276. *Arc Spectrographic Determination of Indium in Minerals, and the Association of Indium with Tin and Silver.*

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For a long time the scarcity of indium has restricted the investigation of its chemistry. By the application of principles based on a study of the association of elements in minerals it was hoped that new and richer sources of the element might be discovered. Since this work was begun, commercial production from the concentrates of an ore not specified (Murray, *J. Ind. Eng. Chem.*, 1932, **24**, 686; *ibid.*, News edn., 1933, **11**, 300; Baldwin, *Brass World*, 1932, **28**, 98; French, *J. Chem. Educ.*, 1934, **11**, 70) has provided a much more plentiful supply, but the results of our investigation are not without theoretical significance, and indicate a possible source of indium richer than any yet worked.

Elements are associated in the earth's crust on account of (i) chemical similarity between elements of the same periodic group, (ii) similarity in atomic or ionic size and consequent ability to occupy equivalent places in crystal structures, (iii) genetic relations such as exist in a radioactive series. Although group characteristics determine the type of mineral in which an element is to be found, differences in atomic size usually prevent the association of the elements of a group in any particular mineral. The other two factors mentioned both result in the association of adjacent members of the same horizontal period, and recent searches for new elements or new sources of rare elements have shown that these horizontal associations predominate over the greater part of the periodic table. Where the influence of ionic size is fortified by a factor comparable to group similarity, as in the rare earths or platinum metals, association is very marked, and this combination of factors is repeated to some extent in the association of elements in the same horizontal period when they exhibit the same valency. That these horizontal associations are not limited to elements in the same valency state, however, is shown by the fact that the mineral germanite, for instance, contains 12 of the 17 chemically active members of the first long period, and also silver ($Z = 47$), cadmium (48), indium (49), and tin (50) in the second (Thomas and Pugh, J., 1924, **125**, 816). The mineral is essentially a copper thioarsenate and thiogermanate with zinc as its next main constituent and an abnormally high gallium content (0·5—0·76%), *i.e.*, its main metallic constituents are the first-period representatives of groups IB to VB. A similar association in the first long period has been shown to exist in enargite (Brewer, Papish, and Holt, *J. Amer. Chem. Soc.*, 1927, **49**, 3028), and the present paper establishes a striking example in the second.

Since its discovery in the Freiburg zinc blendes, indium has been reported as occurring in other blendes, notably those carrying cadmium and gold, in zinc carbonate minerals, and in various ores of iron (including chalcopyrite, $Cu_2Fe_2S_4$), manganese, and tin. Its association with cadmium has been further demonstrated by Papish and Holt (*Z. anorg. Chem.*, 1930, **192**, 92), who found it to the extent of 0·117% in a sample of commercial cadmium oxide, and by Hirschel (*Chem. and Ind.*, 1933, **11**, 797), who pointed out that indium is always present in the cadmium residues obtained during the purification of lithopones. In this connection also it is significant that Paschen (*Ann. Phys.*, 1909, **29**, 625) records a strong line at 4511 A. in his investigation of the infra-red spectrum of cadmium. As no other investigators appear to have observed this line, it is probable that Paschen's cadmium also contained indium. As he does not record any wave-lengths shorter than this, it is not possible to say whether any of the other characteristic indium lines were present or not, but it is noteworthy that in the analysis of the cadmium spectrum given in Kayser's " Handbuch der Spektroscopie," Vol. VII, this line is not allotted to any cadmium transition. Although the ore worked by Murray (*loc. cit.*) is not defined, it is described as containing sulphides of lead, zinc, copper, iron, silver, and gold, the indium remaining on concentration with the zinc. The average yield is given as 1·93 oz. per ton (French, *loc. cit.*), *i.e.*, less than 0·01%, which is low compared with some other sources reported. A statement, as yet unsubstantiated, has been made by Romeyn (*J. Amer. Chem. Soc.*, 1933, **55**, 3899) that certain pegmatite dikes in Utah contain 1—2·8% of indium, probably replacing aluminium in cordierite. If this is true it is unique in respect of both quantity and association. Hoppe-Seyler detected indium in wolfram from Zinnwald (*Annalen*, 1866, **140**, 247), but Atkinson (*J. Amer. Chem. Soc.*, 1898, **20**, 797) has shown that its occurrence in tungsten ores is not typical. The association of wolfram with tin ores and the particular source of this wolfram are interesting, however, in the light of Garrett's discovery (*Proc. Roy. Soc.*, 1927, **114**, *A*, 289) that all samples of metallic tin which he could procure contained traces of indium. This observation was confirmed by Green (*Nature*, 1927, **119**, 893).

