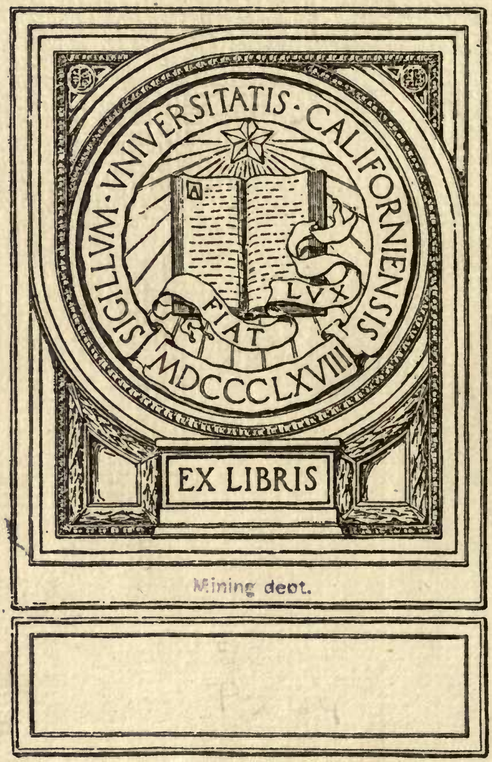
THE ASSAY OF TIN AND ANTIMONY

L. PARRY, A.R.S.M.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The Assay of Tin and Antimony.

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Introduction.

HAVING regard to the high price of the metal, it is a most remarkable fact that the methods usually described in text books, taught in school and classes, and in common use, for the separation and analytical determination of tin, are as a rule both unpractical and unreliable.

In commercial work it is, in general, of far greater importance to employ methods which can be relied upon to yield results accurate to within a quarter or a half per cent. in every case, and in a few hours at most, or in which the possibilities of error are definitely limited to a known minimum, rather than to spend three or four days in finicking with methods which are, properly speaking, only suitable for atomic weight determinations or other academic research, in order to obtain results which may possibly be exact to two or three decimal places and possibly inexact to the extent of 10 per cent. Gravimetric methods possess the single advantage over volumetric that one can weigh with greater precision than one can measure; the difference is absolutely immaterial in most cases, as far as buying and selling are concerned, and in every other respect volumetric methods are far more reliable and are much more rapid than gravimetric, involving fewer and less complicated separations; speaking generally, and having regard to differences in the *kind* of error involved in gravimetric as against volumetric assays, it is not going too far to say that in commercial work gravimetric assays should be avoided as far as possible—they leave too much to chance unless used with great discrimination. In an atomic weight determination one starts with pure chemicals, in assaying there are too many unknowns, involving too many assumptions, for *rapid* and *accurate* gravimetric work. It may as well be pointed out here that very few combining weights are known with certainty beyond the first decimal place, or nearer than 1 part in 1,000. In the majority of analytical methods greater accuracy than 1 part in 1,000 is a physical and chemical impossibility; in very many the limit may be put at 1 part in 500—indeed, a method of analysis which is properly systematised and capable of this degree of accuracy is a most excellent method, and, what is more, a *rara avis.* For instance, a really good method may enable us to report 50·1 per cent., or even 50·15 in very rare cases, in preference to 50·0 per cent. or 50·2 per cent.; but such a result as 50·12 per cent. is a scientific absurdity in the second decimal place.

if anyone doubts this let him study carefully Ostwald's "Foundations of Analytical Chemistry."

As regards tin, the commonest and most glaring source of error is undoubtedly the indiscriminate and unreasoning abuse of the estimation by weighing as Stannic Oxide (SnO_2). It is, or should be, perfectly well known to chemists that the usual methods employed in order to obtain tin as SnO_2 involve at the same time the contamination of the stannic oxide with SbO_2, As_2O_5, P_2O_5, Fe_2O_3, PbO, and even with SiO_2 and WO_3, and occasionally CuO, unless special methods are adopted which ensure the quantitative separation of these elements. The separation of tin for volumetric estimation is easy and certain; on the other hand, its separation for gravimetric estimation as SnO_2 is complicated, tedious, and unreliable. The result is that the presence of impurities in stannic oxide is very commonly ignored unless they are in *very* obvious quantities. Thus, it is usual to assume that solder is composed of tin and lead, whilst as a matter of fact nearly all the tinman's and plumber's solder which is made to-day contains from 1½ to 3 per cent. antimony; in consequence, determinations of tin in solder are very generally too high, either because the antimony is simply allowed to score fully as tin, or because an imperfect separation of tin and antimony is employed; moreover, such determinations are usually too high on account of the presence of PbO in the SnO_2, to the extent of about 1 per cent., as it is a common error to assume that treatment of solder with HNO_3 is a quantitative separation of tin from lead, or of tin and antimony from lead. When worked without a due appreciation of its limitations, there is probably not a more unreliable analytical method in common use than the gravimetric estimation of tin as SnO_2; yet in certain special cases it is undoubtedly useful. No wet method of assaying tin can be considered justifiable which does not exclude the interference of Sb, As, Fe, Pb, Cu, W, and Si, to mention the most usual sources of error, and weighing as SnO_2 does not permit of this with certainty. It is probably in consequence of the general use of this method that errors of 5, 10, and even 20 per cent. in tin and antimony assays (reported to two decimal places) are of common every-day occurrence.

Tin ores are very frequently sold on a dry assay basis. Any dry assay of tin is, however, rather misleading as a valuation basis unless it is combined with a wet assay for *Sn*, of the button of *metal* obtained in the crucible. Mere oxidation with HNO_3 and weighing the residue as SnO_2 will not do—common sense should teach that; it is necessary to use a method which will show the percentage of *Sn* and exclude the possibility of any possible impurity scoring as *Sn*. If this is done, the result obtained (as in any crucible *assay*) must of necessity be lower than the actual tin contents of the ore. If it is not done—if the metal button is simply weighed as tin, or if the percentage of *Sn* is determined negatively by assaying the button for one or two impurities, or positively by oxidation with HNO_3 and weighing the residue as SnO_2—the result will in many cases be too high. It is a common practice to report the percentage of tin in tin ore as so many per cent. "fine tin." The use of this term appears to be sanctioned by buyers and sellers alike, though it is scientifically an indefensible expression with a far too indefinite meaning. One man's idea of "fine tin" may include tin of 5 per cent. of impurities, while another man may think of "fine tin" as something containing 99¾ per cent. or over of the definite entity *Sn*, and altogether it is scarcely advisable to expect concordance of results between two assayers, one of whom reports the percentage of "fine tin," and the other the percentage of *Sn*. As regards tin ores, the only method of assay which would, in the opinion of the writer, receive the mutual assent of buyers and sellers, if they could be brought to see the technical points involved, would be reduction to metal in hydrogen combined with a volumetric or electrolytic determination of the tin. There can be no certainty about any method not involving complete solution of the ore.

The originator of the Ferric Chloride titration for estimating tin is unknown to the writer, who became acquainted with the process many years ago; at that time its application was rather limited, and the greater number of assay methods involving this titration, and described in Chapter V., as well as many important points about the titration itself, were elaborated in detail by the writer in conjunction with Mr. H. Hocking.

Chapter I.

Miscellaneous Facts bearing on the Assay of Tin and Antimony.

Sn = 119. Sb = 120. (O = 16.)

(1.) *OXIDES.*—Oxides of tin formed in the wet way are soluble in HCl. Oxides of antimony are much less easily soluble. The oxides of both metals are soluble in alkalies (soda and potash, not ammonia), and in alkaline sulphides.

SnO_2 obtained in the wet way by the action of HNO_3 on metals or sulphides is liable to hold Sb, As, P, as oxides, also PbO, Fe_2O_3, CuO, WO_3, SiO_2, and Bi_2O_3. Oxides of tin and antimony are almost insoluble in acids after ignition. Oxide of tin exhibits many modifications according to the method of preparation. Thus the rapid action of dilute HNO_3 on tin (with the aid of heat) yields a product different from that obtained by the slow action of dilute HNO_3 in the cold, which yields an unstable compound containing nitric acid. The action of HNO_3 on SnS_2, the addition of KOH to $SnCl_4$, the evaporation of $SnCl_2$, with excess of HNO_3, the cautious addition of HCl to solutions of alkaline stannates, and the addition of NH_4NO_3 or Na_2SO_4 to $SnCl_4$, all yield some form of stannic oxide. Insoluble stannic oxide results from the ignition of any of these products or by burning stannic sulphide or tin, in air or oxygen. The hydroxide precipitates obtained by adding AmOH or NaOH to solutions of $SnCl_2$ or $SnCl_4$ are soluble in excess of NaOH, and partly soluble in acetic acid, but are insoluble in AmOH. Soluble in tartaric acid. Stannic acid is slightly soluble in HNO_3, and therefore to ensure the complete separation of SnO_2 by HNO_3 it is sometimes necessary to evaporate to complete dryness, and is always safer. The dilute nitric acid extract from this will be quite free from tin.

Two acids derived from stannic oxide are generally recognised; ordinary stannic acid, H_2SnO_3, which can exchange all its hydrogen for metals, is formed by neutralising solutions of alkaline stannates with acids, and also by the addition of $CaCO_3$ to $SnCl_4$; metastannic acid, which results by oxidising tin with nitric acid, is $H_{10}Sn_5O_{15}$, 5 H_2O at ordinary temperatures and $H_{10}Sn_5O_{15}$ when dried at 100°C., and only one-fifth of its hydrogen is replaceable by metals. Both these substances are soluble in H_2SO_4 or in HCl. The H_2SO_4 solution contains stannic sulphate, and on dilution a hydroxide precipitate forms; on boiling the diluted solution, all the tin is said to be thrown down as metastannic acid. The HCl solution is not precipitated by dilution. Ignited and native stannic oxides are only partly acted on by strong H_2SO_4 or boiling alkalies, and cassiterite is not completely opened up even by fusion with potassium bisulphate. When oxides of tin and antimony are dissolved in fixed alkaline solutions, alkaline salts of the particular oxides are formed. When the oxides are dissolved in alkaline sulphides, mixtures of sulpho and oxy-salts are formed.

(2.) *SULPHIDES.*—Sulphides of tin, arsenic, antimony, are all soluble in alkalies and alkaline sulphides, from which solutions they are all precipitated by cautious addition of HCl.

Sulphide of arsenic is insoluble even in strong HCl and is completely precipitated by H_2S on standing, from a strong HCl solution of either As_2O_3 or As_2O_5. Sulphides of antimony are precipitated from fairly concentrated HCl solutions, but on boiling with strong HCl both dissolve with formation of $SbCl_3$.

SnS is an inconvenient form in which to precipitate tin, and stannic sulphide SnS_2 is precipitated completely only from fairly dilute solutions. These sulphides readily assume a colloidal form and pass into solution when washed with pure water; hence, when washing is necessary, they should always be washed with some salt solution (NaCl or NaĀc)—see Ostwald, "Foundations of Analytical Chemistry." Sulphide of tin (SnS_2) is not precipitated from solutions containing excess of oxalic acid whilst sulphides of As and Sb are precipitated under these circumstances. Sulphides of tin are readily soluble in HCl and are oxidised to SnO_2 by treatment with HNO_3.

(3.) *OXYCHLORIDES.*—Solutions of $BiCl_3$ and $SbCl_3$ in HCl are precipitated by dilution with water, the oxychlorides being formed; they redissolve on the addition of more HCl. A solution of $SnCl_4$ in HCl is not precipitated by dilution, but solutions of $SnCl_2$ readily absorb oxygen from the air, and in a neutral or only faintly acid solution a deposit of tin oxychloride forms; if the solution of $SnCl_2$ is freely acid with HCl no precipitate is formed, but the solution becomes converted into $SnCl_4$. A solution of $SbCl_5$ in HCl is precipitated by dilution with water, some form of antimonic acid (said to be probably orthoantimonic acid H_3SbO_4) being thrown down; the precipitate is only redissolved by HCl with difficulty, especially after standing some time. Oxychloride of tin which has been long precipitated is also difficult to dissolve in HCl. The presence of tartaric acid or of alkaline tartrates prevents the precipitation of oxychlorides of tin and antimony. A solution of $SbCl_3$ in HCl gives Sb_2O_3 with KOH, soluble in large excess, easily soluble in presence of tartaric acid, forming potassium antimonyl tartrate, which is tartar emetic $\left(\begin{smallmatrix}\mathrm{CHOH.\,CO.\,OK} \\ \mathrm{CHOH.CO.O(SbO)}\end{smallmatrix}\right)$. The use of organic acids in inorganic analyses is much too frequent, and is simply a fad with many chemists. Complications which are not always properly understood are very often introduced, and it is a safe rule to avoid the use of such compounds as much as possible—at any rate in commercial work.

(4.) *REDUCING ACTION OF STANNOUS OXIDE.*—An alkaline solution of SnO (in potash) reduces a solution of cupro-potassic tartrate with precipitation of Cu_2O. An alkaline solution of As_2O_3 acts in the same way, but no other metallic oxide. A solution of SnO in KOH also reduces $Bi(NO_3)_3$ with deposition of suboxide, according to Tilden. Further, such a solution appears to reduce itself, to use a rather loose expression, depositing tin and giving a solution of stannate.

SnO in either alkaline (bicarbonate) or acid (HCl) solution reduces a solution of iodine, forming a stannate or stannic chloride and HI.

$SnCl_2$ in HCl solution reduces $AsCl_3$ with precipitation of a brown deposit of arsenic containing 4 to 5 per cent. of Sn; reduces solutions of $AuCl_3$ and $PtCl_4$ to metals, solution of $HgCl_2$ to first Hg_2Cl_2 and then Hg; (in presence of KI, $SnCl_2$ does not reduce $HgCl_2$); reduces CrO_3 and Mn_2O_7 to Cr_2O_3 and MnO; reduces $SbCl_5$, $CuCl_2$, and $FeCl_3$ to $SbCl_3$, Cu_2Cl_2, and $FeCl_2$ respectively. Also reduces $BiCl_3$ to metal.

