277. *The Extraction of Indium from Cylindrite, Chalcopyrite, and Metallic Tin.*

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IN the preceding paper it was shown that indium is present in unusually large amounts in the mineral cylindrite, in large traces in some chalcopyrites, and as a general impurity in metallic tin. We now describe the extraction and concentration of indium from these sources.

Extraction from Tin.—This was carried out partly as a check on the accuracy of the initial spectroscopic determination, and partly to show how indium would behave analytically in the presence of a large excess of tin. This information was needed before the profitable extraction of indium from the very limited supply of cylindrite available could be attempted. Two methods of concentration were used.

(a) *Sulphide separation.* Although the difference in the solubility of indium and stannous sulphides is no doubt sufficient to effect a separation on a large scale, with both elements present in similar quantity, yet the probability that small quantities of indium sulphide would be coprecipitated on the stannous sulphide was considerable (cf. Kolthoff and Moltzau, *Chem. Rev.*, 1935, **17**, 293). Preliminary experiments showed that this was so. 1 G. of indium-bearing tin was dissolved in concentrated hydrochloric acid, diluted so that the acid was 0·2*N*, and stannous sulphide precipitated with hydrogen sulphide. The precipitate was washed with a solution of the gas. A few mg. of sodium chloride were then added to the filtrate, to give a residue on evaporation that could be placed on a spectrographic arc, and the solution evaporated to dryness. A second sample of 1 g. was treated in the same way, except that it was oxidised to the stannic condition before precipitation as sulphide. The stannic sulphide precipitate, examined spectroscopically, was free from indium, but the residue from the filtrate showed the line at 4511 A. more strongly than the original tin. With the tin precipitated as stannous sulphide, some concentration had taken place in the filtrate residue, but the precipitate still showed traces of indium. Concentration of the indium in a 10-g. sample of the tin was carried out successfully bv the stannic sulphide separation. After solution of the tin in hydrochloric acid, chlorine was passed in to convert it into the stannic condition. The sulphide precipitation was repeated on the filtrate and washings after they had been concentrated by evaporation, and the solid which separated from them redissolved in hydrochloric acid. A few mg. of aluminium nitrate were added to the final filtrate, and the indium coprecipitated on aluminium hydroxide by addition of ammonium hydroxide solution. As the hydroxide is not a suitable form of indium for spectroscopic examination, the precipitate was dissolved in hydrochloric acid and evaporated to small bulk. It showed the indium lines strongly, along with lines due to sodium, calcium, magnesium, and traces of copper. Repetition of this extraction with 500 g. of tin showed that the oxidation of the last part of the tin by chlorine is very slow, and the reaction was therefore completed by the use of mercuric chloride. The sulphide precipitation on this scale was slow and laborious, and the bulky precipitate carried down some indium sulphide with it.

(b) *Chloride separation.* The b. p. of stannic chloride is 114·1°, but indium chloride does not volatilise appreciably below 440°. These substances can therefore be separated effectively by a single distillation. Chlorine was led over 300 g. of tin in a large distilling flask, and the stannic chloride formed distilled off simultaneously. The small residue was extracted with concentrated hydrochloric acid, the solution evaporated to small bulk, and made up to 10 c.c. Four further solutions were made from this by successive ten-fold dilutions, 0·1 c.c. of each solution was evaporated on a graphite arc (Brewer and Baker, *loc. cit.*), and their spectrographs compared with indium standards. The line at 3256 was clearly visible with the third of the five solutions, but had faded in the fourth. As there was still considerable tin present from a spectroscopic standpoint, this indicated an approximate content of 0·001 mg. of indium in 0·1 c.c. of the third solution, or a content in the original tin of 0·003%.

Extraction from Chalcopyrite, and the Separation of Indium from Iron.—Sufficient chalcopyrite from the New Cook's Kitchen mine, Camborne, Cornwall, was available for a small-scale separation. In preliminary experiments, the copper was removed as sulphide, and separations of the indium from the residual iron attempted. The most satisfactory method appeared to be that of Mathers (*J. Amer. Chem. Soc.*, 1908, **30**, 209), in which iron is removed in 50% acetic acid by nitroso-β-naphthol. As copper also forms an insoluble complex with this reagent, the sulphide separation was afterwards omitted. Mathers claimed that the indium so separated is free from iron, though traces of the indium originally present may remain on the iron precipitate.

1 G. of finely-ground chalcopyrite was dissolved in aqua regia, treated with ammonium hydroxide until a precipitate appeared, and cleared with the minimum quantity of hydrochloric acid. 4 G. of nitroso-β-naphthol in 200 c.c. of 50% acetic acid were added, the solution left over-night, and then filtered. The precipitate was washed with 50% acetic acid, then with water, the indium appearing at first sight to have been concentrated successfully in the filtrate. This method was therefore applied to the removal of iron later, in the extraction of indium from cylindrite. It was observed in that separation, however, that if the iron complex with nitroso-β-naphthol was ignited, there was a larger proportion of indium adsorbed on the carbon residue than had been observed by Mathers. These experiments made it clear that, although this method might serve to separate traces of iron from indium, yet it is unsatisfactory as a means of extracting small quantities of indium from iron. The use of iron minerals as a source of indium was consequently not likely to prove convenient, owing to the difficulties inherent in the separation.

