

THE EXTRACTION OF TIN FROM ITS ORES AND
THE PREPARATION AND BEHAVIOR OF CERTAIN
PURE SALTS OF TIN.

by

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INTRODUCTION.

The existence of isotopes has explained a great many discrepancies in the theory of atomic structure. It has also definitely settled the validity of the whole number rule for the atomic weights of the elements. Hence any experimental work which will corroborate the existence of isotopes, will be of great importance in strengthening the proof of the atomic Theory.

F. W. Aston, by using the positive ray spectograph, and plates of increased sensitivity to positive rays, has found it possible to definitely prove that a group of eight lines, corresponding approximately to atomic weights of 116, 117, 118, 119, 120, 121, 122, 124, was due to Tin. It is extremely likely that these eight isotopes do exist in the case of tin, but as yet no direct chemical evidence has proven their existence.

One method of attacking this problem is to determine the atomic weight of tin in its different ores. Due to extremely different geological formation there may be wide variations in the concentration of the isotopes in these different ores. Such a variation might be detected by separate atomic weight determinations of the tin in the different samples.

This was the original problem attempted. However, the extraction of tin from its ores proved to constitute a problem in itself, and this thesis will deal largely with this part of the work, together with the preparation of pure tin from the material extracted.

Considerable work has been carried out towards evolving a convenient and generally applicable method of analysing tin ores. This search has brought forth many methods of disintegration and may be briefly reviewed under two headings:

- A. Reduction methods in which the oxide is reduced to metallic tin.
- B. Salification methods in which advantage is taken of the acid properties of stannic oxide in the formation of alkali stannates.

A. Reduction Methods:

Cornouailles first used carbon as a reducing agent for tin ores. The process has been studied by Levol and Moissenet,² but it is best described by Beringer.⁴ He also suggests the addition of a little powdered fluor spar to assist the fusion of refractory slags.³

The method of reduction in hydrogen or illuminating gas is due to Hampe,⁵ but has been described in some detail by Parry.⁶ Fawns⁷ considers it the most practical method of reduction.

Reduction with potassium cyanide has been used by assayists for some time. Parry⁶ and Bayerlein-Essen⁸ have outlined their methods of analysing tin ore with this reagent.

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G. M. Henderson has found that this method of fusion is out of the question for low grade ores. C. Boy¹⁰ ascribes this inefficiency for low grade ores to the presence of sulphur or silica, and modifies the procedure by first roasting to remove sulphur, and then boiling with hydrofluoric acid to remove silica.

B. Salification Methods:

Fusion with sodium carbonate and sulphur to form soluble sulpho-stannates, has been worked out by Golick¹¹ and Corti.¹²

J. Gray¹³ has found this to be an accurate method, but describes it as "dirty, tedious, and slow." This conclusion has been affirmed by S. Fawns who also adds that for this reason the method is never used.

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E. V. Pearce¹⁴ suggested the use of sodium hydroxide for the disintegration of tin ores and worked out a scheme of analysis based on this method of fusion. The present accepted method is a slight modification of Pearce's original procedure and is called the Pearce-Low¹⁵ method. R.J. Morgan¹⁶ also uses the alkali fusion method for dissolving tin ores and finds that consistent results are obtainable using this process. J. Gray has obtained accurate results for low grade ores with sodium hydroxide whereas potassium cyanide is entirely unreliable.

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G. M. Henderson used sodium peroxide instead of the hydroxide and found that the speed of the analysis was greatly increased. The peroxide was also discussed by J. Gray¹³ who claims its advantage over the hydroxide is only in special cases, as when chromite is present.

EXTRACTION OF TIN FROM ITS ORES.

1. Occurrence of Samples.

Tin occurs in Nature in three forms: (1) as Cassiterite or stannic oxide, (2) as stannite, the combined sulphides of Iron, Copper and Tin and (3) as native Tin.

