

|    | PER CENT    | MOLECULAR RATIOS |        |
|----|-------------|------------------|--------|
| As | 69.80       | .933             | } 1.78 |
| S  | 0.21        | .007             |        |
| Fe | 29.40       | .530             | 1      |
|    | <hr/> 99.41 |                  |        |

The slight deficiency of the analysis is due to the presence of calcite in small amount which was not determined. Sulphur is practically absent. There is insufficient arsenic, as shown by the molecular ratios, to yield exactly the 2 : 1 ratio of löllingite. Such a deficiency is common in analyses of this mineral and has generally been accounted for by assuming the presence of varying amounts of the leucopyrite molecule,  $\text{Fe}_3 \text{As}_4$ . In this case calculation shows the presence of 14% of leucopyrite.

The authors are very glad to acknowledge the considerable help given by Professor Charles Palache in the preparation of this paper.

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## THE PREPARATION OF OPTICALLY CLEAR SELENIUM FOR USE IN INDEX MEDIA<sup>1</sup>

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### ABSTRACT

In the preparation of selenium-sulphur mixtures for use as index media, one is encountered with the difficulty of obtaining selenium which is optically clear when melted into thin films. Minute particles of another phase are commonly present which interfere with the index determinations. These have been identified as selenium dioxide, and a method is described for the removal of this material by distillation in an atmosphere of carbon dioxide.

### INTRODUCTION

In the determination of the optical properties of minerals, by the immersion method, materials frequently are encountered the refractive indices of which lie above those of the usual immersion media. For index determinations between values of 2.05 and 2.75 sulphur-selenium mixtures have been recommended.<sup>2</sup>

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<sup>2</sup> Larsen and Merwin; *Am. J. Sci.*, 34, 42, (1912).

These are prepared by mixing carefully weighed portions in accordance with the index-composition curves of Larsen and Merwin, melting to a uniform material and, after cooling, rechecking the index by some standard procedure.

In the immersion method a small amount of the powdered medium is placed on the slide and the material whose index is to be determined is scattered on it. A cover glass is placed upon the mixture and the slide is heated over a small flame until the medium is liquid. It can then be pressed readily into a thin film and the determination made. There is but little danger of change in the index due to volatilization of either the sulphur or selenium.

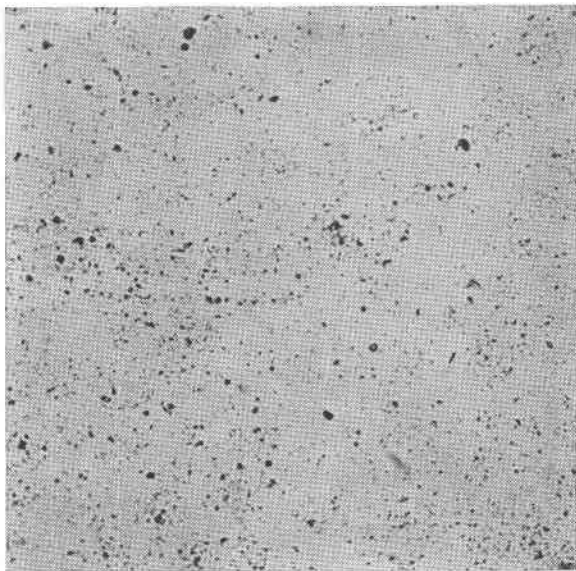


Fig. 1.  
Appearance of thin film of commercial "pure" selenium, x 200.

In making such media it was found that the selenium contained some foreign material in amounts which prevented the transmission of sufficient light for standardization; and this impurity made impossible exact determination of the indices. In a thin film of the selenium the impurity appeared under the microscope as black opaque grains as shown in Figure 1. Upon closer examination, many of these grains were identified as aggregates of very

small particles; and small individual particles were scattered through the whole field. The present investigation was undertaken therefore to establish a method for the purification of selenium by means of which the opaque particles would be removed.