Cylindrite.—*Analysis.* This mineral is essentially a sulphide of lead, tin, and antimony. Frenzel, who discovered it (*Jahrb. Min.*, 1893, **2**, 124), found silver and iron were also present, and, assuming they were replacing lead, formulated the mineral as $3PbS,Sb_2S_3,3(PbS,SnS_2)$. His analyses were not confirmed by Prior (*Min. Mag.*, 1904, **14**, 21), who gave the formula

$3PbSnS_2,SnFeSb_2S_8$. Ahlfeld and Moritz (*Jahrb. Min.*, 1933, **66**, 206) showed that both the zinc blende and the iron sulphide present were impressed into the laminated pencils of the mineral proper. They therefore ignored the iron content, but otherwise adopted Prior's formula in preference to Frenzel's. As there seemed to be some doubt as to the actual constitution of the mineral, it was thought desirable to carry out analyses for the principal constituents. Only three specimens could be obtained for chemical treatment. Of these, the first was a small 3-g. sample, homogeneous in appearance, which was all used in preliminary separations. The other two differed considerably in appearance. The larger (A, 280 g.) was apparently fairly pure cylindrite, but the smaller (B, 150 g.) had a considerable quantity of hard rocky matter associated with it. The first main separation of indium was carried out on this sample, and a few selected " pencils " of the sulphide material used for a determination of antimony, tin, lead, and sulphur. The values found for antimony and sulphur agreed with Frenzel's, and although there was some discrepancy with the tin and lead, the atomic ratios were in as good agreement with his proposed formula as his own results had been. Mr. E. G. J. Hartley, of this laboratory, carried out an analysis of the larger sample, making a preliminary separation of the constituents before estimating them quantitatively. His results agreed well on the whole with those of Prior, and confirmed the formula proposed by him. As our value for tin in sample B differed from that found by Frenzel, Prior, or Hartley, this metal was determined by us in sample A, the value agreeing exactly with that of Hartley. It therefore seems that there are two substances described as cylindrite : the pure material analysed by Prior, and typified by our larger sample, and an altered material with a definitely lower antimony content, corresponding to that originally discovered by Frenzel. The methods of analysis and summarised results of our own and the other investigations are given below.

Lead : 1 G. of the mineral (sample B) was dissolved in concentrated hydrochloric acid containing a little bromine. The solution was evaporated to 20 c.c., diluted with water, and left until the lead chloride precipitate had settled out. This was filtered on a Gooch crucible, washed with dilute hydrochloric acid, then with cold water, dried at 120° and weighed. To the filtrate and washing were next added 5 c.c. of concentrated hydrochloric acid, the solution evaporated to 100 c.c., and 1·5 g. of tartaric acid added to keep the antimony in solution. The solution was made alkaline with sodium hydroxide, a slight precipitate cleared with the minimum of hydrochloric acid, and the lead precipitated as sulphide at 60°. The precipitate was filtered on a Gooch crucible, washed with sodium sulphide solution, digested with nitric acid (*d* 1·2), the solution filtered, and the lead precipitated finally as sulphate. 1 G. of cylindrite gave 0·2576 g. $PbCl_2$ (= 0·1919 g. Pb) plus 0·2850 g. $PbSO_4$ (= 0·1946 g. Pb) ; total Pb = 0·3865 g., or 38·65%.

Antimony : This was determined by potassium bromate solution which had been standardised against pure metallic antimony (0·1528, 0·1512 g. Sb required 24·75, 24·5 c.c. ; hence 1 c.c. $KBrO_3$ = 0·006172 g. Sb). 1·4765 G. of cylindrite required 18·5 c.c. $KBrO_3$; *i.e.*, Sb = 0·1142 g. or 7·74%.

Tin : This was estimated by reduction with antimony in a stream of carbon dioxide, and titration of the resulting stannous chloride with 0·1*N*-iodine solution. Blanks were done for the antimony and acid used, and the iodine was standardised against A.R. tin. For sample B : 0·3619 g. contained 0·07759 g. Sn or 21·44%. For sample A : 0·2944 g. contained 0·07399 g. Sn or 25·13% (Hartley found 25·06%).

Sulphur : This was determined by roasting the cylindrite in a stream of air, absorbing the resulting sulphur dioxide in potassium hydroxide, oxidising it to sulphate with hydrogen peroxide, acidifying with hydrochloric acid, and boiling off any carbon dioxide present. The sulphate was then precipitated as barium sulphate. The residue in the boat was extracted with alkali, and the sulphate precipitated from acid solution as barium sulphate. 0·40 G. of cylindrite gave a total of 0·6916 g. $BaSO_4$; S = 23·75%.

Analysis of cylindrite, %.

				Hartley.*	Authors.	
	Frenzel.	Prior, I.	Prior, II.	Sample A.	Sample A.	Sample B.
Pb	35·41	35·25	34·58	33·97	—	38·65
Fe	3·00	2·81	2·77	3·47	—	—
Ag	0·62	0·50	0·28	nil	—	nil
Sn	26·37	25·65	25·10	25·06	25·13	21·44
Sb	8·73	12·31	12·98	11·92	—	7·74
S	24·5	23·83	23·88	24·39	—	23·75

* Hartley's values were corrected for 1·62% of insoluble residue (SiO_2).