(5.) *ACTION OF $KMnO_4$ AND $K_2Cr_2O_7$.*—In acid solution oxidise Sb_2O_3, As_2O_3, SnO, FeO, Cu_2O.

(6.) *ACTION OF A SOLUTION OF $FeCl_3$ IN HCl.*—Liberates iodine from a solution of KI, converts Cu_2Cl_2 into $CuCl_2$, converts $SnCl_2$ into $SnCl_4$ and dissolves ppted Sb, As, and Cu, with formation of $SbCl_3$, $AsCl_3$, $CuCl_2$. Does not oxidise HCl solutions of Sb_2O_3 or As_2O_3, but on the other hand $FeCl_2$ reduces HCl solutions of Sb_2O_5 and As_2O_5 under some conditions. $FeCl_2$ does not reduce $HgCl_2$. $SbCl_5$—$FeCl_3$ $CuCl_2$ are in the order of reducibility by $SnCl_2$, which in a hot HCl solution containing all three of the above chlorides, reduces first the $SbCl_5$, then the $FeCl_3$, and lastly the $CuCl_2$. $FeCl_3$ does not under similar conditions oxidise HCl solutions of $SbCl_3$ or As_2O_3, but oxidises solutions of Cu_2Cl_2 or $SnCl_2$. $CuCl_2$ in such solutions does not oxidise $SbCl_3$ or $FeCl_2$, but oxidises $SnCl_2$. Cu_2Cl_2 reduces $SbCl_5$ before $FeCl_3$, and has very little, if any, action on HCl solutions of As_2O_5. In alkaline solution As_2O_3 reduces CuO as does SnO also. In acid solution As_2O_3 does not reduce CuO. A solution of $SbCl_3$ in HCl seems to be permanent, a solution of $FeCl_2$ or As_2O_3 gradually oxidises in the air, and solutions of Cu_2Cl_2 or $SnCl_2$ rapidly oxidise—we should expect from the above that $SnCl_2$ would be less stable than Cu_2Cl_2, but it is not; we should also expect that $FeCl_2$ would reduce $SbCl_5$ and As_2O_5, and to a certain extent and under some conditions this appears to be the case. KI reduces $SbCl_5$, $FeCl_3$, $CuCl_2$, and As_2O_5 in HCl solution, but not $SnCl_4$, whilst iodine oxidises Sb_2O_3, As_2O_3, SnO, in alkaline solution. The behaviour of arsenic in HCl solutions is very peculiar, depending much on the amount and concentration of the HCl present. $FeCl_3$ does not oxidise As_2O_3 in HCl solution, and excess of $FeCl_2$ reduces As_2O_5 in a strong (saturated) HCl solution (Fischer-Hufschmidt distillation process), so that the place of arsenic would appear to be before iron in order of reducibility. $SbCl_5$ is certainly more rapidly and completely reduced by KI in HCl solution than is As_2O_5, the reaction in the case of As_2O_5 only moving to completion as fast as the liberated iodine is removed, and being reversible unless the iodine is removed; further, HCl solutions of As_2O_3 (in which, by the way, the arsenic is supposed to exist as As_2O_3 unless the liquid is saturated with HCl, when it exists as $AsCl_3$) show a strong oxidation tendency, so that we should arrange the order of reducibility thus: $SbCl_5$—As_2O_5 (in HCl)—$FeCl_3$—$CuCl_2$—$SnCl_4$, and the order of permanency or stability of the lower chlorides would, of course, be $SbCl_3$—$AsCl_3$—$FeCl_2$—Cu_2Cl_2—$SnCl_2$. But, on the other hand, if a little $FeCl_3$ or $CuCl_2$ be added to a solution of arsenic acid in fairly strong HCl, and the solution titrated with $SnCl_2$, the $FeCl_3$ or $CuCl_2$ are at once reduced, and would therefore appear to be under these conditions more readily reduced than As_2O_5; it also follows that $FeCl_2$ does not reduce As_2O_5 under these conditions. Again, the reducing effect of $SnCl_2$ on HCl solutions of arsenic acid is very doubtful, and, further, As_2O_3 reduces even CuO in alkaline solution. From this we should arrange the order of reducibility thus: $SbCl_5$—$FeCl_3$—$CuCl_2$—As_2O_5—$SnCl_4$. SO_2 reduces Sb, As, Fe, from -ic to -ous in HCl solutions, but neither Cu (unless in presence of KCNS) nor Sn. As_2O_5 may be also reduced by PCl_3. Also, it would appear from the foregoing that if we have $SbCl_5$, As_2O_5, $CuCl_2$ in hot strong HCl solution and titrate with $SnCl_2$, the $SbCl_5$ is first reduced, then any trace of $FeCl_3$, then $CuCl_2$, at which point the solution becomes colourless; this suggests an obvious and very easy estimation of Sb in alloys containing Cu and As, when the Cu is known, the As making no difference. The strength of solutions of $SnCl_2$ may be checked with $FeCl_3$, $CuCl_2$, $K_2Cr_2O_7$, $KMnO_4$ or with iodine. Some of the foregoing reactions are applied in the "Weil" assays of Fahl Ores, described in "Sutton's Volumetric Analysis." These oxidising and reducing actions are extremely complicated, and for the elucidation of a satisfactory theory of them much investigation is needed, but the subject is well worthy of it.

(7.) *METALLIC PRECIPITATION.*—From HCl solutions of —ic chlorides.

Copper	precipitates	Hg, Ag, As, Sb, not Sn.
Iron	,,	Hg, Bi, Sb, Cu, and (in presence of $SnCl_4$) As, and reduces $FeCl_3$ and $SnCl_4$ to $FeCl_2$ and $SnCl_2$.
Tin	,,	As, Sb, Cu, Hg.
Lead	,,	Cu, Hg, Sb, Bi.
Aluminium	,,	Cu, Sb, and most of the common metals.
Zinc	,,	Sn, Sb, Cu, Pb, As, Cd, Hg.
Magnesium	,,	Fe, Zn, Co, and Ni, and most of the common metals.

Zinc evolves a considerable proportion of the As and Sb as hydrides, as does iron, though to a less extent, very little SbH_3 being formed with iron. Even magnesium does not appear to completely evolve As and Sb as hydrides, though Crookes states that it does.

(8.) *SOLUTION OF METALS.*—Arsenic, antimony, copper, bismuth, mercury, are insoluble in HCl either strong or dilute, hot or cold, when in a coherent form; from alloys a certain amount of As is evolved as AsH_3, and certain tin copper alloys are completely soluble in HCl giving a solution of $SnCl_2$ and Cu_2Cl_2; in presence of oxidising agents such as free Cl the above metals are all soluble. Finely divided Sb and Cu readily oxidise in contact with air and moisture, and the oxides are, of course, then readily dissolved by any HCl present, thus often giving rise to the appearance of solution of the metals themselves in HCl. The above metals are all soluble in aqua regia.

Tin, zinc, cobalt, nickel, iron, cadmium, aluminium, are readily soluble in strong HCl, and lead is also completely soluble, though slowly. When antimony is dissolved in HCl and $KClO_3$ it gives $SbCl_5$; when it is dissolved in HCl and iodine, $SbCl_3$ is formed.

Zinc, iron, cobalt, nickel, cadmium, readily dissolve in dilute H_2SO_4. Tin, copper, mercury, and finely divided arsenic and antimony are soluble in hot strong H_2SO_4, forming in the case of arsenic and antimony solutions of the lower oxides. Sulphides of As, Sb, Sn, are also soluble, forming in the case of Sb and As solutions of Sb_2O_3 and As_2O_3. In the case of Sn a solution of stannic sulphate is produced unless the metal is in excess.

Copper, lead, zinc, iron, cobalt, nickel, bismuth, mercury, cadmium, are dissolved by HNO_3 with formation of nitrates; tin and antimony (and in presence of tin) phosphorus and arsenic remain as insoluble oxides, though a little tin may go into solution if the liquid is not evaporated to dryness, and the residue is also liable to hold varying amounts of other metallic oxides, especially those of lead and iron. In absence of tin, arsenic and phosphorus go into solution as arsenic and phosphoric acids.

Aluminium is not easily soluble in H_2SO_4 or HNO_3.

(9.) *PRESENCE OF PHOSPHORUS AND ARSENIC IN TIN ASSAYS.*—When Sn^{Tv} and As^{v} or P^{v} in solution in HCl are treated with iron, the precipitate holds tin. In the case of As, the ppted metal holds 3 or 4 per cent. Sn. When Sn and As, or Sn and P, in any soluble form, or as metal or sulphide, are evaporated with HNO_3 insoluble $2\,SnO_2$, As_2O_5, and $2\,SnO_2P_2O_5$ are formed, soluble in strong HCl.

(10.) Arsenic acid is not reduced by HCl, as is sometimes asserted, at any rate not under ordinary circumstances, and HCl solutions of arsenic acid may be boiled freely without any loss of arsenic by volatilisation.

Ferric chloride does not convert precipitated Sb into $SbCl_5$, but into $SbCl_3$.

The low boiling point of $SnCl_4$ (114° C.) is no bar to the boiling or evaporation (unless carried very low) of HCl solutions of SnO_2—as experiment has shown that any such loss is entirely negligible under all ordinary circumstances, and the possibility of such loss can always be checked. Crookes states that when a Sn—Sb—As alloy is boiled with HCl the residue contains only Sb, that all the As is evolved as AsH_3, but the statement requires considerable qualification.

(11.) *PURITY OF CHEMICALS* used in the ensuing tin and antimony assays:—Sheet zinc must be absolutely free from tin, and must not contain more than small traces of arsenic or antimony.

Hydrochloric acid should be as concentrated as possible and free from As, HNO_3, or Cl.

Ferric chloride should be free from Cl, HNO_3, As, or $FeCl_2$.

Soda ash and caustic soda used for fusions should be free from chlorine.

Water used for diluting should be boiled and free from oxygen. Iron used should be either best piano wire or soft iron rod.

(12.) *METHODS OF SEPARATING TIN—ANTIMONY—ARSENIC* from one another.

Separation of Tin.

1.—In a moderately strong warm HCl solution, containing excess of oxalic acid (20 grms. oxalic acid for each grm. of tin) H_2S pptes. As and Sb,—Sn remains in solution. This method, which was devised by Mr. F. W. Clarke, is tedious and unsuitable for commercial work, though accurate. For Carnot's modification, using thio-sulphate as a precipitant, see "Crookes' Select Methods."

2.—Iron wire in an HCl solution of As, Sb, Sn, precipitates As and Sb as metals, though a certain amount of SbH_3 and AsH_3 are formed. The *arsenic* precipitated contains 3 or 4 per cent. Sn. Except where more than 10 per cent. of As is present, this is the best practical method of separating tin from arsenic and antimony.

3.—Strong boiling HCl dissolves tin and lead, but not arsenic or antimony. This is a good rough separation, provided not more than 5 per cent. As and Sb are present.

4.—Electrolytic separation (see "Classen").

5.—Fractional separation with H_2S. As is ppted in a concentrated HCl solution and Sb on slight dilution. Sn not ppted in a strong solution. (Doviton's Method ?)

6. Winkler's separation with $CaCO_3$ and KCN (see Menschutkn). Method unpractical and not suitable for commercial work.

7.—Fusion of oxides of As, Sb, Sn, with caustic soda. Stannate and arsenate soluble in water, antimonate insoluble. This is a thoroughly unpractical and unreliable method.

In practice, methods 2 and 3 are the most useful, methods 1 and 4 rarely.

Separation of Antimony and Arsenic.

N.B.—Antimony can be readily estimated in presence of tin.

1.—When an alloy or an arsenious compound is distilled with a solution of $FeCl_3$ and $CaCl_2$ in HCl, the arsenic is all evolved as $AsCl_3$ at a temperature of 125° C. By adding a solution of $ZnCl_2$ the antimony can then be all evolved as $SbCl_3$ at a temperature of about 190° C. (Gibbs' method). In distilling off arsenic there is no loss of $SnCl_4$.

(*a*) When a solution of arsenic acid saturated with HCl is distilled with $FeCl_2$ the arsenic is quantitatively evolved as $AsCl_3$ (Fischer-Hufschmidt process). By distilling with a mixture of $FeCl_3$ and $FeCl_2$ in concentrated HCl and $CaCl_2$ solution the whole of the arsenic may be obtained as $AsCl_3$, not only from alloys but from any arsenic compound. These distillation separations are chiefly used in the assay of arsenic.

(*b*) Arsenic may also be separated from HCl solutions with metallic copper, and the copper-arsenic then distilled with ferric-chloride mixture.

2.—HCl dissolves sulphides of antimony and tin on boiling, whilst sulphide of arsenic is left undissolved. An imperfect method, though very convenient sometimes.

3.—As_2S_3 is completely precipitable by H_2S in a strong HCl solution, leaving Sb and Sn in solution. This is a good and useful method in special cases. (Rose's method.)

4.—By addition of magnesia mixture to an ammoniacal tartarate solution of Sn, Sb, As (ic), the As is precipitated as Mg, NH_4, AsO_4. It may also be precipitated from an alkaline sulphide solution, with MgO mixture.

5.—Sulphide of arsenic is soluble in Am_2CO_3 solution. Sulphides of tin and antimony are insoluble. A rough practical method, though imperfect.

6.—The gallic acid separation of antimony is unsuitable for commercial work except in special cases, but is a good method.

7.—Electrolytic separation (see "Classen").