#### EXPERIMENTAL METHODS

The methods of purification of selenium described in the literature are concerned mainly with the removal of sulphur and tellurium. The latter may be used to form a series of index media with selenium, the range of which lies above 2.75. Accordingly neither of these two materials is detrimental in selenium to be used for index determinations. But since they are the most difficult common impurities to remove (as reported) due to their similarity to selenium, some of the methods of their separation were applied to the further purification which is necessary to remove the opaque material.

One of these methods depends on the oxidation of the selenium to the dioxide and the subsequent reduction of the dioxide to the element. The selenium was oxidized readily by dissolving it in nitric acid. After filtration, the solution was evaporated to dryness, the dioxide sublimed and dissolved in water. It was then reduced: in one case by sulphur dioxide; in another by hydrazine. There seemed however to be no diminution in the amount of impurity after such treatment.

Purification by distillation was then attempted. The element melts at about 220°C. and boils at about 688°.³ Distillation was carried out in large glass test-tubes, bent to form an angle of about 120°, and held in such a position that the outlet was slightly inclined. The distilled selenium was collected in a suitable receptacle placed beneath the mouth of the tube. It was found to contain the impurity even after several such distillations.

During the previous operation it was noticed that long needles collected in the test tube near the mouth. These crystals had indices greater than 1.76, possessed a high birefringence, showed parallel extinction, and gave a uniaxial positive interference figure. Accordingly they belonged to the tetragonal or hexagonal systems. Determinations on the selenium dioxide obtained by oxidation showed identical optical properties.

Therefore it was assumed that the impurity in the selenium

³ *Internat. Critical Tables*, Vol. I, 104, 102, (1926).

was selenium dioxide. Distillation was again attempted from tubes constructed similarly to those used before, but suction was applied to the cold end with an attempt to exclude any oxygen. Due to difficulties in sealing the tube, air was constantly being drawn into the selenium vapor and the distilled material had considerable impurity in it. Furthermore, due to the high temperature and the reduced pressure within the tube, it collapsed readily and in that respect the method was not satisfactory.

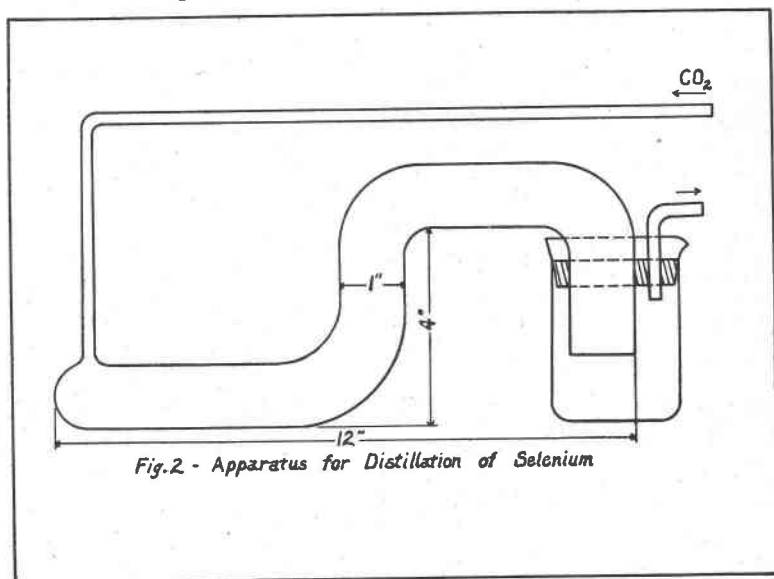


Fig.2 - Apparatus for Distillation of Selenium

Distillation in an inert gas was suggested. Carbon dioxide seemed most desirable. A tube of heavy glass was constructed, as shown in Figure 2, one inch in diameter and about 12 inches long. The carbon dioxide was passed through the smaller tube directly over the selenium for several minutes before beginning the distillation, and continued throughout the entire operation. The tube was put into a muffle furnace with the beaker for collecting the selenium just outside. Asbestos paper was used to close the furnace and shield the beaker. The charge was comparatively small (about 200 grams) and distillation proceeded rapidly. The temperature of the furnace did not greatly exceed that of the boiling selenium.

