PREPARATION AND PURIFICATION OF THE TRI-IODIDES OF ANTIMONY AND ARSENIC FOR USE IN IMMERSION MEDIA OF HIGH REFRACTIVE INDEX

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In order to determine the indices of refraction of minerals, the indices of which are between 1.68 and 2.05, amorphous mixtures of piperine and the iodides of antimony and arsenic may be used (1). It is possible to use liquids only up to an index of 1.868, and those with refractive indices above 1.778 (methylene iodide saturated with sulphur) change rather rapidly by evaporation. As piperine and iodide mixtures remain constant in refractive indices a few months after they are prepared, they are especially useful.

To make these preparations, three parts by weight of antimony tri-iodide and one part of arsenic tri-iodide are mixed with the required proportion of piperine to give a mixture of the desired refractive index based upon the composition—index of refraction curve of Merwin (1). The weighed mixtures which become fluid a little above 100 degrees C. are introduced into a suitable container and heated, while being stirred, until homogeneous. After cooling, their refractive indices may be checked by means of a goniometer.

To use such mixtures as imbedding media, a small fragment of the previously prepared mixture and a few fine grains of the mineral to be examined are placed on a slide which is gently heated over a low flame, or on a hot plate. As the mass melts, the grains are mixed with it and it is covered with a small cover glass. The slide is then allowed to cool, and at the same time the mixture is pressed into a thin film which, if the mineral grains were fine enough, is sufficiently transparent to permit the microscopic determination.

Immersion media thus prepared have not been found suitable, due to numerous microscopic inclusions which cause difficulty in determining the indices of refraction of the mineral fragments. By first purifying the piperine and the iodides it has been possible to prepare media, which although not entirely free from impurities, have been found quite satisfactory.

Piperine from different sources was tried and a coarsely crystalline variety of rather large fragments gave the best results. One sample obtained from a chemical company in the powdered form, was found satisfactory only after it was twice recrystallized from ethyl alcohol. As piperine is rather soluble in hot alcohol (23 grams per 100 cubic centimeters at 60 degrees C.), and much less soluble in cold alcohol, recrystallization is readily accomplished. By filtering the hot alcoholic solution before cooling, mechanical impurities are removed.

The tri-iodides of antimony and arsenic are not obtainable from all chemical houses. Therefore, it was found desirable to prepare them.

Mellor (2) states that antimony tri-iodide can be synthesized directly from metallic antimony and iodine. This was accomplished in the following manner. The correct proportions of finely powdered antimony and iodine were mixed in a mortar and introduced into a large test tube, the lower third of which, only, was filled. Combination was caused to take place by gently heating the bottom of the tube over a low flame. The reaction takes place with some vigor and vapors of iodine are liberated; the greater part of the antimony and iodine combine. The heat of reaction is sufficient to cause the melt to remain liquid for a few moments, permitting it to be mixed by shaking the tube before solidification.

Antimony tri-iodide thus prepared was found to be unsatisfactory without purification. Attempts were first made to accomplish this by distillation from a small retort. The distilled material was found unsatisfactory. Various organic solvents were tried and at the suggestion of Dr. Merwin (3) carbon disulfide was chosen. After several trials a technique was developed whereby a pure recrystallized product was obtained. Antimony tri-iodide is only slightly soluble in carbon disulfide at room temperatures, but at 45 degrees C., just below the boiling point of the latter, it dissolves fairly readily. The crushed iodide was introduced into a 500 cubic centimeter Erlenmeyer flask with about 300 cubic centimeters of carbon disulfide. A cork stopper was inserted loosely in the mouth of the flask and it was placed in a constant temperature oven maintained at 45 degrees C. The flask was shaken from time to time until no further solution appeared to take place. Excess of uncombined antimony readily settled to the bottom of the flask and free iodine dissolved in the liquid causing a dark color. The iodine in solution reacts with metallic antimony in a short time to form more iodide. If metallic antimony was not present, a small amount (finely powdered) was added. When the dark color of the solution due to iodine was completely discharged, all solid material was allowed to settle while the flask containing the solution was kept at a temperature of 45 degrees C. After sufficient settling (two or three hours) the clear supernatant liquor was rapidly poured into a clean dry Erlenmeyer flask which was covered with a dark cloth to exclude light. This precaution was found necessary to prevent formation of light colored, fine grained decomposition products. The decanted solution was allowed to cool to room temperature and finally cooled in ice water. This temperature change caused crystallization over the bottom and sides of the flask. The cooled mother liquor was then poured back into the first flask and allowed again to act on undissolved iodide. The dissolving and decanting operations were repeated as often as necessary to produce the desired amount of pure material. Crude pulverized iodide was introduced as required. Crystals thus obtained were again purified by a second recrystallization.

According to Mellor (4) arsenic tri-iodide also can be prepared by direct union of the elements. This was found to be the case and crude arsenic tri-iodide was formed by the same method described for antimony tri-iodide. In the case of arsenic tri-iodide, the reaction of combination was not as vigorous as that taking place when antimony and iodine unite. Arsenic tri-iodide was found to be sufficiently soluble in carbon disulfide at 45 degrees C. to enable a good yield of the crystalline compound to be obtained by allowing the saturated solution, after decantation, to cool and evaporate slowly. As in the case of solution of the iodide of antimony, uncombined iodine reacts with metallic arsenic in the presence of carbon disulfide to form iodide. It was again found necessary in order to obtain a pure product, to exclude light while crystallization was taking place. With arsenic tri-iodide the last few cubic centimeters of mother liquor in contact with crystals were rejected and the crystals were rinsed rapidly with a small amount of fresh carbon disulfide.

In preparing melts of the iodides and piperine, it was found absolutely essential to avoid heating the mixtures above 135 degrees C. to prevent decomposition by excessive temperatures as pointed out by Merwin (1) and Larsen (5). The melts were best prepared in a short test tube immersed in a "Nujol" oil bath with a thermometer, the bath being heated by an electric hot plate.

For approximate determinations and comparison of refractive indices of piperine-iodide melts, the indices of which are within the range $n=1.85$ to $n=2.05$, a number of minerals have been found useful. In employing these minerals it should be recognized that the optical constants of most of them may vary from published values, due to possible changes in composition as a result of solid solution. Minerals used for this purpose include,—fayalite (pure–$2FeO \cdot SiO_2$), monazite, siderite (pure–$FeO \cdot CO_2$), zircon, synthetic $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (6), cerargyrite and cassiterite. The writer is indebted to Dr. Wm. J. McCaughey for samples of the minerals named.

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