8.—Strong H_2SO_4 dissolves As, Sb, Sn—the Sb compound separates on cooling.

9.—$KHSO_3$ dissolves freshly precipitated As_2S_3 or As_2S_5. Sulphides of Sn and Sb are not dissolved. Method is unpractical.

10.—AsH_3 and SbH_3 when passed into $AgNO_3$ act differently. AsH_3 forms H_3AsO_3, and Ag is precipitated. SbH_3 gives a deposit of $SbAg_3$. (Houzeau's method.) This reaction is of doubtful value except as a qualitative test, as it is seldom possible to depend upon the quantitative evolution of arsenic and antimony as hydrides.

In practice, the first four are the most useful methods.

We might add here that most of the text-book methods of separating arsenic are quite useless in presence of tin, as they usually involve solution of the arsenic in HNO_3, which is impossible from a tin arsenic mixture.

Chapter II.

The Assay of Tin.

SUMMARY OF SEPARATIONS.

When necessary, tin is best separated from accompanying elements as follows:—

1.—From Chlorine—
  (*a*) Evaporation with excess of HNO_3.
  (*b*) Boiling with Na_2CO_3.

2.—From Sulphur—
  (*a*) Evaporation with HNO_3 (tin ore).
  (*b*) Solution in aqua regia.

3.—From Tungsten—
  (*a*) Reduction of HCl solution with iron.
  (*b*) Solution of unignited WO_3 in Am_2CO_3 or AmOH.

4.—From Antimony, Copper, Bismuth—
  (*a*) Boiling the metals with HCl (rough).
  (*b*) Reduction of HCl solution with iron.

5.—From Cobalt, Nickel, Iron, Phosphorus—
  By pption with H_2S in dilute HCl solution.

6.—From Arsenic—
  (*a*) Iron wire in HCl solution.
  (*b*) H_2S in HCl—oxalic solution.

(*c*) H_2S in strong HCl solution.
(*d*) MgO in tartaric solution.
(*e*) Distillation of metals with $FeCl_3$.

7.—From Lead, Zinc—
No need to separate for volumetric assay, but Sn and Pb are best separated by alkaline sulphide pption, and Sn and Zn by HNO_3 in cases where it is necessary to estimate Pb or Zn.

8.—From Silica—
By evaporation with HF.

9.—From PbO, Fe_2O_3, CuO—
Stannic oxide may be roughly separated by evaporation to dryness with nitric acid and extraction with dilute nitric. All the SnO_2 is in the residue, but is very impure.

SUMMARY OF CHIEF METHODS OF DETERMINATION.

1. Dry Assays—
   (*a*) Ferrocyanide assay.
   (*b*) Cyanide assay.
   (*c*) Carbon reduction assay in carbon-lined crucibles.

2.—Gravimetric determination as SnO_2.

3.—Gravimetric assay by electrolysis.

4.—Volumetric assay by titration of $SnCl_2$ with ferric chloride.

5.—Volumetric assay by titration of $SnCl_2$ with iodine in acid solution.

6 and 7.—Volumetric assay by titration of $SnCl_2$ with $KMnO_4$ or $K_2Cr_2O_7$, with or without addition of $FeCl_3$.

8.—Titration with iodine in alkaline solution.

9.—Solution of metallic tin in $FeCl_3$ and titration with $KMnO_4$ or $K_2Cr_2O_7$.

10.—Titration of stannic chloride with ferrocyanide.

The dry assay should, of course, in every case be combined with a wet assay of the button of metal obtained, otherwise it is not an assay at all, but a mere guess of a somewhat greater degree of approximation than a vanner's test for "black tin." Ia is a safe buyer's assay for tin ashes and tin slags, is quick, convenient, and fairly reliable within certain limits. In some cases Ib is more accurate for tin ashes—*e.g.*, in the case of irony tin dross. Ib and Ic are fairly good assays for tin ore if the button is assayed for tin by a volumetric method. The dry assay of tin ore is rapid, and the results are fairly consistent, but of course always rather lower than the actual percentages of tin present. If the buttons are *not* assayed for tin, the results are quite unreliable, and generally too high.

Method No. 2, though occasionally useful, is a thoroughly unreliable method for general use, for reasons given in the introduction. Method No. 3 is accurate, but tedious, and more suitable for a clean, quiet research laboratory than for ordinary use in commercial work. Method No. 4 is at once the most accurate and practical method of estimating tin, involving in general only one filtration, and that from a slight precipitate, or in some cases two filtrations, is rapid and for large numbers of assays is cheap and convenient. Its accuracy is inherent, and is probably almost absolute when the assay is worked under proper conditions, the titration figures being strictly proportional to the amounts of Sn present.

Method No. 5 is a very good one, but it is unreliable to the extent that an assumption not justifiable *a priori* has to be made, and it is one that is not readily capable of direct verification—viz., that all the tin tetra-chloride in every assay is reduced to stannous chloride by 20 to 30 minutes' reduction with iron in warm dilute HCl solution. It is a most elegant method requiring but little apparatus and few chemicals and no filtrations, is rapid and in practice it is found to yield results which as a rule agree closely with those got by ferric chloride assay, though it does not possess the inherent accuracy of that method.

Methods 6 and 7 are workably accurate but not as convenient as the two previous methods, though titration with $KMnO_4$ is useful for checking the working strength of standard solutions of stannous chloride.

Methods 8, 9, and 10 are not to be recommended in practice.

General Summary of Wet Assay of Tin.

Tin occurs as (*a*) metal, (*b*) sulphide or arsenide, (*c*) soluble oxide or soluble salts, (*d*) silicate, (*e*) insoluble oxide.

Solution can always be effected as follows :—

(*a*) Removal of combined silica by evaporation with hydrofluoric acid (seldom necessary except with slags).

(*b*) Treatment of residue by boiling with HCl and HNO_3. All the tin not present as insoluble oxide is then obtained in solution as stannic chloride.

(*c*) Reduction of the residue of stannic oxide to metal, in a stream of hydrogen or coal gas, at a low red heat.

(*d*) Solution of reduced metal in HCl and HNO_3.

(*e*) Fusion of any slight siliceous residue with $KNaCO_3$ or soda ash, and borax, in a platinum crucible, and solution of the melt in HCl.

The method of effecting solution of insoluble tin oxide by fusion with caustic alkalies or caustics, alkalies and sulphur in porcelain vessels is a dirty, tedious, and unreliable method.

SEPARATION.

1.—As, Sb, Cu, W are separated by heating the acid solution with iron, when As, Sb, Cu are precipitated in the metallic form and tungsten as blue oxide.

2.—When it is desired to separate tin from Fe, P, Co, and Ni, precipitate with H_2S in dilute HCl solution. The sulphides of Sn, As, Sb, Cu are redissolved in HCl and $KClO_3$, and the As, Sb, Cu separated with iron.

ESTIMATION.

(a) For titration with ferric chloride the filtrate from the iron reduction is precipitated with strip zinc, the precipitated tin and lead and undissolved zinc are dissolved in pure HCl, and the solution containing the tin as $SnCl_2$ is titrated at the boiling point with ferric chloride.

(b) For titration with iodine, the solution is not filtered from the iron deposit, but is cooled, the iron rod withdrawn, and the solution containing the tin as $SnCl_2$ titrated in the cold with iodine, using starch paste as indicator.

Chapter III.

The Dry Tin Assay.

A.—TIN ASHES AND SOLDER ASHES.

The fire assay gives low results with ashes which contain chlorine, grease, sulphur, or zinc, or much lime, slag, or fine carbonaceous matter.

The general method is to fuse.

50—100 grms. ashes with 5—30 per cent. potassium ferrocyanide,
10—20 per cent. soda ash,
5—10 per cent. borax.

in a G Cornish crucible, adding a little fluor and white arsenic if necessary. A high temperature is necessary, and the best fuel is gas *carbon*. When the fusion is complete the assay is allowed to cool in the crucible, which is broken up when cold. The button of metal usually consists of a soft or non-irony portion and of a hard or irony portion It is weighed, and the soft portion is melted away in a hand ladle and poured into a small hemispherical mould; the iron button is weighed and the weight of the soft portion calculated by difference. Both portions are assayed for tin by the direct ferric chloride assay (see Wet Assay of Tin, Chapter V., A.), the iron portion being pounded in a mortar and the non-irony portion broken in two and filed across the centre. As a rule the soft portion holds about twice the percentage of tin that the iron holds, but if the iron button is very arsenical, it is always very poor in tin, and if only small in amount may be sometimes neglected altogether.

Speaking generally, the iron portion is an iron—tin—antimony—arsenic alloy, while the soft metal is a lead—tin—copper—antimony alloy, which, however, may contain 10 to 20 per cent. Fe in the absence of lead. If lead is present in any quantity the soft portion is as a rule free from iron. If sulphur is present a matte-speise may be formed as well as a soft portion. In ashes containing chlorine, sulphur, zinc, there is usually considerable loss of tin by volatilisation. If thought desirable, chlorine may be removed by boiling the ashes with carbonate of soda, and the effect of sulphur removed by evaporation with dilute HNO_3 previous to the fusion in the crucible. The poorer the ashes and the greater the amount of lime and silica they contain, the greater the loss of tin in the slag. Very carbonaceous ashes also give low results, and if free from zinc and chlorine may with advantage be calcined previous to reduction. The best results are obtained from ashes which are mainly composed of metal and metallic oxides. Ashes which are practically pure oxide of tin, and irony tin dross containing S and As may be with advantage assayed by the cyanide method as in the case of tin ores.

This combination of fusion with ferrocyanide and direct ferric chloride assay of the button is at best a rough method, though it is a safe buyer's assay; the result will always average 1 or 2 per cent. lower than a complete wet assay both on account of loss by volatilisation and in slag, and to a slight extent on account of the rough nature of the separation of the tin from Sb, As, Cu, adopted in the wet assay of such buttons. It is a purely commercial matter, whether in any particular instance it is worth while to adopt a complete wet assay of the ashes in place of the dry assay, depending mainly on the size of the lot. It is certainly not worth while from any buyer's point of view to adopt a complete wet assay for a lot of two or three hundredweight of solder ashes. In ashes poor in lead the iron button, being the heavier, is the bottom portion; but if the ashes are leady the iron button is lighter and is found above the soft. The irony portion does not, as a rule, contain copper unless much arsenic or sulphur, or much copper, is present. Copper gives a white crystalline fracture to the buttons from tin ashes, easily recognisable after a little experience. Antimony gives a white lustrous, crystalline fracture in rich tin buttons rather different in appearance from the copper fracture. Zinc gives a bluish crystalline fracture to the metal, and a bluish flame during the progress of the assay. Arsenic gives a graphitic-looking fracture to solder buttons. In the absence of Cu and Sb. the fracture of a rich tin button is dull grey and holocrystalline.

B.—TIN SLAGS.

50 grms. slag.	5 grms. white arsenic.
30 grms. ferrocyanide.	5 grms. fluor.

5 grms. soda ash.

Mix, transfer to a G crucible, add a little borax, and fuse in the hottest fire possible. When in a state of tranquil fusion, remove from the fire and allow to cool in the crucible. When cold, break the crucible, knock off the slag, weigh the button of iron—tin—arsenic alloy and assay for tin. This is an excellent comparative method for works purposes, but the results are of course low, as it is quite impossible to reduce all the tin to metal.

C.—TIN ORE.

The dry assay of tin ore is only to be recommended for works purposes, mines, or for prospectors. It is not accurate enough for buying and selling on equitable terms, having regard to the amount of money hanging on a single assay and the increasing keenness of competition.

THE CYANIDE ASSAY is of the most general applicability, but (*a*) where the ore is poor and contains much Fe_2O_3 it should be digested with strong HCl provided the tin is present as cassiterite. (*b*) If much pyrites is present it should be evaporated to dryness with HNO_3 before extraction with HCl. These operations may be conveniently performed in a 6-in. evaporating basin with a clock glass cover. Oxide of lead, if occurring in tin ore, is very difficult to extract completely even with strong hot HCl, whilst HNO_3 often removes only half of it. Take 20 grms. dried ore, 20 c.c. of strong HNO_3, and about the same amount of water, and evaporate cautiously to complete dryness. Add 100 c.c. strong HCl and digest for half-an-hour just below the boiling point. Dilute with an equal bulk of water, filter and wash by decantation until the washings are free from HCl. Ignite the filter paper and add the ash to the cleaned residue of ore in the dish. The HCl extract will *usually* contain *most* of the iron, arsenic, antimony, &c., and will in general be free from tin, but should always be tested or assayed for tin (see Wet Assay). It is *never* safe to assume that the cleaned residue is free from metallic oxides other than SnO_2, though the assumption is frequently made. Dry the cleaned ore and mix it with an equal weight of cyanide (98 per cent. Au—not commercial cyanide). Take a small dry crucible and charge in 10 grms. cyanide, then the above mixture, and finally 10 grms. cyanide as a cover. Place in a fire at a low red heat and fuse gradually, increasing the heat to bright redness at the finish of the fusion, which should not take more than ten minutes. Allow the assay to become quite cold in the crucible, and when cold break out the button and either remelt it by dropping it into a crucible containing melted borax, or under palm oil in a ladle, or cut it in two and boil out the adhering cyanide with water. The button should in every case be assayed by a *wet* method for *tin*, otherwise the result is a mere guess and may be very misleading, no matter how much the ore has been cleaned, or however pure the ore is supposed to be, or however clean the metal appears to the eye. The use of the term "fine tin" has been already referred to in the introduction, and it is only necessary to add here that Sn is a definite entity, while "fine tin" is an expression which awaits definition. Further, it is quite as bad to assay such a button by oxidation with HNO_3 and weighing the oxide residue as SnO_2—that would be merely making the same unjustifiable assumptions (in another form) as to absence of certain impurities, which are involved by weighing the prill as *tin*. The button must be assayed positively for tin by a method which shall ensure the elimination of the interference of every possible impurity, and that, in practice, means assaying the button for tin by a volumetric method. Of course, if this procedure is systematically followed (and any other is illogical as an assay, and so uncertain as a valuation basis as to be inexcusable on account of the high price of tin), the results will always favour the buyer. The remedy is, not to attempt to counteract this "low" tendency, which is inherent in any dry assay, by balancing an unknown "high tendency" (impurities) against it (the net result of which is, in practice, to favour the seller), but to use a wet assay throughout.

