technique has been reported¹ to produce gallium in which no impurities are detectable spectroscopically. Although this method is very effective in removing oxides and surface contaminants, semiconducting material made of gallium subjected only to leaching indicated little reduction in the concentration of metallic impurities. Zone-refining, however, appears very effective in removing trace metallic impurities, but comparatively ineffective in removing the surface oxide film. Consequently, the method evolved consists of acid leaching to thoroughly clean the surface, followed by zone-refining to remove metallic impurities.

The low melting point and relatively high thermal conductivity of gallium introduce some difficulty in maintaining frozen and molten zones in zone-refining. To accomplish this, it is found necessary to reduce the effective ambient temperature by circulating ice water in coils about the regions that are to be kept frozen, while heat is supplied to the molten regions by resistance coils. The power supplied to the heating coils is regulated by a constant-voltage transformer and a variable autotransformer. Both heating and cooling coils are mounted on a transite base. The gallium ingot is held in a closed pyrex tube sliding inside the heating and cooling coils, the reciprocating method of Tanenbaum et al.⁴ being employed to move the molten zones through the ingot at a rate of 2 in. per hr. This apparatus is shown in Fig. 1.

Fig. 1—Gallium zone-refiner. The cooling coils are covered with asbestos.

Table I. Spectrographic Analysis

Gallium Treatment	Pb, Pot
As-received	0.00X
Acid leached	0.00X
Purified end of zone melt	0.000
16 cm from pure end of zone melt	0.000
24 cm from pure end of zone melt	0.00X
32 cm from pure end of zone melt	0.00X

The results of a spectroscopic analysis⁶ of a zone-refined ingot, as well as of the material as-received and after acid leaching, are shown in Table I. The ingot was 32 cm in length, and received 37 molten-zone passes, the molten zone being about 4 cm long. The only impurity found was lead, the following elements being reported also as checked but not found in the pure material: Al, Sb, As, Ba, Be, Bi, B, Cd, Ca, Cr, Co, Cb, Cu, Ge, Au, Fe, Mg, Mn, Mo, Ni, Pt, Si, Ag, Na, Sr, Sn, Te, Ti, W, V, Zn, and Zr. There thus appears no indication of pickup of Al, Mg, or Si from the pyrex boat as reported by Zimmerman² in his fractional crystallization.

Thus it appears that definite removal of lead from gallium occurs during the zone-refining process. It also may be concluded that a more sensitive analytical procedure than spectroscopy is required to evaluate quantitatively the purity of zone-refined metals. One such procedure which is proposed for use in the near future is the measurement of very low temperature resistivity. Although this will not identify the impurities present, it offers a very sensitive check of total impurity.

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References

¹F. Sebba and W. Pugh: *Journal of the Chemical Society* (1937) p. 1373.

²W. Zimmerman, III: *Science* (1954) **119**, p. 411.

³W. G. Pfann: *Trans. AIME* (1952) **194**, pp. 747, 861; *JOURNAL OF METALS* (July, August 1952).

⁴M. Tanenbaum, A. J. Goss, and W. G. Pfann: *Trans. AIME* (1954) **200**, p. 762; *JOURNAL OF METALS* (June 1954).

⁵F. Montariol, R. Reich, P. Albert, and G. Chaudron: *Comptes Rendus* (1954) **238**, p. 815.

⁶Spectroscopic analysis performed by the W. B. Coleman Co., Philadelphia.

D. P. DETWILER, formerly associated with The Franklin Institute Laboratories, Philadelphia, is now associated with the New York State College of Ceramics, Alfred, N. Y., and W. M. FOX is associated with The Franklin Institute Laboratories, Philadelphia.
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