We have confirmed the occurrence of indium in chalcopyrite by both spectroscopic observation and chemical separation, and have investigated other sources of iron, manganese and cadmium, with negative or doubtful results. In addition, we have carried out a systematic study of tin ores, since, in view of Garrett's work, these seemed to be the most promising and the least investigated, and we have made a preliminary survey of a few silver minerals. The spectrum of the laboratory supply of tin was photographed and found to contain an appreciable quantity of indium. An estimate (0·01—0·001%) was made by comparison with standard photographs, and confirmed by further examination after chemical concentration. Cornish tinstones and associated minerals, kindly supplied by the East Pool and Agar Co. Ltd., and other tin samples were next examined, but no rich source was indicated. The occurrence of tin as oxide is, however, anomalous for a B sub-group element, since these metals occur predominantly as sulphides, and it was therefore considered more important to examine the much rarer tin sulphide minerals, especially those containing other metals in the second long period. Attention was focused particularly on cylindrite and franckeite, which are sulphides of lead, antimony, and tin; these were found to have an indium content probably higher than anything yet reported, that in the former being estimated as 0·1—1·0%. While the work was in progress, a complete microscopic and crystallographic account of these minerals was published by Ahlfeld and Moritz (*Jahrb. Min.*, 1933, **66**, 206), who discuss the constitution and association of the minerals and point out that the zinc blende which is impressed into the crystals of cylindrite has a high cadmium content. (We were able to show by a spectrographic examination of picked crystals that the indium was in the cylindrite itself and not in the zinc blende.) Also the occurrence of these minerals is confined to the Bolivian tin belt, where argentiferous thiostannates are found. Hence in this mineral are found associated the " adjacent " elements silver, cadmium, indium, tin, and antimony. A further point is that in the similarly occurring teallite, a sulphide of tin and lead containing no antimony, there was found only a very small trace of indium. According to Ahlfeld and Moritz, the only mine from which cylindrite can be obtained in quantity (Santa Cruz, Poopo, Bolivia) has been closed down, and as most of the specimens known are museum specimens, only a few hundred g. of the crude material could be obtained for chemical separations. This yielded enough indium sulphide, however, to confirm the preliminary estimate.

Indium was also found in some silver minerals not containing tin, and this association will receive further investigation.

EXPERIMENTAL.

For the detection of indium, materials were examined visually with a Hilger constant-deviation spectroscope, after excitation in an arc between poles of pure iron. These give a clear field for the easily visible line at 4511 A. For photographic work, a Bellingham and Stanley quartz spectrograph was used, and the electrodes were of Hilger Acheson graphite. Estimates of the amount of indium present were made by the persistence method. This depends on the fact that, with the same conditions of excitation and recording, the number of lines appearing gives a measure by reference to standard exposures of the actual amount of an element on the arc. Though not as accurate as the more refined methods now in general use, this gives a rapid method for exploring a large field of minerals.

Comparison Standards and Limits of Sensitivity.—Solutions of known indium concentration were prepared by dissolving a 10% indium–silver alloy in nitric acid, precipitating the silver as chloride, and suitably diluting the filtrate. Electrodes carrying from 1 to 0·0001 mg. of indium were prepared by evaporating on them 0·1 c.c. of the appropriate solutions. Spectrographs of these solutions were then taken on a single plate, and the persistence of the lines determined. These are tabulated below. Ilford special rapid panchromatic plates were used; exposure 15 secs.; arc voltage 100; max. current 3 amps.

As silver minerals were among those to be investigated, standards were also made from the solutions before precipitation of the silver. It will be seen from the table that the line sensitivity appears to be diminished by the presence of silver, but the difference may also have been due in part to the formation of the non-volatile In_2O_3 on evaporation of the nitric acid solution. The effect of excess tin, added as stannous chloride, was also examined. The intensity of the most persistent lines was affected to some extent even in hydrochloric acid solution. This is presumably due to the greater volatility of the tin. Excess of copper, lead, zinc, or iron, or the presence of gallium salts appeared to have little effect on the indium spectrum. (For the effect of gallium on the spark spectrographic determination of indium, see Dennis and Bridgman; *J. Amer. Chem. Soc.*, 1918, **40**, 1531.) It should be noted that Garrett (*loc. cit.*) and Green *loc. cit.*) found the most persistent line to be at 4102 A., whereas de Gramont had given 4511.

Persistence of lines for pure indium.