By far the most abundant source of this element is Cassiterite and hence this mineral has been studied in some detail. Stannite occurs usually in much smaller quantities and often in small proportions along with the oxide. It is very seldom used as a source of Tin not only because of its rarity but also because of its low tin content. Hence it has not been studied in the same detail.

Hence in effecting the disintegration of the mineral, the methods already in use in connection with Cassiterite were tried, and similar ones in the case of the Stannite.

The sample of Cassiterite referred to was obtained from the Consolidated Mining and Smelting Company, from their Sullivan mine, at Kimberley, B. C. It had been concentrated from their tailings and was a fairly rich ore. A sample of Stannite was obtained from the Snowflake mine, situated twenty miles north of Revelstoke. It was taken from a quartz vein and was of low quality.

These two ores seemed to fulfill the conditions laid down above as to difference in conditions of formation.

2. The Disintegration of Cassiterite Sample.

The methods of treating Cassiterite are varied and have been discussed by H. Milou and R. Fouret,¹⁷ and J. Gray.¹³

The tin oxide may be reduced by carbon, hydrogen, illuminating gas, zinc or potassium cyanide. Of these carbon and cyanide were tried. The finely ground ore was well mixed with powdered charcoal and placed in a porcelain crucible well lined with the reducing agent. The dross was heated till redness and kept at this temperature for ten minutes. On cooling the reduced tin was found to exist in very small particles which had to be separated by sluicing.

The cyanide method was next tried and since the results obtained in this case were most satisfactory, the pursuit of a better method was discontinued. A 25 gram sample was well mixed with an equal quantity of Potassium Cyanide and placed in a 3 inch porcelain evaporating dish. On both top and bottom of the mix was placed a layer of pure cyanide. The crucible was heated, slowly at first and then more rapidly, until the whole mass had fused. The temperature was finally raised to a bright red heat and then the crucible and its contents were allowed to cool gradually. The whole operation required about thirty minutes. The melt was then leached out with water and the metallic tin button found on the bottom of the crucible.

It has been noted above that the Pearce Low method of fusion with Sodium Hydroxide gives the most accurate results, especially with low grade ores, and seems to be the best method

thus far suggested. While the cyanide fusion is not an accurate analytical method, it is relatively most effective in the separation of the tin from other constituents and for this reason was adopted.

3. The Disintegration of Stannite.

Very little study has been made of the disintegration of stannite ores. Accordingly those methods which are successful in fusing Cassiterite, were also tried with stannite with varied results.

A small sample of finely ground ore was boiled with aqua regia for sometime but was not attacked.

Potassium nitrate is a powerful oxidizing agent and is often used successfully for this purpose. In order to test out the method, fifteen grams of ore and an equal quantity of the nitrate were well mixed and placed in a fire clay crucible of two hundred c.c. capacity. An upper and lower layer of pure potassium nitrate was used and the crucible heated gently in a muffle furnace until fusion. The temperature was then raised and maintained at red heat for ten minutes longer. On cooling the charge was found to have changed somewhat in color and appearance, and had become extremely hard and brittle. It was found to be very difficult to remove by mechanical means, i.e., with hammer and chisel, and could not be dissolved by any of the ordinary acids or aqua regia. Therefore this attempt was considered unsuccessful.

The Cyanide fusion was used in a manner similar to that outlined above. When the cyanide was leached out with water in the customary manner, the finely divided ore came out as well, still in the form of a fine black powder. The ore had not been attacked. The duration of the heating period after fusing did not seem to assist the process of reduction.

It has been already noted that the sodium hydroxide fusion is the standard method of disintegrating and analysing Cassiterite. About thirty grams of broken Sodium Hydroxide was mixed with five grams of finely divided ore and the mixture fused for half an hour in a porcelain crucible. The melt was first softened with water and then with HCl. The ore did not dissolve even on boiling.