Extraction of Indium from Cylindrite.—A concentration of the indium in a 1-g. sample of the mineral was carried out to ascertain how the indium would behave in the proposed separation. The finely powdered mineral was dissolved in 15 c.c. of hydrochloric acid, leaving a slight siliceous residue. The solution gave no reaction for stannous tin. The filtered solution was therefore diluted to make the acid $2N$, and hydrogen sulphide passed in. The precipitate of lead, antimony, and stannic sulphides was filtered off. Further dilution to 130 c.c. and treatment with hydrogen sulphide gave more of these sulphides. Spectroscopic examination of the precipitates and filtrates showed that, although the greater part of the indium was obviously in the final filtrate, yet the second precipitate also contained appreciable traces of it. Reprecipitation of the sulphides from the second precipitate at a rather higher acid concentration effected a separation of the indium. The final filtrate and washings were evaporated to 10 c.c. At this point a few crystals of hydrated stannic chloride separated and were removed, a further small crop being removed later. The final brown residue was dissolved in hydrochloric acid and prepared by suitable dilutions for spectrographic examination. The indium lines fell off in intensity more rapidly than the preliminary inspection of the mineral had suggested, and to avoid any error due to the presence of residual tin, the indium was further separated on aluminium hydroxide, redissolved in hydrochloric acid, and examined again. The persistence of the lines indicated a probable content of 0·125 mg. of indium in the solution, corresponding to 0·1% in the mineral. The spectrograph also showed that there was present in the final solution considerable iron, together with some calcium and sodium.

Separation from sample B. 100 G. of picked material from this sample (which had associated with it much that was obviously not cylindrite) were finely ground, and extracted with 500 c.c. of hydrochloric acid and a few c.c. of bromine on a water-bath for several hours. After cooling, the precipitate of lead chloride was filtered off and again extracted with acid. The main filtrate was evaporated to 150 c.c. and more lead chloride filtered off. These crystals showed only a very slight trace of indium spectroscopically, and this was associated with the retained mother-liquor rather than with the crystals themselves. Tin, antimony, and the remaining lead were then precipitated as sulphides in *ca.* $3N$-acid, filtered off, and washed with hydrogen sulphide solution. Indium precipitated on these sulphides was shown spectroscopically to be negligible. The combined filtrates from the sulphide precipitations were evaporated to a dark brown syrup, and a quantitative spectrographic test carried out. This indicated the presence of 0·1—1 g. of indium, and also showed that zinc had been highly concentrated in the separation, the lines at 4682, 4722, and 4811 A. being intense.

The hydroxides of iron, zinc, and indium were next precipitated by ammonium hydroxide and filtered off, a little hydrated iron oxide separating from the filtrate on standing. This showed a minute trace of indium spectroscopically. The main precipitate, containing practically the whole of the indium, was redissolved in hydrochloric acid. After neutralisation of the solution, the iron was separated by nitroso-β-naphthol. This involved the use of rather large volumes, and left a solution containing considerable nitroso-β-naphthol, which was extracted with benzene. A thiocyanate test showed that the bulk of the iron had been removed, but on concentration of the solution and examination of the residue it was found necessary to make a further separation. After removal of organic matter from the residue with benzene, the zinc hydroxide was dissolved in concentrated ammonium hydroxide, and the indium separated from the iron as the insoluble basic sulphite (Bayer, *Annalen*, 1871, **158**, 372). Conversion of the sulphite into sulphide showed that iron had not been entirely removed even by this process, as some ferrous sulphide was carried down by the indium sulphide in dilute acetic acid solution. It was found that this could be removed by treating it with hydrogen peroxide until the black colour disappeared, and so converting it into ferric acetate. This left the indium sulphide along with residual sulphur, which was extracted with carbon disulphide, and the last traces removed by gentle ignition. The final weight of indium sulphide was only 0·0185 g., which represented one-tenth of the indium indicated by spectrographic tests. The rest of the indium was found mainly on the nitroso-β-naphthol precipitate, which was very bulky, and its indium content was not apparent until it had been ignited and the carbon residue extracted with acid.

Separation from sample A. This was the larger sample, and richer than B in cylindrite. It was treated in a similar manner for the separation of the sulphides, after which the iron, zinc, and indium hydroxides were precipitated with concentrated ammonium hydroxide, and the zinc hydroxide dissolved in excess of the same reagent. The bisulphite separation was used to free the indium from iron, and, with the larger amount of indium, was more successful than it had been with sample B. Two bisulphite separations were necessary, and the product contained a little iron, but not enough to cause contamination of the indium sulphide when this was precipitated from acetic acid solution. Spectrographic examination of the final product showed that it was reasonably pure, small traces of calcium, iron, and zinc being the main impurities. 269 G. of the crude mineral yielded 0·2048 g. of pure indium sulphide. A still higher yield might be obtained with large-scale extraction.

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