Of other dry methods of assaying tin ore, the Cornish tin assay is no doubt useful on mines as a comparative test, where the quality of the ore remains fairly uniform, whilst the vanning test is also most useful to prospectors and on mines.

The German assay of tin ore by mixing with oxide of copper and fusion for white metal, does not appear to possess any advantages over the cyanide assay as regards accuracy, and is an exceedingly complicated method.

The method of fusing tin ore with Na_2CO_3 and borax in a luted carbon lined crucible, in the muffle, is said to give very perfect reduction of the tin.

Hallet's method—fusion with KHF_2, solution in H_2SO_4 and precipitation of the tin as metastannic acid on dilution and boiling—seems to be a good assay, but is in reality a wet method.

Chapter IV.

The Wet Assay of Tin.

GRAVIMETRIC ASSAY BY WEIGHING AS SnO_2.

Bi, Pb, As, Sb, Fe, W, Si, should be absent.

The tin from 1 grm. of material, separated either as metal or sulphide, is treated with 20 c.c. of dilute HNO_3 (1 : 1) in an evaporating dish, and evaporated almost to dryness. It is diluted with

50 c.c. hot water and boiled, then filtered, the residue well washed with hot water, dried, and ignited in the muffle in a small porcelain dish. When cold, weigh the SnO_2. It contains 78.7 per cent. Sn.

The tin in bronze coins and tin copper alloys free from Sb, Pb, As, may be estimated this way, but its application to solder, metal from crucible assays of tin ore, and the sulphide precipitate from tin slags is inaccurate.

If solder is treated in the above manner the residue consists of SnO_2 and SbO_2 and some PbO. Multiply the weight of residue from 1 grm. of solder by 78.7, and the result, less 1 per cent. deduction for lead, may be taken as the sum of the percentages of tin and antimony in the solder.

GRAVIMETRIC ASSAY BY ELECTROLYSIS.

This assay is fully described in Classen's "Chemical Analysis by Electrolysis."

VOLUMETRIC ESTIMATION WITH FERRIC CHLORIDE.

When ferric chloride is added to a strong hot HCl solution of stannous chloride it is immediately reduced to ferrous chloride, and stannic chloride is formed at the same time. *One drop* in excess of the ferric chloride gives a decided yellow colour to the previously colourless solution, provided the solution is hot and strongly acid. The nearer the boiling point and the greater the concentration of HCl in the solution the more rapid is the completion of the reaction. A solution of $FeCl_3$ in dilute HCl, of which 100 c.c. = 2 grms. Sn, is employed. In the assay the addition of $FeCl_3$ from the burette cools the solution somewhat, so that the finish is rather slower than the commencement of the reaction, both owing to dilution and consequent lowering of the temperature, and to the presence, in increasing concentration, of ferrous chloride in the solution, but in any case the titration should never take more than a minute, if worked as directed. $FeCl_3$ gives a far stronger colouration in a hot, strongly acid solution than in a cold, faintly acid solution. The titrations cannot be done by gas light or electric light, and should always be effected in the daytime. In an emergency they may be done by magnesium light.

The equation representing the chemical change is $2\ FeCl_3 + SnCl_2 = 2\ FeCl_2 + SnCl_4$. The presence of chlorides of lead, zinc, aluminium, iron (ous), cobalt, nickel, antimony (ous), copper (ous), cadmium, does not affect the quantity of $FeCl_3$ required; the presence of $FeCl_2$ in quantity somewhat retards the finish and lessens the delicacy of the colour indication; Cu_2Cl_2 reduces $FeCl_3$ with formation of $CuCl_2$, but $SnCl_2$ reduces $CuCl_2$, and the net result of this is that not a trace of $CuCl_2$ is formed until all the $SnCl_2$ is converted into $SnCl_4$—the next drop of $FeCl_3$ forms a trace of $CuCl_2$, which gives a similar colour indication to that of $FeCl_3$ itself; $CoCl_2$ and $NiCl_2$ give highly coloured solutions which render the recognition of the end point difficult—one way of remedying this is to dilute the solution somewhat, with boiling water, which removes the blue colour, but of course renders the reaction slower and lessens the colour intensity of the drop or two excess of $FeCl_3$; $SbCl_3$ is not converted into $SbCl_5$ by $FeCl_3$, and under the conditions of the assay neither $SbCl_3$ nor $SbCl_5$ ever occur in the solution; Cu_2Cl_2, $CoCl_2$, $NiCl_2$ are rarely present, also $CdCl_2$ and Al_2Cl_6; $FeCl_2$ is often present to begin with, and $ZnCl_2$ and $PbCl_2$ are generally present in greater or less amounts. $BiCl_3$ and $HgCl_2$ are reduced to metal by $SnCl_2$, but Bi and Hg would be separated with iron. Precipitated Sb, Cu, As, are attacked by hot acid ferric chloride and blue oxide of tungsten is affected by it, but the assay method excludes the presence of these substances during titration. Acid solutions of $SnCl_2$ very readily oxidise by exposure to air; the method of dissolving the tin from the state of metal by boiling with HCl in an atmosphere free from oxygen excludes the formation of $SnCl_4$, if the operation is carried out as subsequently directed, and if the solutions are titrated as soon as ready and at the boiling point the oxidation tendencies are completely eliminated. Briefly, the best conditions are: (1) Solution from the state of metal as rapidly as possible in a non-oxidising atmosphere, the solution being brought to the boiling point before the solution is complete. (2) Use of strongest and purest HCl. (3) Bulk 150—250 c.c. (4) Titration rapid and at the B. Pt. (5) Strength of $FeCl_3$ 100 c.c. = 2 grms. (6) Absence of precipitated Sb, As, Cu in the solution.

From the dilute peroxidised HCl solution of Sn, Sb, Hg, Bi, As, Cu, Pb, Cd, Zn, Co, Ni, Fe, P, the Sn, Sb, As, Cu, Hg, Bi, and some Pb and Cd are separated as sulphide by H_2S if it is desired to separate from Co, Ni, Fe, P. The sulphide precipitate is redissolved in HCl and $KClO_3$, and the solution reduced by heating with iron wire. The As, Sb, Cu, Hg, Bi are precipitated in the metallic form, and the solution (which must be strongly acid to avoid precipitation of $SnOCl_2$) is filtered and neutralised with thin strips of zinc. The action finished, the mother liquor, after testing for tin with H_2S water, is poured off as completely as possible, and the residue of spongy metallic tin and lead and undissolved zinc, is dissolved in the same flask in about 200 c.c. of pure HCl, the flask being provided with a rubber cork and leading tube, and the liquid is brought to a boil as rapidly as possible; a piece of pure zinc about the size of a pea is added to assist in preserving a non-oxidising atmosphere of hydrogen and hydrochloric acid in a flask until the liquid clears and boils. As soon as everything is in solution and the liquid is boiling, the flask is removed from sandbath or plate and titrated immediately with ferric chloride. The ferric chloride should be free from ferrous chloride, nitric acid, chlorine and arsenic, and the solution should contain 300—500 c.c. HCl in two litres. It is best made up from a concentrated stock solution in HCl, made by dissolving piano wire as directed subsequently. If the assays turn dark greenish after titration the $FeCl_3$ solution is contaminated with HNO_3. The $FeCl_3$ may be made up also by dissolving 180 grms. of the yellow commercial lump salt, which is Fe_2Cl_6 12 H_2O, in about 200 c.c. HCl and evaporating it to dryness. The residue is dissolved in 300 c.c. HCl and diluted to two litres. The solution is standardised against 1 grm. of the purest tin obtainable, filed with a fine file. This is weighed into an 8 oz. flask, and the flask is about three parts filled with pure HCl, rubber cork, and leading tube inserted, and boiled (but not too rapidly) until solution is complete; then titrated at once.

Pure tin is more readily obtained from smelters of tin ore than from dealers in chemicals—the writer once ordered some "pure tin for standardising purposes" from a firm of wholesale chemists and received metal holding 3 per cent. Sb.

It is rarely necessary to complicate the assay by separating the tin as sulphide—having once got everything in solution, reduce with iron wire, filter, and precipitate on zinc. This method has been repeatedly checked on made up metals of known composition containing varying amounts of Sn, Pb, Cu, Sb, and the results are in every case so close as to leave no doubt whatever that the method is extremely accurate; indeed, it is much more accurate than the electrolytic assay on account of the complicated separations which the latter involves, and is incomparably quicker.

The favourite objection to the ferric chloride assay is the oxidation tendency of solutions of $SnCl_2$—the method if properly worked overcomes this completely. It has also been objected that five or six drops of ferric chloride solution are necessary to give a perceptible colour indication. This is quite incorrect—one drop in excess of $FeCl_3$ is ample if the operator possesses normal colour vision. It is also stated that Sb dissolves in HCl—this is not the case. It is true that finely divided Sb in contact with air and HCl slowly dissolves, but even then, $FeCl_3$ does not oxidise $SbCl_3$, and, further, under the conditions of the assay the absence of Sb is ensured by the iron wire separation. In direct ferric chloride assays on solutions from metal filings, the assays so far from being too high through Sb dissolving, are too low because of Sn retained with the black powder (Chapter V., A.), and it should also be remembered that metallic tin precipitates antimony from solution.

VOLUMETRIC ESTIMATION WITH IODINE IN ACID SOLUTION.

The dilute acid solution of metallic chlorides, which should not be more than about 50 c.c. in bulk, and should be contained in a 4-inch beaker, is reducted by heating with a clean piece of iron rod resting in the solution against the side of the beaker, which is covered by a watch glass. The whole is heated to 80° or 90° C. (not to boiling) over a Bunsen flame; five or six assays may be conveniently heated in a small frying-pan sandbath. The assays are heated for 20—30 minutes after they have lost their original red, yellow, or greenish colour. The Sb, As, Cu, are precipitated, and the $SnCl_4$ is assumed to be reduced to $SnCl_2$; in practice this assumption is found to be justified, though it is really one of the weak points of the assay. The assays are cooled in a basin of cold water, and when cold the watch glass and rod are rapidly washed with a little cold boiled water, starch paste added, and the solution titrated rapidly with iodine. It is not necessary to remove the black precipitate of Sb, As, Cu, as the finishing point in the case of $SnCl_2$ and iodine is so sharp; but the finely-divided metallic precipitate sometimes seems to *slowly* remove the blue colour. The iodine solution is made up by dissolving 21.32 grms. iodine and 45 grms. pure KI in about an inch of water in a small beaker and diluting to one litre. 100 c.c. = 1 grm. Sn. Not more than .5 grm. Sn should be present in the assay. It has been proposed to increase the accuracy of this assay by titrating in an atmosphere of CO_2.

Mr. A. H. Low states ("Technical Methods of Ore Analysis," 2nd Edition, page 185) that copper and iron in contact precipitate tin. He does not, however, state the conditions which obtained when he made the observation, and the writer wishes to emphasise the fact that in a freely acid (HCl) solution (a *sine quâ non* in tin assays), no such precipitation of tin ever takes place.

Titanium and tungsten both interfere with the ferric chloride and tungsten with the iodine titrations for tin, as titanium sesquichloride, Ti_2Cl_6, and the blue oxide of tungsten, WO_2, are peroxidised in HCl solution by ferric chloride, and WO_2 by iodine. Titanium sesquichloride is not affected by iodine, and titanium does not interfere with the iodine titration. Hence Ti and W, if present, must be separated for the $FeCl_3$ assay, and W must be separated for the iodine assay. WO_2 is precipitated with antimony by iron, and Ti_2Cl_6 remains in solution when tin is precipitated on zinc provided the liquid is distinctly acid with HCl when poured off from the precipitated tin. Uranium does not interfere with either iodine or ferric chloride assays. Uranic salts in HCl solution are reduced by iron, but uranous chloride is not oxidised by iodine. Uranous chloride which makes boiling HCl solution greenish, is peroxidised slowly by $FeCl_3$ after the tin has been peroxidised; as in the case of Cu_2Cl_2, the colour change to yellow takes place as soon as the tin is peroxidised, so that uranium, if present, does not affect the titration reading. In this case, however, the colour due to $FeCl_3$ slowly goes as the uranium is peroxidised, and is replaced by the much fainter yellow of uranic chloride; so that the exercise of considerable care is required in noting the finish of the tin titration. Further, zinc precipitation leaves the uranium in the mother liquor if this is kept sufficiently acidulated. Molybdenum interferes with both iodine and ferric chloride assays, and tin requires to be separated from it by zinc precipitation, the mother liquor, if sufficiently acid after separation of the tin, containing the molybdenum. Molybdous compounds colour a boiling HCl solution reddish; on titration with ferric chloride the colour changes to green, finishing a strong yellow.

Chapter V.

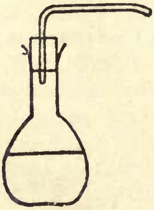
Specific Tin Assays.

A.—Direct Ferric Chloride Assay.—Applicable to alloys of lead, tin, zinc, aluminium, iron, arsenic, antimony, copper, cobalt, and nickel, with less than 5 per cent. Sb, As, Cu, and to certain tin copper alloys.