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J.H. Walton and H.A. Scholz found that many refractory substances could be easily decomposed by fusion with Sodium Peroxide. Their experiments included a Titanium Tin ore. This method as applied to Cassiterite has been highly ¹³ recommended by Gray.

In general, even where the sodium hydroxide fusion is successful, the peroxide has been found to produce a surer, safer, and more complete fusion, for not only is a better mix possible, but the combined effect of an oxidizing and salification agent is obtained.

Accordingly twenty-five grams of ore were well mixed with an equal quantity of Sodium Peroxide and the mixture transferred to a fire clay crucible. Ignition of the mix was obtained by heating gently in a muffle furnace for three

or four minutes. The molten mass was allowed to cool somewhat and was then poured carefully into about six litres of water. Violent ebullition took place at first, but soon subsided. The remainder of the melt was easily chipped from the crucible and added to the solution. This mixture still appeared partially undecomposed but on acidifying with HCl and warming, complete solution was obtained, yielding a clear yellow liquid. To remove silica this solution was evaporated until the large jelly which precipitated, became quite viscous. The mixture was then diluted, and the silica separated by decantation. The silica was then further extracted with dilute Hydrochloric acid until the solution obtained was no longer yellow.

This method of fusion has proven to be quite satisfactory for the disintegration of stannite ore. It is exceedingly rapid and requires only a relatively small amount of fusing material. Since the material is to be later purified, another important feature is to be noted. No foreign material which would be difficult to remove later on, is introduced.

4. Purification of Cassiterite Tin.

The metal is obtained from the cyanide fusion in the form of a shiny button. All the cyanide is first carefully dissolved out with water and the metal then dissolved by warming in HCl. The tin is precipitated from this solution as the sulphide by passing in hydrogen sulphide gas, iron and other group (3) metals remaining in solution. The

precipitate was filtered, washed, and dissolved by warming with ammonium polysulphide. When copper is present in large quantities, it is dissolved to a small extent by this reagent, but there was no indication of its presence in the sulphide as it appeared a bright yellow and perfectly homogeneous. The ammonium sulpho stannate was then filtered and the stannic sulphide reprecipitated by acidifying the filtrate with dilute hydrochloric acid. The large yellow precipitate obtained was washed free of acid and then treated in a beaker with conc. Nitric Acid. Small pieces of yellow amorphous sulphur were left undissolved even on warming. These were filtered off, washed and rejected, the wash water being added to the main solution. The solution of the tin in nitric acid was then evaporated almost to dryness, a clear transparent jel being obtained. This jel gave a fine white flocculent precipitate of metastannic acid when agitated with a large excess of water. Dilute nitric acid was added to increase the solubility of any impurities and the precipitate most conveniently filtered by decantation. Antimony forms a corresponding pentoxide which however is insoluble only after ignition. Hence this procedure should remove the last possible traces of any impurities.

To obtain the tin in a metallic form, the precipitate (H_2SnO_3) was dissolved in concentrated hydrochloric acid, diluted, and electrolysed. As Platinum is dissolved somewhat by nascent chlorine, it was necessary to substitute some other resistive material which is not attacked, for an anode.

Tantalum metal is not attacked by aqua regia or chlorine, hence would be quite useful for the purpose. A thin strip, one mm. in width and ten cm. long was obtained, and was substituted for the anode, and a fine platinum rod used as cathode. The tantalum however, on imposing an E.M.F., was found to take on an iridescent blue film of the oxide, which was quite impervious to the passage of the current. It is remarkable that the current was found to pass in the opposite direction with the tantalum serving as a cathode.

A spectroscopically pure carbon electrode, fifteen cm. long and one half cm. in diameter was obtained from Adam Hilger Ltd., and substituted for the anode. It was found to be very satisfactory and resisted the action of the chlorine quite well. The platinum rod was again used as cathode.

The tin deposited in shining leaflets which were collected daily and stored in distilled water. To obtain in a more compact form the crystals were placed in a porcelain boat and fused in a current of pure dry hydrogen. A shiny metallic button was obtained. This completed the purification.