	Indium, mg.						Indium, mg.			
λ, A.	1.	0·1.	0·01.	0·001.	0·0001.	λ, A.	1.	0·1.	0·01.	0·001.
4511·37	S	S	V	V	?FF	2753·98	V	F	F	
4101·82	S	V	V	V	FF	2714·00	V	F		
3258·55	V	V	V	F		2710·31	S	V	F	
3256·03	S	S	V	V	F	2601·90	V	F		
3039·36	S	V	V	F	FF	2560·22	S	V	FF	
2957·14	V	V	F			2522·99	V	F		
2932·62	S	V	F	F		2468·01	V	F		
2837·01	V	F	F			2460·06	V	F		
2775·35	F	F	FF							

Persistence of indium lines in presence of excess silver.

λ, A.	1.	0·1.	0·01.	0·001.	0·0001.	λ, A.	1.	0·1.	0·01.	0·001.
4511·37	S	S	V			3256·03	S	V	V	V
4101·82	V	V				3039·36	S	S	F	F
3258·55	S	V	F			2932·62	S	V		

Persistence of indium lines in presence of excess tin.

	Indium, mg.							Indium, mg.			
λ.	1.	0·1.	0·01.	0·001.	0·0001.	Nearest Sn line.	λ.	1.	0·1.	0·01.	Nearest Sn line.
4511·37	S	S	V	F	?FF	4525	2837·01	F	F		2840
4101·82	S	V	V	FF		3801	2775·35	S	F	F	2779
3258·55	V	F	F	F		3262	2753·98	V	F	F	2779
3256·03	V	V	V	F	?FF	3262	2714·00	V	FF		2707
3039·36	V	V	V	?F		3034	2601·90	V			2594
2932·62	V	F	F			2913	2560·22	V	F	FF	2558

S = Strong; V = easily visible; F = faint; FF = very faint.

Garrett's and Green's material was almost entirely metallic tin, and since in the presence of metallic tin we find that the line at 4511 is the more persistent, it would seem that the condition of excitation affects their relative intensities. As regards the most persistent lines, at 3039 and 3256 A., and the limit of sensitivity (0·0001 mg. In), our results are in agreement with those of Papish and Holt (*loc. cit.*), who used essentially the same method, but differ from them with respect to the persistence of the lines at 4102 and 4511 A.

Spectrographic Analysis of Metallic Tin and Minerals.— Metallic tin. A spectrogram of the laboratory supply of granulated tin (taken on a copper arc) showed the lines at 4511, 4102, and 3256 quite clearly, and the sample gave a bright but not very persistent line at 4511 in the spectroscope. It was estimated spectrographically that the tin contained 0·01% of indium. The extraction of indium from this sample was used later to investigate the chemical behaviour of traces of indium in the presence of a large excess of tin, all separations being followed spectroscopically or spectrographically. Crude metal ingots and a specimen of A.R. tin, all of unknown geographical origin, were also examined, the former showing a doubtful trace of, and the latter no appreciable, indium. It is possible that Garrett's more sensitive method would have revealed faint traces, but as a rich source was being sought, no attempt was made to concentrate any indium that may have been present in these samples.

Cassiterites, etc. Six cassiterites from the East Pool and Agar Company's mines (Cornwall) were next examined, three showing traces of indium. One of these was a practically pure tinstone, with iron as the only other metal easily detectable; the second contained in addition to tin and iron, arsenic, manganese, tungsten, and a trace of niobium; and the third, in which the indium content was markedly lower, contained iron, manganese, aluminium, and a fair amount of copper. Of the three free from indium, two resembled the pure tinstone, and the third contained arsenic, aluminium, and iron. This indicated that there was no immediate connection between the presence of indium and other contaminating elements. A wolfram and a scheelite-wolfram from the same source were found to be indium-free.

An extremely pure cassiterite from the Roche Beam mine, Cornwall, also appeared to be free from indium (there was a doubtful line at 4511 only), but a sample of Cornish stream tin, which is geologically distinct from the tinstones, showed the lines at 4511, 4102, and 3256 A. more strongly than any of these had done. Three foreign cassiterites from Pahang (Malay), Bolivia, and Tasmania all showed small traces (0·01—0·001%) of indium, but in no case was there as much as in the stream tin. Two Nigerian samples of tin oxide minerals (Ilorin, pegmatite, and Jarava Hills, alluvial) contained traces of indium. The laboratory stannic oxide and A.R. stannous chloride were indium-free.

The oxide not proving a profitable source, attention was turned for reasons given above to tin sulphides and other minerals containing elements in the second long period, particularly silver and antimony. No greenockites were available, but as these do not occur in large masses, their omission was not serious. In addition, a number of iron, zinc, and manganese ores were examined, in most cases without revealing any indium.

Tin sulphide minerals. Cylindrite (Santa Cruz mine, Poopo, Bolivia), $Pb_6Sb_2Sn_6S_{21}$: iron and zinc also present. Indium : five persistent lines 3039—4511, all fairly strong for 10 mg. of solid; estimated content 0·1—1% In.