Solder, Terne, Pewter, Capsule Metal, &c. Buttons obtained in dry assay of Tin Ashes.

The sampling of alloys of lead and tin and antimony is quite as important as the assay, on account of the pronounced liquation phenomena which these alloys exhibit. Wherever possible the sample should be taken from the molten kettle of metal. Where there is no option but to sample from the pigs, chips may be taken from the centre of opposite top and bottom longitudinal edges, and the chips melted in a ladle. The sample for assay should be cast in a *small* hemispherical or rectangular mould (not in long thin strips) and cut transversely in two with a chisel. Filings are taken with a clean and fairly fine cut file across the surface of fracture, and the filing should be done gently. Very brittle alloys such as irony arsenides may be pounded in a steel mortar. The objection sometimes raised against filing, that the use of a file involves the contamination of the sample with particles from the file, is more imaginary than real, and in practice may be ignored quite safely.

The Assay.—Weigh up 1 grm. of filings into a clean 8-oz. flask and add about 200 c.c. of pure HCl (s.g. 1.16). Close the flask with a rubber cork with leading tube attached as shown, and boil the assay on a sandbath enclosed in a fume cupboard, over a moderate fire. As the object is to obtain the tin in solution as stannous chloride, precautions are necessary in order to prevent oxidation. The assay should not boil too rapidly, or the HCl becomes weakened in strength before it has had time to thoroughly attack the metal, and any black residue is broken up so finely that it settles afterwards only with great difficulty. Neither should the assay come to a boil too slowly, as in that case the metal may be completely attacked while there is still air in the flask, with attendant formation of $SnCl_4$. The tin goes into solution as $SnCl_2$—tin, lead, zinc, aluminium, iron (forming $FeCl_2$), cobalt, nickel, all dissolve, and in some cases copper (forming Cu_2Cl_2) whilst arsenic, antimony, copper (also bismuth and mercury) are left undissolved as a black powder, also often considerable quantities of iron, and a certain amount of unattacked tin and lead occluded by the powder.



Some As is evolved as AsH_3, but in general the As remains as a brownish flocculent residue, while only faint traces of SbH_3 are formed. Certain tin copper alloys are completely soluble in HCl, giving a colourless solution of $SnCl_2$ and Cu_2Cl_2. Cu_2Cl_2 is oxidised to $CuCl_2$ by $FeCl_3$, but its presence does not affect the tin titration, as was explained in the previous chapter. The presence of $SbCl_3$, $PbCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, has no effect on the titration figures. Alloys containing only lead, zinc, tin, and aluminium go completely into solution in fifteen to twenty minutes, and may then be immediately titrated with ferric chloride; such alloys yield perfectly accurate results by this method.

In the presence of a residual black powder the results will always be too low, though when the percentage of antimony and copper is low the results are near enough for many purposes, as, for example, in the assay of buttons got in the fire from tin ashes and solder ashes.

Thus solders with 20—60 per cent. Sn and 1½—4 per cent. Sb yield results for tin by this method which are ½—1 per cent. too low. Alloys of iron and tin are also difficult to attack completely, and further the presence of much $FeCl_2$ in the solution retards and obscures the finish somewhat. $CoCl_2$ and $NiCl_2$ give coloured solutions in HCl which also obscure the colour finish; this may be overcome by adding hot boiled water before titration.

In all cases where solution in boiling HCl is incomplete, the assay is allowed to boil until the metal is completely attacked. This is a matter for the judgment of the operator, and requires experience to determine, but in general the fine stream of gas bubbles is replaced by a slower stream of larger bubbles as solution proceeds. The assays must not be allowed to boil below 150 c.c. or the $FeCl_3$ used in titration may cool the assay so much as to impair the sharpness of the colour indication at the finish of the titration. It is an improvement to allow the leading tubes to dip under water—this may be effected by attaching a straight vertical tube to the ordinary leading tube, with a piece of rubber tubing, or the leading tubes may be made longer and with a second right angle bend; or a rubber tube valve may be fitted on the glass leading tube to prevent air finding its way into the flask.

As soon as the metal is completely attacked, remove the assay to the titrating bench and allow it to stand for a minute or two until the black powder has settled. A slight rotatory jerk, given to the flask when it is removed from the sandbath, assists the powder to collect in the centre of the flask. Remove the cork and leading tube and carefully pour the liquid off into another clean flask, from any black powder—pour off as closely as possible, but so as not to carry over any powder into the other flask. (The black residue of Sb, Cu, As is soluble in $FeCl_3$). Titrate the hot acid solution of tin rapidly with ferric chloride solution from a fast running burette with glass stopcock. The assays must not be allowed to stand off the fire before titrating, for more than two or three minutes. After five minutes the effect of oxidation begins to be perceptible, and the oxidation increases very rapidly on further standing.

The ferric chloride solution should be made up two litres at a time from a concentrated stock solution made by dissolving piano wire in HCl, peroxidising with HNO_3 and evaporating twice with HCl, to dryness, and then dissolving in HCl, and is standardised against 1 grm. of purest tin dissolved by boiling with HCl as usual. The standard solution may also be prepared by dissolving 180—190 grams of the yellow lump salt (which is, roughly, Fe_2Cl_6, 12 H_2O) in 200 c.c. HCl and evaporating the solution just to dryness. The residue is dissolved cautiously, and in a fume cupboard, in 300 c.c. HCl, and the solution diluted to two litres. Evaporation with HCl is necessary to free the solution from HNO_3 and arsenic. Only the purest and strongest HCl should be used in these assays.

As previously stated, in the case of alloys which dissolve completely in HCl the above method is perfectly accurate, but where solution is incomplete (1) the black powder holds Sn, (2) oxidation possibilities are introduced in pouring off into the second flask, (3) a little powder may get over into the second flask, (4) it is impossible to pour off quite clean—though the error from this cause is much less than might be supposed, and may be practically eliminated by pouring a little hot boiled water on to the residue in the first flask immediately after decantation, and decanting off the washings into the second flask at the end of the titration. Admitting that in cases of incomplete solution the results are too low, they are in all cases sufficiently close to render the method very reliable, especially when one considers the extent to which antimony and tin are allowed to act as understudies to one another in so many assays. Briefly, in cases of complete solution, this direct assay is quite accurate, while with incomplete solution the results are low, but provided not more than 5 per cent. Sb and Cu are present they are reliable and within 1 per cent. of the Sn percentage. In the case of plumber's solder and tinman's solder it is a fairly safe rule to add ½ per cent. in the case of plumber's and ¾ per cent. in the case of tinman's; by doing this it is possible to arrive more accurately at the percentage of Sn in solder in half-an-hour than is otherwise possible (except by the next assay to be described) in a week. Tinman's solder very commonly contains 46 per cent. Sn and 3 per cent. Sb. This metal assays 50 per cent. Sn by oxidation with HNO_3 and weighing residue as SnO_2. Plumber's solder often holds 30¾ per cent. Sn and 2 per cent. Sb.

All tin assays for estimation with ferric chloride are finished in the manner just described. The precipitated tin and excess zinc are dissolved up together, over a good fire, in a flask with leading tube, and a granule of zinc is added to assist in keeping a non-oxidising atmosphere in the flask until the assay comes to a boil. In the general tin assay, As, Cu, Sb are always absent, being separated in the iron wire stage, so there is no error through decantation.

Alloys containing zinc or aluminium effervesce violently in the cold, with strong HCl. Tungsten gives a bluish tint to the solution.

Cobalt gives a blue colour much weakened by dilution, and nickel a weaker green colour which goes on dilution.

B.——ALLOYS OF LEAD—TIN—ANTIMONY holding much Sb and but little Cu and As.

TYPE-METAL—ANTI-FRICTION METALS.

Weigh up 1 or 2 grms., according to the probable amount of tin present, into an 8-oz. flask, and boil gently with 50—75 c.c. HCl until action ceases, when most of the Pb and Sn are in solution. Complete solution is effected by the cautious addition of a saturated solution of $KClO_3$. Boil off the excess of chlorine, remove the assay from the bath, and add at once two bunches of fine piano wire. The action in the hot, strongly acid liquid is very rapid, and one minute after the solution turns colourless add a thin strip of copper foil. As soon as a small piece of copper remains bright (after a minute or two) dilute with 30 or 40 c.c. of hot boiled water and boil for a minute. Filter very rapidly into another similar flask, keeping the precipitate as far as possible out of contact with the air, and wash the flask and paper once, with hot dilute HCl. Neutralise the solution (which should be freely acid) with thin strips of zinc—use excess of zinc straight away, as if the neutralisation is effected too slowly tin is apt to remain unprecipitated.

When the action ceases pour a little of the liquor off into a beaker containing a little H_2S water; if the precipitate is white, all the tin has been precipitated. Pour away the mother liquor as closely as possible after allowing any floating particles of metal to settle. The best plan is to empty the liquid from the flask into a beaker, which is then rapidly filled with water from the tap. Larger pieces of spongy tin are pressed against the side of the beaker with a glass rod, after which they readily settle; the addition of a drop or two of ammonia or pouring the liquid to and fro from one beaker to another will generally ensure the settling of the lighter particles. The metal in the beaker is washed back into the flask with 180 c.c. HCl and the liquid brought to a boil as rapidly as possible with the addition of a granule of zinc and using a cork and leading tube. When solution is complete titrate at once with ferric chloride.

Black powder should be absent, as all the As, Sb, Cu are previously separated. This method has been repeatedly checked on made up alloys of known composition, and is perfectly accurate. From start to finish it need not take more than one hour, but the assays require unremitting attention. Copper is best precipitated on iron in a dilute HCl solution, whilst antimony comes down immediately in a strong HCl solution. The arsenic is not really precipitated by iron but by the $SnCl_2$ formed by the action of Fe on $SnCl_4$; iron precipitates Cu and Sb. Copper precipitates As and Sb; tin precipitates As, Sb, and Cu. Phosphorus is said to bring down some tin on iron wire, and in the case of arsenic the precipitated metal holds 3 or 4 per cent. Sn. It may be asked, why reduce the tin to metal; why not stop at the half-way stage when the $SnCl_4$ is reduced to $SnCl_2$? This is actually done in the iodine assay, but the procedure described affords a far surer way of obtaining the tin in solution as $SnCl_2$, and further it is necessary to obtain the $SnCl_2$ in strong boiling HCl solution free from precipitated As, Sb, and Cu, and this can only be ensured by the above method.

C.——In alloys which contain much Cu, and with non-ferruginous mattes, a little HNO_3 may be used instead of $KClO_3$ to effect complete solution, and the reduction by iron wire prolonged in dilute solution.

D.——ALLOYS AND MATTES rich in Fe, Co, Ni, P.

Weigh up 1 grm. and dissolve in 20—30 c.c. HCl and 1 c.c. HNO_3. Heat until solution is complete, boil off red fumes, dilute to 200, and precipitate with H_2S. Allow to stand for an hour or two, filter, but do not wash, as SnS_2 is decomposed by water. (In cases where the filtrate is required wash with NaCl solution.) Test the filtrate with a further stream of H_2S. Wash the sulphide precipitate back into the flask, add 30—40 c.c. HCl and some $KClO_3$, boil, add iron wire, and heat to 70° or 80° for half-an-hour to two hours, or until reduction is complete. Filter, precipitate the tin on zinc, dissolve and titrate with ferric chloride.

E.——ALLOYS, MATTES, AND SPEISES rich in arsenic and iron.

1.—In many cases methods C or D are quite satisfactory provided the assay is well boiled with plenty of iron wire, and is kept freely acid. The assay is too low for tin by 5 per cent. of the arsenic percentage.

2.—Method D is adopted, but instead of dissolving the mixed sulphides in HCl and $KClO_3$ they are boiled with 50 c.c. HCl alone, down to about 30 c.c., diluted and filtered from the insoluble sulphide of arsenic. The filtrate is heated with iron wire to precipitate the Sb, filtered and precipitated with zinc as usual. This is a rough and ready separation, as the As_2S_3 always holds some SnS_2, and if much copper is present the loss is increased by the Cu_2S which is undissolved in HCl.

3.—The arsenic may be distilled off with a solution of $FeCl_3$ and $CaCl_2$, and the tin separated as sulphide from the diluted solution. This is sometimes convenient where the arsenic has to be estimated, as there is no loss of $SnCl_4$.

4.—One grm. 25 c.c. HCl and 2 c.c. HNO_3. Heat till dissolved and boil off the fumes. Add sodium sulphide solution very cautiously until solution is alkaline and precipitate is black, and pass H_2S. Warm, dilute, warm again, filter and wash well with hot dilute Na_2S. (The precipitate if very bulky should be redissolved and reprecipitated.) The alkaline filtrates are cautiously acidified with HCl, the liquid allowed to stand for half-an-hour in a warm place, and the sulphides of Sn, Sb, As are filtered, washed well with NaCl, and washed back into an 8-oz. flask, and boiled down with 50 c.c. HCl to 30 c.c., then diluted and filtered from the As_2S_3. Boil with iron wire, filter and precipitate on zinc.

5.—Or separate with H_2S in acid solution first, and digest the precipitate with Na_2S. Then proceed as before.

6.—Dissolve in 30 c.c. HCl and a little $KClO_3$. Boil off the chlorine, and precipitate with H_2S in strong HCl solution. Allow the solution to stand for some time in a warm place and again pass H_2S. As_2S_3 alone is precipitated (and Cu_2S). Filter through asbestos, dilute and precipitate the SnS_2, &c., with H_2S.

7.—Or having obtained the sulphides of As, Sb, Sn, separate the antimony by electrolysis, the arsenic with magnesia mixture, and the tin by electrolysis. (See electrolytic assay.)