The hydrogen for this purpose was prepared by the action of zinc on sulphuric acid and was purified by passing through a series of wash bottles containing concentrated alkali, and over hot copper gauze.

5. The Purification of Stannite Tin.

The percentage of tin in this ore is very much lower than in the Cassiterite. Hence the procedure had to be modified considerably, as certain separations used in the preparation of pure tin from Cassiterite can not be used where there is only a small quantity of tin, and much larger quantities of other elements.

From the hydrochloric acid solution of the ore, the tin was precipitated as the sulphide along with other group (2) metals, the most serious of these being antimony and copper. This precipitate was filtered off, washed, and then warmed with ammonium polysulphide. Instead of leaving the copper behind as expected, quite a large quantity of it passed into solution. This was indicated by the dark color of the sulphide precipitate obtained by acidifying the solution of ammonium sulpho-stannate with dilute hydrochloric acid. The process of dissolving in ammonium polysulphide and precipitating with hydrochloric acid was repeated, but there was still considerable copper present. Consequently the precipitate was dissolved by warming in dilute nitric acid, the sulphur residue filtered off, and the solution evaporated to dryness. On diluting and agitating the residue with water, a white flocculent precipitate of metastannic acid appeared. By evaporating to dryness, it was found that some of the antimony was rendered insoluble by being converted to the pentoxide. The evaporation had to be carried that far because of the small quantity of tin

present. However, by taking up the residue in dilute nitric acid, the copper and other metals form soluble nitrates, while the tin and antimony remain quite insoluble. The antimony was then separated by taking advantage of the fact that tin can not be precipitated in a solution of a certain acid concentration in which the antimony is readily precipitated. The insoluble residue obtained on evaporation with nitric acid was dissolved in concentrated hydrochloric acid, and the solution diluted with five times its volume of water. The antimony was precipitated by saturating the hot solution with hydrogen sulphide. The tin was then obtained as yellow stannic sulphide by almost neutralizing the filtrate with ammonium hydroxide, diluting, and saturating the cold solution with hydrogen sulphide.

II. THE STABILITY OF STANNIC OXIDE.

The atomic weight of tin has been determined by several investigators ¹⁹ by means of the ratio $\text{Sn}:\text{SnO}_2$; without exception the values obtained by them have been too low, due to absorption of air on so large a surface. In order to determine the accuracy of the method as a means of estimating tin, the temperature of drying and stability of the oxide to heat treatment was investigated.

A small button of C.P. tin, weighing approximately one gram was filed to remove surface oxide and etched with dilute hydrochloric acid. It was then washed with distilled

water, dried, and carefully weighed. The metal was converted to the oxide by warming in conc. nitric acid, the excess of acid being carefully evaporated when the metal no longer remained. The residue when dried at different temperatures gave the following results.

Original weight of Sn button: 0.9923 grams.

	Weight of SnO ₂	Atomic Weight Calculated.
After drying in the oven for two hours, at 150 degrees.	1.2743	116.6
After drying in the oven for twenty-four hours at 150 degrees.	1.2643	116.73
After heating with a blast lamp for half an hour	1.2632	117.21
After heating with a blast lamp for another half an hour.	1.2623	117.60
After heating with a blast lamp for another half an hour.	1.2619	117.78

It can thus be seen from these measurements that prolonged heating tends to decrease the amount of air absorbed, but it is doubtful whether a perfect removal of the absorbed gases can be attained.

III. THE DETERMINATION OF TIN AS CAESIUM CHLORO STANNATE.

Tin forms several complex chlorides with the alkali metals, of which the caesium chloro stannate is insoluble. As the original object of the investigation was to determine the atomic weight of tin in its different ores, the possibility of using the formation of this salt as a method was considered.

The method was investigated in the following manner.

Preparation of Stannic Chloride.