Franckeite (Santa Cruz mine), $Pb_5Sb_2Sn_2S_{12}$: iron also present. Indium : somewhat similar to cylindrite, but lines considerably fainter. Estimated max., 0·1% In.

Teallite (Poopo), $PbSnS_2$. Indium : trace; 3039 and 4102 faint (3256 doubtful).

Stannite (Cornwall), SnS_2,Cu_2S,FeS. Indium : very doubtful.

Antimony minerals. Bournonite (Liskeard, Cornwall), $2PbS,Cu_2S,Sb_2S_3$; jamesonite (Cornwall), $5(PbFe)S,3Sb_2S_3$; nagyagite (Transylvania), $(PbAu)_{16}Sb_3(S,Te)_{24}$; stibnite (Hungary), Sb_2S_3; and tetrahedrite (Hungary), $3Cu_2S,Sb_2S_3$. Indium : nil. See also cylindrite and franckeite (under " Tin ") and dyscrasite, polybasite, and pyrargyrite (under " Silver "). Laboratory samples of antimony and its trioxide and trisulphide were also free from indium.

Silver minerals. Argentite (Gersdorf, Saxony), Ag_2S. Indium : lines at 3039 and 3256 showing with original mineral. After separation of the silver as chloride, the filtrate showed clearly the lines at 4511, 4102, and 3259.

Hessite (Altai, Siberia) Ag_2Te; iron also present. Indium : a doubtful line at 4102 only.

Dyscrasite (Harz, Germany), Ag_3Sb. Indium : after separation of the silver, faint lines showed at 3039, 3256, and possibly 4102.

Argentite (Mexico); polybasite (Copiapo, Chile), $(Ag_2S,CuS)_9,Sb_2S_3,As_2S_3$; and pyrargyrite (Harz, Germany), $3Ag_2S,Sb_2S_3$; indium : nil.

Zinc minerals. Zincite (New Jersey), ZnO. Indium : the doublet at 3256—3259 was visible.

Calamine (two samples of unknown origin), $ZnCO_3$. Indium : one sample was free; the other showed very faint lines at 3256, 3259, and 4102.

Zinc blende (origin unknown), ZnS. Indium : 3039 faint, and 3256, 3259, and 4511(?) with decreasing intensity.

Franklinite (Bohemia), $(FeZnMn)(FeMn)_2O_4$. Indium : lines at 3039 and 4511. Manganese obscures the lines at 3256—3259.

Jeffersonite (New Jersey), $(CaMn)(MgFeZn)(SiO_3)_2$. Indium : very faint line at 3039; lines at 3256—3259, possibly manganese.

Zinc blende with blue fluorspar (Darley Dale, Derbyshire); wurtzite (Bohemia), ZnS; and zincite with franklinite (New Jersey). Indium : nil.

Manganese minerals. Alabandite (Austria), MnS; rhodocrosite (Colorado), $MnCO_3$; and wolfram (Schlaggenwald, Bohemia, and from Cornwall), $(Mn,Fe)WO_4$. Indium : nil. See also franklinite and jeffersonite (under " Zinc.").

Iron minerals. Pyrites (three samples : Cyprus; Goslar, Harz; Mexico), FeS_2. Indium : nil.

Chalcopyrite [(*a*) origin unknown; (*b*) and (*c*) Cornwall, unspecified; (*d*) New Cook's Kitchen Mine, Camborne, Cornwall], $Cu_2Fe_2S_4$. Indium : (*b*) and (*c*) nil; in (*a*) and (*d*) the persistent indium lines were intermediate in intensity between those shown by cylindrite and metallic tin. Estimated max. 0·1% In.

Mispickel (Munzig, Saxony), FeAsS. Indium : a doubtful line at 3039. A hæmatite (Fe_2O_3) and two chalybites ($FeCO_3$) were examined but gave spectra too rich in lines to allow the identification of indium without further separation.

Cadmium. A sample of metallic cadmium appeared to be indium-free, but very faint lines at 3256—3259 were given by a laboratory sample of cadmium oxide.

The results quoted above indicate that the occurrence of indium as a common impurity in metallic tin is due to a fairly general association of indium with tin ores, whereas its association with blendes, and with iron and manganese minerals, is more specific in character. A further investigation of silver ores is necessary before it is possible to say whether this association is general or not. At present it would appear that indium does not necessarily occur with silver or antimony as such, but in the argentiferous thiostannates from Bolivia which have been examined, a markedly high indium content is associated with those minerals which contain antimony as a main constituent.

Separations of indium from cylindrite, chalcopyrite, and metallic tin will be described in a subsequent paper.

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