8.—The oxalic acid separation may also be used with arsenical material. One grm. is dissolved in 20—30 c.c. HCl and 1 c.c. HNO_3. Add 20 grms. oxalic acid dissolved in 100 c.c. water and gas the solution with H_2S, while at the boiling temperature. Two separate gassings are necessary. Filter the sulphides of As and Sb on the water bath and wash with a hot concentrated solution of oxalic acid. Neutralise the filtrate with ammonia, acidify with acetic acid, dilute to 1 litre, warm, and precipitate the tin completely with H_2S. Filter, dissolve in HCl and $KClO_3$, and precipitate with zinc as usual.

F.——GENERAL ASSAY applicable to everything not containing the tin as silicate; suitable for calcined matte and calcined speise, bronze ashes, many tin copper alloys, chloriny and leady tin ashes, sulphide ores, metallic copper.

1 to 5 grms. is evaporated to complete dryness with 10—20 c.c. HNO_3 and some water, in a covered porcelain dish. It is then digested with dilute HNO_3 and filtered. The residue will contain all the tin, and is dried and ignited with the filter paper in the same dish, the ignition being best done in the muffle. The calcined residue is carefully transferred to a porcelain boat and reduced at a low red heat in a current of coal gas for an hour and a half or two hours (see Wet Assay of Tin Ore). The boat and its contents are allowed to cool in the tube in a current of coal gas, and when cold are transferred to an 8-inch beaker, and the metal dissolved in HCl and a little HNO_3, the nitrous fumes boiled off, and the solution filtered. The residue of carbon and silica is dried, ignited, and examined for Sn as a matter of precaution by fusing with $KNaCO_3$ and borax in a platinum crucible, dissolving the melt in HCl, and precipitating with zinc, &c.

The main solution if from 5 grms. is made up to 500 c.c., and 100 c.c. are pipetted into an 8-oz. flask.

(*a*) In presence of *much* arsenic, see Section E. Most of the arsenic is, however, volatilised in the reduction tube.

(*b*) In presence of a little arsenic, precipitate the As and Sb on iron, and the tin on zinc as usual.

(*c*) In presence of much iron or of phosphorus separate the SnS_2 with H_2S in acid solution. (See Section D.)

(*d*) In presence of tungsten, the uncalcined residue obtained by evaporation with HNO_3 is extracted with dilute AmOH or Am_2CO_3, when WO_3 dissolves.

(*e*) Copper, cobalt, nickel, zinc, mostly go into the HNO_3 solution, also much of the lead, whilst usually most of the iron and sometimes half the lead remain with the SnO_2. Some Co and Ni may remain with the tin, in which case a separation with H_2S is advisable as the coloured chlorides of Co and Ni interfere with the appearance of the colour finish in the ferric chloride titration.

In any tin compound or mixture of substances containing tin (except tin slag), the tin may be brought into solution by the above method.

G.——ASSAY OF MISCELLANEOUS ALLOYS.

1.—TIN PLATE—SPELTER—TEA LEAD.—5 grms. is boiled with 300—400 c.c. HCl in a 16-oz. flask provided with cork and leading tube. When the action is complete pour off from any residue and titrate with ferric chloride. In the case of spelter use less acid or more spelter, and bring rapidly to a boil. See article by R. Job, "The Mining Journal," December 12, 1908, p. 743.

2.—TIN FOIL—CAPSULES—BORINGS.—50 or 100 grms. is dropped into a crucible three parts full of melted borax with a little charcoal sprinkled on top. The button of metal is assayed for tin by method A or C, according to composition. The presence of zinc or aluminium in borings is easily recognised by the ease with which they burn in the crucible, and by the violent effervescence with cold HCl.

3. TIN DRILLINGS AND SAWINGS AND FINE BORINGS.—5, 10, 20, or 40 grms. is dissolved in a large beaker in 100—500 c.c. HCl and the minimum amount of HNO_3. When solution is complete, dilute to 500, 1,000, or 2,000 c.c. and measure out the equivalent of 1 grm. Reduce with iron, filter, and precipitate on zinc.

4.—ALLOYS OF TIN AND ALUMINIUM.—May be assayed by method A.

5.—METALLIC COPPER.—Use method E. 4.—separation with Na_2S, or, better, method F.—treatment with HNO_3 and reduction of residue. Take 5 to 10 grms. for assay.

6.—Tin Amalgam and Fusible Alloys.—Weigh up to 5 grms. Treat with dilute HNO_3 and evaporate to dryness—extract with dilute HNO_3—filter—calcine and reduce in coal gas. Dissolve as usual in HCl and a little HNO_3, separate Sb, &c., with iron, and precipitate tin on zinc.

H.—*TIN ASHES.*

Samples of tin ashes should in general be tried for moisture and the tin assay done on the dried sample. In sampling material of this kind a sample weighing from 14 to 28 lbs. is broken up and made to pass through a quarter inch sieve. Large pieces of iron are picked out and weighed and allowed for in making up final calculations. 100 grms. of the dry ashes are pounded in an iron mortar and passed through a sieve with 16 meshes to the linear inch to separate the metallics. The metallics are weighed and the difference from 100 is the weight of the " fine " which is not separately weighed owing to slight loss of dust in pounding. 5 to 10 grms. of the ashes (with fine and metallic in proportion) is weighed out and treated by one of the following methods. Most tin ashes are best assayed by method 1. Method 2 is suitable for chloriny or leady ashes (and for tin ore). Finely divided ashes, if free from chlorine, grease, sulphur, and metallic—*e.g.* tin oxides, may be tried by method 3. Siliceous ashes in which silicate of tin is present are treated by method 4.

1.—General Method.—5 to 10 grms. ashes is weighed into a 400 c.c. beaker, treated with 100 c.c. HCl and 5 or 10 c.c. HNO_3, and allowed to stand in a moderately warm place until the action abates. It is then boiled until the further action is completed. Dilute with an equal bulk of water and filter. If the ashes are leady and $PbCl_2$ clogs the filter, wash with hot sodium acetate, when the $PbCl_2$ dissolves (alternative to the use of method 2). Wash the residue well, firstly with dilute HCl, then with hot water, dry, and calcine with the paper in a porcelain dish in the muffle. Transfer the calcined oxides to a porcelain boat and reduce to metal in a current of coal gas at a low red heat. Time of reduction, 1½—2 hours. Transfer boat and contents to the same beaker when cold, and add 50—100 c.c. HCl and 2 or 3 c.c. HNO_3; boil off the nitrous fumes and dilute. Filter into the first HCl solution and well wash the *residue* which is dried, calcined, and fused with four or five times its bulk of a mixture of $KNaCO_3$ and borax, the fusion being done in a platinum crucible in the muffle. The melt is dissolved in HCl and the residual tin precipitated on zinc as usual. The *solution* is made up to 500 or 1,000 c.c. and the equivalent of 1 gram is measured out with a pipette and reduced with iron wire in an 8-oz. flask, filtered and precipitated with zinc as usual, prior to solution in HCl and titration with $FeCl_3$.

2.—Evaporation with dilute HNO_3 and reduction of the residue in coal gas (see method F). *Leady or chloriny ashes.*

3.—Fine Ashes free from Cl, S, grease, moisture, and metallics. 5 grms. is weighed into a porcelain boat and reduced for 2 hours in a current of coal gas. The reduced metals are dissolved as in method 1.

4.—SLAGGY ASHES.—5 grams is weighed into a platinum basin and evaporated just to dryness with HF. (If the ashes are also chloriny they must be first boiled in a porcelain dish with Na_2Co_3, and the liquid filtered off and, of course, examined for tin.) To the residue from HF add 40—50 c.c. HCl, heat to loosen from the basin and transfer to a 400 c.c. beaker. Add 50 c.c. HCl and 5 c.c. HNO_3 and proceed as in 1.

5.—TIN CHALK, TIN PASTE, TIN MUDS, AND PRECIPITATES in which the tin all exists as soluble oxide, sulphide, oxychloride, or as metal.

10 grams is dissolved in 100 c.c. HCl and a little HNO_3 diluted and filtered. The residue which is small in amount is fused with $KNaCO_3$ and borax. The solution is treated as in 1 unless Sb, Cu, As are known to be absent when the reduction with iron wire is omitted, the measured portion being at once treated with zinc.

6.—TIN GREASE.—5 grms. is washed with benzene in a dish, then filtered, dried, and treated like ordinary tin ashes. Slightly greasy ashes should be treated by method 2.

7.—IRONY SULPHARSENIDE TIN DROSS.—20 grms of the dross is treated with 300 c.c. HCl and 20 c.c. HNO_3 as in the case of ordinary tin ashes. The solution is diluted and filtered and the residue well washed. In this case the residue is washed into a dish without opening out the paper and evaporated to dryness with a little HNO_3, extracted with dilute HNO_3, and filtered through the same filter (not, of course, into the main solution). The residue is then dried and ignited as usual, and may be then reduced in coal gas, or if small in amount may be fused at once with $KNaCO_3$ and borax. The tin is determined in the usual manner—reduction with iron—precipitation on zinc—solution in HCl, and titration with ferric chloride.

8.—VERY CHLORINY ASHES which often contain much $ZnCl_2$ and large fragments of metal ("tin scruff") should not be assayed on the dry material, as this is extremely hygroscopic. Weigh out 100 or 200 grams of the ashes, *wet, on sampling*, boil with NA_2CO_3 and filter. The washings are made acid with HCl and a measured fraction precipitated on zinc. The residue is dried and separated into fine and metallic. The *fine* is dried by method 1 or 2. The metallic is melted with reducing agents in a clay crucible and the button assayed for tin by A or C. If the ashes are chloriny but without large fragments of metal, weigh up 10—20 grms. wet and treat with 200 c.c. HCl and 100 c.c. HNO_3 in a large beaker.

K.—*ASSAY OF TIN ORE.*

Tin ores are often exceedingly complex; they may contain in addition to stannic oxide, ferric oxide, and silica, some or all of the following substances—bismuth, copper, pyrites, iron pyrites, mispickel, wolfram, titanic acid, lead oxide, antimony oxide. Antimony and arsenic are common impurities, especially in South American ores. Contrary to a statement in "Crookes' Select Methods," the writer's experience is that antimony is almost invariably associated in small quantities with tin ore. It should be apparent that complete solution of the ore is absolutely essential in every case, in order to systematically ensure the complete extraction of the tin and its quantitative determination. Any method which does not involve complete solution of the ore is quite unreliable as a *method*, although it may often yield correct results. Further, the final determination of the tin should always be effected volumetrically; if a gravimetric estimation is adopted the assay develops into an academic research, owing to the number and complicated nature of the separations necessary to ensure that no possible impurity may score as tin; while if such thorough separation is neglected, the results obtained are quite unreliable.

The following methods have been proposed and used for the wet assay of tin ore:—

1.—Fusion with alkalies or alkalies and sulphur in nickel, silver, platinum, or porcelain crucible.

2.—Continued agitation with zinc and HCl.

3.—Reduction of the cleaned stannic oxide in hydrogen and calculation of the tin from the loss in weight, which is assumed to represent only the oxygen of the stannic oxide.

4.—Cleaning with HCl and reduction with cyanide in a porcelain crucible.

5.—Fusion with potassium hydrogen fluoride, solution in sulphuric acid and precipitation as metastannic acid by dilution and boiling.

6.—Reduction in coal gas or hydrogen and extraction with HCl and HNO_3, combined with fusion of the siliceous residue with Na_2CO_3 and borax in a platinum crucible and solution of the melt in HCl.

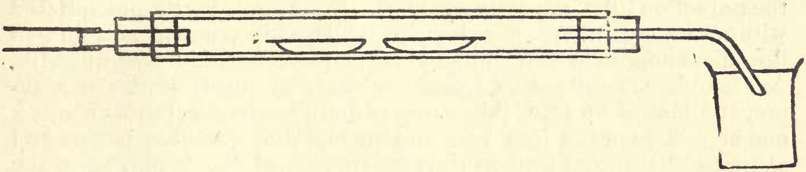
7.—Fusion with caustic soda in an *iron crucible.*

The first method is now hardly ever used, being tedious and uncertain. The second method, agitation with zinc and HCl, is very slow; it may occasionally give all the tin, but there can be no certainty whatever about such a method, and the same remark applies to the third method, calculation of the tin from the weight of oxygen lost by reducing the stannic oxide in hydrogen after presumably purifying it from other metallic oxides by cleaning the ore with acids; rapidity is claimed for this method, but the assumptions as to complete reduction of the tin and absence of other metallic oxides reducible by hydrogen, are vital objections, and render the method unsound from either a scientific or commercial standpoint. Method four, reduction of cleaned ore with cyanide, is in reality a dry assay, notwithstanding the use of the porcelain crucible, and when the metal obtained is assayed for tin, must necessarily give results which are lower than the tin contents. It is not denied that in many cases the results will only be very slightly under the actual percentage, but one can never be certain of this; often, indeed, results obtained in this way are 2 or 3 per cent. too low. If the button of metal is not assayed for tin, the results obtained may be either a little too low, correct, or up to as much as 4 or 5 per cent. too high. The method is not sufficiently certain for the commercial valuation of tin ores. Method 5 (Hallet's method) is logically admissible provided that the precipitated metastannic acid is not merely ignited and weighed as stannic oxide, but is redissolved and the tin carefully separated. This, however, complicates the method somewhat. Method 6 is the most practical method of assaying tin ore, which ensures at the same time accuracy and reliability as a *method*, and it alone will be considered here in detail. Method 7 (the Pearce-Low method), which consists of fusion with caustic soda in an iron crucible, solution in HCl, reduction with iron, and titration with iodine, is a workable and an exceedingly rapid method *for isolated assays;* one assay can be done in an hour easily (see Low, "Technical Methods of Ore Analysis," 2nd Edition). The above italics are mine, and I consider it necessary to emphasise this point, as Mr. Low claims that the method is at once the quickest and most accurate assay of tin in tin ores. It is undeniably quicker for isolated assays, though it is not as economical of time as the reduction method, since one can do seven or eight reduction assays in conjunction with other work in the course of a working day, which is scarcely possible with the above fusion method. With regard to accuracy, the method compares favourably with most other assays, but is scarcely as accurate as the reduction assay.