This product was examined and appeared better than any previous sample. It was redistilled three times and the final

product had practically no foreign material in it. The amount of the impurity present was so small that it in no way hindered the determination of the indices of refraction of high index materials.

Upon reexamination of the original selenium with the oil immersion objective whereby a magnification of at least 900 diameters was obtained, the particles larger than 1 or 2 microns in diameter were transparent and birefracting while only at lower magnifications did they appear opaque. This birefringence of the particles forms additional evidence that they are selenium dioxide since it likewise is birefracting. The opaque appearance at lower magnifications is probably due to the small size of the particles and the difference in index of refraction between them and the surrounding selenium.

Crystalline selenium also is birefracting, and it was thought at one time that the particles might be small crystals of selenium itself. However, when crystallization of selenium begins it spreads from a center; such spreading from the opaque particles was never evident. Furthermore crystallization in the film on slides only begins after a comparatively long time whereas the minute particles are always found in the selenium immediately after the slide has been made. In a film of purified selenium the particles were never found, as long as the film was heated just above the melting point. If they were the crystalline form of selenium they should not only occur in the unpurified material but in the purified samples as well.

Upon oxidation and reduction of some of the purified selenium there seemed to be as many of the opaque particles present as in the original samples. And when the purified selenium was distilled in air they reappeared also. In fact in any sample of optically clear selenium which was treated under any oxidizing conditions the particles were always found after such treatment.

Finally some crystals of selenium dioxide were intimately ground with purified selenium and a film of such a mixture was found to appear similar to a film of commercial selenium. The finer particles of the dioxide appeared opaque under low magnifications while only under the highest magnifications could any birefringence be detected.

All evidence, therefore, seems to indicate that selenium dioxide,  $\text{SeO}_2$ , is responsible for the apparently opaque particles which are found in commercial selenium.

## SUMMARY

All selenium obtainable on the market, so far as examined, contains a trace of selenium dioxide. This dioxide appears under the microscope as small nearly opaque particles when the selenium is used as an index medium, and renders the material unsuited for such a purpose.

Several methods of purification have been attempted, and it has been found that the dioxide may be removed by distillation from a suitable container in an atmosphere of carbon dioxide. The distillate is then practically optically clear when melted into thin films such as are used in index determinations.

The author wishes to express his gratitude to Dr. R. H. Bogue for his advice and cooperation in outlining and directing this problem.

Further acknowledgement is due Dr. Herbert Insley for his interest in the work and his aid in the identification of the materials, and to Mr. F. W. Ashton for the preparation of the photomicrograph.

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ELLSWORTHITE CRYSTALS FROM  
HALIBURTON COUNTY, ONTARIO<sup>1</sup>

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Some months ago the writer received from Charles G. Earle of Haliburton, Ont., a few ounces of small, loose crystals which electroscopes tests showed to possess considerable radioactivity, and which were immediately suspected of being either ellsworthite or betafite. The crystals received are free from gangue but are more or less coated with a yellowish brown decomposition or resorption product, as well as with small crystals of apatite, which along with calcite may also be included in part or completely within the crystals themselves. One fragment of a crystal, however, was entirely free from any superficial coating or alteration and showed clean, sharp, bright faces. The crystals vary from slightly less than  $\frac{1}{4}$  inch to  $\frac{1}{2}$  inch in diameter and in general exhibit a rounded octahedral habit, with the octahedron most prominent in combination with small cube faces and with rather frequent occurrence of small faces of the dodecahedron and the tetragonal trisocta-

<sup>1</sup> Published by permission of the Director of the Geological Survey, Canada.