A small button of tin corresponding to about one gram was filed until all the surface layer had been removed. It was then etched in dilute hydrochloric acid and washed in distilled water. After drying and desiccating, the button was accurately weighed. It was then dissolved in a covered beaker in concentrated hydrochloric acid with gentle warming, and the stannous chloride oxidized by passing in chlorine, the temperature of the liquid being kept as low as possible by running water. Previous tests have shown that a corresponding quantity of tin can be oxidized in this manner in half an hour, so in the present case one hour was considered as sufficient.

Preparation of Caesium Chloride.

The caesium used for the purpose was obtained from Dr. E.H. Archibald in the form of caesium sulphate. It had originally been used for the determination of the atomic weight of caesium. To convert this material to caesium chloride the calculated weight of recrystallized barium chloride necessary was added to it. The precipitation was carried out in a total volume of two litres and both solutions were kept hot during the mixing. After stirring and digesting the precipitate for sometime, it was filtered off and the filtrate of caesium chloride evaporated to a small volume. To remove possible traces of sulphate, the caesium chloride was reprecipitated from the solution by saturating it with HCl gas. The crystals, after washing and drying were ready for use.

Method.

A slight excess of the calculated amount of caesium chloride was weighed up and dissolved in twenty-five c.c. of water and added a little at a time to the stannic chloride. The caesium chloro-stannate came down as a fine white precipitate. It was filtered off and washed with pure water in a tared Gooch crucible, which had been prepared with an asbestos mat. The crucible and its contents were then dried in an oven for several hours at 150°C , and weighed.

The first results calculated from the ratio $\text{Sn}:\text{Cs}_2\text{SnCl}_6$ gave a value for the atomic weight of tin which was much too high, indicating that the weight of the precipitate was correspondingly low. Moreover, on evaporating the filtrate and wash water a number of crystals settled out. As the filtrate should contain nothing but a slight concentration of caesium chloride, it was concluded that the low results could be attributed to the solubility of caesium chlorostannate.

Two more determinations were made taking greater precaution to decrease an error due to solubility and more accurate values were obtained. This justifies the assumption that the error is due at least in part to solubility.

As very little work has been done on this compound it was considered necessary to obtain more definite information on its solubility in various concentrations of hydrochloric acid and caesium chloride. Such information would enable us to state more definitely whether this method is suitable or

not for atomic weight determinations, and if so, the most suitable concentration for precipitation. Accordingly, this has constituted another phase of the investigation.

IV. THE DETERMINATION OF THE SOLUBILITY OF CAESIUM CHLOROSTANNATE.

Apparatus.

In order to agitate the solutions at a constant temperature until the equilibrium of saturation was obtained, a granite kettle of forty litres capacity was nearly filled with water and covered with a thick layer of felt to prevent radiation. The water was maintained at constant temperature by a tungsten lamp which was controlled by a thermostat and relay. The temperature remained within $.05^{\circ}$ of 20° with this apparatus. Pyrex test tubes of twenty-five c.c. capacity were used and rubber stoppers which had been previously boiled for several hours with ammonium hydroxide.

Method of Determination.

To the tubes were added twenty-five c.c. of solution, and somewhat more of the caesium chlorostannate than would dissolve in that particular concentration. The salt was prepared as in the determinations above. The rubber stoppers were then wired in and the tubes attached to the stirring apparatus and rotated for twenty-four hours.

In order to determine how much of the salt had dissolved, the test tube was placed in the bath so that the top just stood above the water. After the excess solid had settled to the bottom, the liquid was drawn up into the calibrated

pipette and two ten c.c. portions withdrawn. The tip of the pipette was prepared by tying a filter paper around it with a small piece of silk thread. In this manner the possibility of solid particles being drawn off was eliminated.

The twenty c.c. portions of liquid were carefully evaporated in small porcelain crucibles, and the amount dissolved taken as the weight of the residue obtained on evaporation.

The results as far as they have been carried at the present time are given in the following table.

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