The foregoing remarks have reference to the assay of dressed tin ores in the main; in previous editions it was omitted to clearly point this out. It is for dressed tin ores that fusion assays in general are so objectionable, owing to the possibilities of slight losses by spurting, creeping, volatilisation, &c., which on rich material introduce errors of commercial importance; on poor material this objection does not exist, and the writer must certainly admit that *for poor mine stuff up to 5 or 6 per cent. of tin* the Pearce-Low method is certainly *the* method, and as slight losses in fusing do not here appreciably affect the result, a batch of such assays may be worked off very rapidly. On the other hand, the writer must still maintain his opinion that for dressed tin ores, the reduction assay, with fusion of the siliceous residue, as herewith described, is the only admissible method from a commercial standpoint, as it favours neither buyer nor seller.

DESCRIPTION OF METHOD.

Tin ores may be either pyritic or non-pyritic. Pyritic ores must be, and non-pyritic ores may be, treated with NHO_3 before reduction, as sulphide of tin is volatile at a red heat. 5 grms. ore, ground as finely as possible in an agate mortar, is treated in an evaporating basin with clock glass cover, with 20 c.c. dilute HNO_3 and carefully evaporated to complete dryness. The residue is digested with dilute HNO_3 and filtered. The washed residue is dried, ignited in the dish, transferred to a porcelain boat and heated to a low red heat for 2 hours in a current of hydrogen or coal gas. Coal gas is much more convenient to use and quite as effective as hydrogen. The boat is 2½ inches by ½ inch, and two at a time are placed in a porcelain or glass tube 12 inches long and ¾ inch bore, which is then placed in the reduction furnace. A very convenient form of gas reduction furnace with clay body, brass gas jets, and asbestos rings to fit over the ends of the tube against the clay covers, is made in 6-inch lengths by Messrs. Fletcher, Russell, & Co., of Warrington. The ends of the tube should project about 3 inches from each end of the furnace and should be closed with rubber corks fitted with glass tubes as shown; the escaping gas (about 2 bubbles per second) is passed through dilute HCl.



The water through which the gas escapes should not be thrown away, but saved, and every now and then the tube should be washed out with HCl and $KClO_3$, and the two solutions tested for tin as a check, against, for instance, loss by volatilisation through sulphur in the coal gas. A two-way gas branch is used; one jet supplies gas to the tube, the other supplies the gas for heating to the jets of the furnace. The boats are allowed to cool in the furnace, and when cold each boat and its contents is transferred to a 400 c.c. beaker and treated with 100 c.c. HCl and 5 c.c. HNO_3, the assay being allowed to stand in a warm place until the action abates, when it is boiled for a few minutes, diluted with an equal bulk of water and filtered. The residue is well washed with hot acid water, then with hot water, is dried, ignited, and fused with four or five parts of a mixture of fusion mixture or sodium carbonate (free from chlorine) and borax, in a platinum crucible, and the melt dissolved in HCl and precipitated with zinc as usual. The residue rarely holds more than ½ per cent. of the total tin in the ore.

Instead of fusing the residue with $KNaCO_3$ and borax in a platinum crucible, it may be fused with about 2 in. of stick caustic soda in an iron crucible over a bunsen burner. The melt is dissolved up in HCl and precipitated on zinc as usual. (See K 1, paragraph 2.)

The main solution is made up to 500 c.c. and the equivalent of 1 grm. is pipetted into an 8-oz. flask, reduced with iron wire and filtered; the filtrate is precipitated with strips of sheet zinc as usual, and the metallic sponge dissolved in HCl and titrated with ferric chloride.

Except with impure ores the reduction with iron wire may be omitted, as it is always an advantage to save a filtration when possible. In this case the aliquot part of the solution is at once precipitated with zinc. The boiling HCl solution for titration with $FeCl_3$ must, however, be free from black powder of Cu, Sb, &c., and from tungsten blue in suspension or solution. (N.B.—Lower oxides of tungsten in solution give a brownish pink or light claret-coloured solution.) During precipitation with zinc the solution should be freely acid to start with, and in presence of Ti, or Mo, should be distinctly acid when poured off. (See Section B, p. 27.)

Any copper in the tin ore is found in the HNO_3 solution, though traces may remain with the SnO_2. In the iron wire stage, the arsenic which escaped extraction with HNO_3 and volatilisation in the reduction tube, is partly evolved as AsH_3 and partly precipitated with antimony in the metallic form. It comes down as a brown flocculent deposit which contains 3 or 4 per cent. of its weight of tin. As there is generally only a few per cent., at most, of As in a tin ore, the loss of tin from this cause is quite negligible, but as a check one should save the iron wire and precipitates and filter papers and examine them from time to time for tin; it will be found, as in the case of the deposit in the tube and the dilute HCl through which the escaping gas bubbles, that only the merest traces of tin are lost in these operations. Further, the HCl solution of the reduced metal may be done in a conical flask with rubber cork and leading tube dipping under water, to assure oneself that there is no appreciable lose by volatilisation of $SnCl_4$.

If the ore contains wolfram, the tungsten is mostly found as WO_3 in the residue from HCl and HNO_3 extraction of the reduced metal, from which it may be removed before fusion, with AmOH. Any tungsten which gets into the main solution comes down as blue oxide with the iron wire precipitate, and any which is fused with $KNaCO_3$ and borax should be removed by reducing the HCl extract of the melt with iron wire, before precipitating with zinc. In general, all the antimony and some of the lead in the ore will be found in the main HCl solution, whilst some of the lead will be obtained in the HNO_3 extract.

Note.—After the HNO_3 evaporation the residue may be boiled with HCl (40 or 50 c.c.), diluted and filtered, though in this case the extract must be tried for tin as a matter of precaution. It will in general hold all the copper and most of the arsenic, antimony, lead, and iron, though one can never be sure that the residue is free from the oxides of these metals. Occasionally this HCl extract will hold a little tin. The residue is reduced in the usual manner.

K 1.—THE ASSAY OF POOR SILICEOUS ORES, BATTERY TAILINGS, AND SILICEOUS RESIDUES HOLDING LESS THAN 2 PER CENT. OF TIN.

Siliceous material very poor in tin is best assayed by a fusion method of which either of the following will serve:—

1.—.5—1 grm. of finely-powdered ore is fused in a platinum crucible with soda ash (free from chlorine) or $NaHCO_3$, and borax. The melt is dissolved in dilute HCl, transferred to an 8-oz. flask, and heated with ten 2½-in. iron nails until the colour goes; it is then allowed to stand in a moderately cool place for 20 minutes to half-an-hour, poured off into a clean flask containing CO_2, and titrated with one-tenth strength iodine.

1*a*.—Or, the HCl solution of the melt is precipitated with zinc, for the usual ferric chloride titration.

2.—Mr. A. H. Low's method is a very useful one. .5 grms. fine ore is fused over a bunsen burner in an iron crucible with 3 or 4 inches of stick caustic soda. The melt is extracted with water and solution effected with HCl. The solution is reduced with iron nails as above, and titrated with iodine as above.

A blank assay with iron nails and dilute HCl must be done, as it has been found in practice that when using ten or a dozen 2½-in. iron nails and digesting these with HCl as above, the liquid requires .1 to .2 c.c. iodine, even in absence of tin.

The solution of the melt may also be precipitated with zinc and the metallic residue dissolved in HCl and titrated with $FeCl_3$.

K 2.—REVISED ASSAY OF DRESSED TIN ORES.

In order to avoid the preliminary evaporation of pyritic black tin with nitric acid, the following procedure may be employed: The ore is weighed direct into the porcelain boat and reduced as usual. After reduction the deposit in the tube is washed out with HCl and $KClO_3$ and mixed with the water (which should have been acidified with HCl before starting the assay), through which the gas bubbled, and the joint solution reduced with iron or zinc and assayed for tin by either the iodine or ferric chloride assay; the amount so found being calculated on to the percentage determined from the solution of the reduced ore.

This procedure applies to all dressed tin ores holding not more than 2 per cent. sulphur; that is to say, it applies to ninety-nine out of every hundred buying samples of black tin or tin barilla. In such exceptional samples as may hold more sulphur than this, evaporation with nitric acid must precede reduction.

As we have already mentioned in these notes, the reduction of the main assay solution with iron wire may in most cases be omitted, and it will be found that in this amended procedure we attain with the gas reduction and ferric chloride assay the following conditions:—

1. The minimum of manipulation of the main portion of the assay both before and after solution.
2. Complete solution of the ore.
3. The use of a method of determination by which only tin can score as tin.

The first two of these conditions which ensure the elimination of all sources of loss, protect the seller's interests; while the third, which is at the same time absolutely fair to the seller, protects the buyer.

L.—ASSAY OF TIN SLAGS.

1.—HYDROFLUORIC ASSAY.—The slag is pounded up finely in a steel mortar; the more siliceous the slag the finer it should be powdered. 2 grms. slag is weighed into a platinum basin and about 20 c.c. HF (pure and strong) added in a fume cupboard and the assay evaporated to bare dryness. Most of the SiO_2 is removed and the tungsten remains as blue oxide, other metallic oxides being left in a form easily soluble in acids. The residue is treated in the basin with 30 or 40 c.c. HCl, and after warming, the contents of the basin are transferred to a 400 c.c. beaker, the basin being cleaned out with a rubbered glass rod and as small a quantity as possible of hot water. Add *1 c.c.* of HNO_3 and boil for *2 or 3 minutes*, dilute to about 350 c.c. and pass a rapid stream of H_2S for about 10 minutes. The SnS_2 should come down granular if these instructions are adhered to. Allow to stand for a few minutes and filter, but do not wash. (If the SnS_2 comes down in a very finely divided form, the assay must be allowed to stand for two hours and again gassed.) Tin should never be separated as SnS. Wash back the precipitate into the beaker and dissolve by boiling with 30 c.c. HCl and a little $KClO_3$. Boil with iron wire, filter and precipitate on zinc as usual. Dissolve in HCl, adding a granule of pure zinc and bringing rapidly to a boil, and titrate with ferric chloride.

2.—HYDROFLUORIC ACID AND REDUCTION.—In the case of certain very rich slags the tin may be present either wholly or in part in a form insoluble in HCl after removal of SiO_2 with HF. In such cases dilute the HCl extract to 75 c.c. and filter; reduce the residue in coal gas, dissolve, the reduced metal in HCl and a little HNO_3 and filter the solution into the first HCl extract. If there is still a residue it may be fused with $KNaCO_3$ and borax. The main solution (if from 5 grms. slag) is diluted to 250 or 500 and 1 grm. pipetted out and precipitated with H_2S. Filter, dissolve in HCl and $KClO_3$, reduce on iron and precipitate with zinc as usual. If the insoluble residue is small in amount it may be fused at once with $KNaCO_3$ and borax, after removal of WO_3 with dilute ammonia. In the case of leady slags the HF residue may be treated with HNO_3 according to general method F. In the case of slags containing prills of metal the metallics must be sieved out, from a portion of 100 grms. Weigh the fine and metallic in proportion.

3.—FUSION ASSAY.—Melt 5—10 grms. NaOH in a nickel (or, better, iron) basin and dust in 2 grms. of the finely powdered slag. Cover and heat to bright redness for 10 minutes with the aid of a foot blowpipe. Cool, loosen the melt, and transfer to a beaker; dissolve in HCl and a little HNO_3, precipitate with H_2S and proceed as before.

M.—IODINE ASSAYS.

The general method consists in—

(*a*.) Obtaining the tin in dilute HCl solution as $SnCl_4$, bulk 50—60 c.c. in a small beaker.

(*b*.) Reduction of this solution to $SnCl_2$ by a piece of soft iron with precipitation of As, Sb, Cu, as metals.

(*c*.) Titration with iodine and starch indicator in the cold.

The method is reliable, quick, neat, and cheap, requires little apparatus or room, but has not the certainty of the ferric chloride assay. The preceding general methods and separations remain unaltered in most cases, as far as obtaining the tin in HCl solution as $SnCl_4$.

1.—In the case of ALLOYS and MATTES, &c., .5—1 grm. filings or powder is weighed into a 4-in. beaker with watch glass cover and covered with about an inch of HCl; then boil gently until action ceases, on a frying pan sandbath over a bunsen burner. Add a crystal of two of $KClO_3$ to complete solution, boil off the chlorine, add an equal bulk of water and a piece of soft iron (3 in. by 3-16 in.), cover with watch glass and allow to simmer gently for 20—30 minutes after the solution becomes colourless (which is an indication that all the iron in solution is present as $FeCl_2$). At this point we assume (a weak point of the assay) that all the tin is reduced to $SnCl_2$. The Sb, Cu, and As are, of course, precipitated by the iron. Cool the assay quickly in a basin of cold water, wash the rod and cover with a rapid stream of cold boiled acid water saturated with CO_2, add a little starch paste and titrate at once with iodine, made by dissolving 21.32 grms. pure iodine, and 45 grms. KI free from iodate, in a little cold water, and diluting the solution to 1 litre .100 c.c. = 1 grm. Sn. In standardising take .5 grms. tin, and dissolve in 1 in. of HCl in a small beaker. Dilute, insert a piece of iron, reduce gently for five minutes, cool, wash cover and rod rapidly and titrate at once. The oxidation tendency is the important source of error in these assays. Precipitated Sb and Cu are not dissolved by iodine (except slowly) in a cold dilute solution, and therefore their presence as precipitated metal does not matter except that they darken the liquid, if in any quantity, and obscure the starch blue until the assay has stood for a moment. The iodine is more safely standardised by comparison with $KMnO_4$ of known strength, or against pure As_2O_3.

2.—ASHES AND ORES.—The measured portion of the HCl solution should not be too bulky; it is reduced in a beaker by an iron rod as in the process just described.

3.—SLAGS. (*a.*) HF ASSAY.—Tungsten blue should be filtered off. The HCl solution of the HF residue may be reduced by iron, filtered, and again reduced.

(*b.*) FUSION ASSAY.—The HCl solution is reduced and filtered from the tungsten blue, then reduced again and titrated. H_2S separation seems to be unnecessary with iodine assays.

Chapter VI.

The Assay of Antimony.

SUMMARY OF METHODS OF DETERMINATION.

1.—Gravimetric estimation as SbO_2 (unreliable).

2.—Gravimetric estimation by electrolysis.

3.—Titration of Sb_2O_3 with iodine in alkaline solution.

4.—Titration of iodine liberated by action of $SbCl_5$ on KI in HCl solution.

5.—Solution of precipitated Sb in H_2SO_4 and titration with $KMnO_4$.

6.—Titration of precipitated Sb with $FeCl_3$ in a boiling HCl solution.

7.—Titration of precipitated Sb with bichromate after solution in $FeCl_3$.

8.—Dry assays (*a*) iron reduction (*b*) carbon reduction.

The electrolytic assay is useful in special cases, as are 5, 6, 7. The dry assays are also useful in their proper place. The ordinary gravimetric estimation is a bad method. Methods 3 and 4 are of the most general applicability, and are both accurate and practical.

SOLUTION from speises, mattes, metals, is easily effected by HCl and $KClO_3$ or HNO_3; from oxides by reduction to metal with KCN or coal gas and solution of the reduced metal in HCl and $KClO_3$, by fusion in a silver basin with caustic alkali and solution in HCl, by extraction with alkaline sulphides (with or without a sulphurising fusion), and sometimes with the help of tartaric acid which dissolves the oxides and oxychloride; also by oxidising metal or sulphide with HNO_3 and solution of the oxide in alkalies or alkaline sulphide.

SEPARATION.—When necessary, H_2S in a not too concentrated HCl solution separates from Fe, Zn, Co, and Ni. Extraction with Na_2S dissolves sulphides of As, Sb, Sn. Sulphides of As, Sb, Sn, are dissolved in HCl and $KClO_3$ and $H\bar{T}$, AmOH, and AmCl added; then magnesia mixture, when the arsenic is separated as Mg, NH_4, AsO_4. Antimony may be readily estimated in presence of tin. Arsenic may also be distilled off from a metal, with a solution of $FeCl_3$, and $CaCl_2$ in HCl. As_2S_3 may be precipitated in a concentrated HCl solution, Sb remains in solution. Sb may be precipitated in the metallic form by iron.

Chapter VII.

Specific Antimony Assays.

A.—Alloys of Tin—Lead—Antimony—Copper with but little Arsenic.

TYPE METAL—SOLDER—ANTI-FRICTION METALS.

$SbCl_5$ in HCl solution oxidises KI. The liberated iodine may be titrated with stannous chloride—*not with Hypo.*

In this method the presence of tin (as $SnCl_4$) and lead has no effect whatever on the titration; indeed, the titration is done with $SnCl_2$. Copper, arsenic, and iron, when present in solution in their highest state of oxidation, score as antimony, and should be separately estimated and allowed for, this being preferable to separating the Sb from them. Fe is rarely present, but in the case of alloys with *more than* 1 *per cent.* As, it is advisable to dissolve in aqua regia and separate the Sb and As as sulphides, as it appears that in some cases when an alloy rich in arsenic and tin is boiled with HCl there is a considerable evolution of H_3As. This matter is under investigation. Arsenic, however, is rarely present in the above alloys in quantities greater than 1 per cent. 1—3 grms. of fine filings is weighed into a 16-oz. flask and boiled gently with 150 c.c. HCl until action ceases and most of the Pb and Sn are dissolved; to complete solution add cautiously a cold saturated solution of $KClO_3$, which also peroxidises the metals. After solution is complete, add a little $KClO_3$ and make sure that excess of chlorine is present. The solution is diluted with rather less than an equal bulk of water and boiled until free from chlorine. In practice half-an-hour is a sufficient length of time; the most practical and most delicate test of the absence of free chlorine in the cold solutions is the sense of smell. The assays should not be boiled below 150 c.c. as a matter of precaution, on account of the volatility of chloride of antimony. Allow the assay to cool; when quite cold, fill the flask with CO_2 from a Kipp charged with marble and HCl, add 20 c.c. of a fresh 20 per cent. solution of KI, and titrate as rapidly as possible with stannous chloride. This is made by dissolving 10 grms. of tin, or 20 grms. $SnCl_2$, 2 aq., in 300 c.c. HCl, and diluting to 1 litre. It should be kept under CO_2, and must be standardised every time it is used, against a standard solution of bichromate made by dissolving exactly 16 grms. of pure $K_2Cr_2O_7$ in 1 litre of distilled water. 100 c.c. Bic. = 2 grms. Sb, and 100 c.c. $SnCl_2$ = about 1 grm. Sb. The assays, if overdone, are brought back with the standard bichromate (rapidly), but should only require a few drops at most, otherwise the accuracy of the assay is impaired.

The assays have a great tendency to absorb oxygen, after titration, and reoxidise; hence the necessity for a CO_2 atmosphere and rapid titration, especially in presence of As and Cu. Further, the reaction in the case of As is not instantaneous, and only proceeds to completion as fast as the liberated iodine is reduced by $SnCl_2$—being to some extent reversible. Acid solutions of $AsCl_3$, Cu_2Cl_2, $FeCl_2$, and KI, readily absorb oxygen from the air; $SbCl_3$ is scarcely affected. The bichromate remains quite constant, and it may be standardised against pure iron as a check on the weighing up. In standardising the stannous chloride, pour a little KI solution and starch paste into an 8-oz. flask, fill the flask with CO_2 and run in rapidly, 20 c.c. $SnCl_2$ from the burette. Then titrate rapidly with $K_2Cr_2O_7$.

$$As = Sb = Cu_2 = Fe_2 = O.$$

1 per cent. As = 1.6 per cent. Sb. 1 per cent. Cu = 0.945 per cent. Sb.
1 per cent. Fe = 1.03 per cent. Sb.

HCl solutions of Sb (ic) As (ic) Cu (ic) and Fe (ic) oxides are all reduced by KI to the corresponding —ous compounds, with liberation of an equivalent amount of iodine. These (—ous) solutions, as well as a solution of KI in HCl and of $SnCl_2$, absorb oxygen from the air, and therefore necessitate a CO_2 atmosphere. The solution requires to be more strongly acid in the case of arsenic. $SnCl_4$ is not reduced by KI, hence the liberated iodine may be titrated with $SnCl_2$. In assaying type metal for Sb the assays generally have a slight yellow colour after boiling off all the chlorine. This may be due to either Cu or traces of Fe, but is not due to $SbCl_5$. Rich type metals sometimes contain a little Fe, and a little iron may get in from the file, but it has been proved that any error arising from the use of a file is quite negligible. Alloys of the above class which are rich in As appear, in some cases at any rate, to lose much or most of their As or AsH_3, during the action of HCl. The matter is being investigated, but the possibility of such loss of As may be guarded against by adding solution of $KClO_3$ before the HCl, and by keeping the solution saturated with chlorine until solution is complete.

The arsenic in such alloys may be always estimated by distillation with a solution of $FeCl_3$ and $CaCl_2$ in HCl (see Beringer, "Text-book of Assaying"). According to Mr. A. Gibb, after removing the As as $AsCl_3$ in this manner, the solution, if mixed with $ZnCl_2$ and redistilled yields all Sb (as $SbCl_3$) at 184° C. Since $SnCl_4$ boils at a much lower temperature than either $AcCl_3$ or $SbCl_3$, it seems strange that $SnCl_4$ is not distilled off in this assay, but the probability is that it forms a thick double salt.

The above method is both rapid and accurate, but it requires considerable judgment and experience in performing the titrations. The titration must be done as rapidly as possible, but not too rapidly; it must be borne in mind that the finish is more or less gradual, and especially so in presence of arsenic. Sometimes in running in a rapid stream of $SnCl_2$ the blue colour vanishes, but reappears like a flash the moment after. In such cases, one should go on titrating, as the assay is still unfinished. If the flask is not properly filled with CO_2, after-bluing will take place in any case, and it requires long experience to distinguish in every case between a finished and unfinished titration. Duplicate assays should always be done; the bichromate solution itself should be standardised against pure iron wire, which contains 99.6 per cent. Fe. Take the at. wt. of Fe as 56 and that of Sb 120 in calculating the strength of the bichromate.

B.—Alloys of antimony and iron with arsenic and copper.

(*a.*) The As is estimated by the distillation assay.

(*b.*) The Cu by the usual means.

1.—1 grm. metal. Dissolve in 20—30 c.c. HCl and 1 or 2 c.c. HNO_3 in an 8-oz. flask. Add sodium sulphide till alkaline and pass H_2S. Warm, dilute, and filter. Redissolve the Cu_2S, PbS, FeS, &c., and reprecipitate. Filter, mix the filtrates, and precipitate the sulphides of As, Sb, Sn by cautious addition of HCl. Filter, dissolve the precipitate in 100 c.c. HCl and $KClO_3$. Boil until solution is complete, dilute, filter, add $KClO_3$, and boil off the excess of chlorine. Cool, add KI and titrate with $SnCl_2$, making the equivalent deduction for As.

2.—1 grm. metal, 40—50 c.c. HCl and a little HNO_3. Dilute to 120 when solution is complete, and pass H_2S, thus separating from Fe but not from Cu. Dissolve the precipitate in HCl and $KClO_3$, and proceed as in 1.

C.—Mattes and sulphurous compounds generally, of Fe, Cu, Pb, As, Sb, Sn. Antimony ore, &c. (if impure).

In these the As cannot be estimated by the direct distillation assay, and must be separated. Solution is effected as usual. The sulphides of As, Sb, Sn, obtained by precipitation of an alkaline polysulphide solution with HCl, are filtered and dissolved in 20 c.c. HCl and a little $KClO_3$ and the Cl boiled off. 5 grms. AmCl and

5 grms. $H\overline{T}$ dissolved in 20 c.c. water are added, and then AmOH until the solution is alkaline. (If a precipitate forms on adding AmOH, more AmCl and $H\overline{T}$ are needed.) The solution, which should not be more than 60 or 70 c.c. in bulk, is mixed with 20 c.c. of magnesia mixture and allowed to stand for 24 hours. The Mg, NH_4, AsO_4, is filtered off and the filtrate acidified with HCl, diluted to 1 litre and precipitated with H_2S. Allow to stand in a warm place for an hour or two. Again pass H_2S and filter the sulphides of Sn and Sb. Dissolve the precipitate in HCl and $KClo_3$ as usual. Add KI and titrate with $SnCl_2$.

D.—ANTIMONY ORE (with but little As).—1 grm. ore, 30 c.c. HCl, 2 c.c. HNO_3. Add NaOH till alkaline, as soon as the ore is completely attacked, and pass H_2S. Warm, filter, and wash with hot dilute Na_2S. The precipitate if bulky should be redissolved and reprecipitated. Precipitate the filtrate with HCl, filter, wash with NaCl, boil the precipitate well with HCl alone (As_2S_3 left undissolved), dilute, filter, peroxidise with $KClO_3$, boil off the free chlorine, cool, add KI and titrate with *$SnCl_2$*, or boil off the iodine, cool, add Rochelle salt, neutralise, make alkaline with bicarbonate and titrate with *Iodine*.

E.—OXIDES. Calcined antimonial material. Boil with HCl and $KClO_3$, dilute and filter. (*a*) Dry, ignite, and fuse the residue with NaOH in a silver dish. Extract with HCl and mix with the main solution; (*b*) or reduce the insoluble oxide to metal in coal gas at a very low red heat, or in a small porcelain crucible with KCy, and dissolve the reduced metal in HCl and $KClO_3$, and mix with the main solution. Proceed as in C if arsenic is present or as in B_2 if no arsenic is present.

F.—The electrolytic assay has been already referred to. (See Chapter IV.)

G.—ROUGH VOLUMETRIC ASSAY BY TITRATING PRECIPITATED ANTIMONY WITH $FeCl_3$.

This method is chiefly useful as a rapid approximate determination of antimony in *solder*, and is used as an adjunct of the direct ferric chloride assay of tin in such alloys. It depends upon the fact that $FeCl_3$ dissolves finely divided Sb with the formation of $FeCl_2$ and $SbCl_3$. After pouring off the hot acid solution of $SnCl_2$ from the black powder (see Chapter V., A.), pour on to the latter, immediately, a little hot boiled water to prevent aerial oxidisation of the Sb. When the tin titration is finished, pour back on to the black powder and retitrate. (Cu if present is also converted into Cu_2Cl_2—as soon as any $CuCl_2$ is formed it gives the colour indication.) The percentage of Sb is two-thirds of the apparent tin percentage, equivalent to the extra ferric chloride used—in absence of copper.

H.—VOLUMETRIC ASSAY BY DISSOLVING PRECIPITATED SB IN H_2SO_4 AND TITRATING WITH $KMnO_4$.

Useful for *type metal* and *solder*. Cu does not interfere, but As should be absent. The method is used as an adjunct of the iodine tin assay. The antimony adhering to the iron rod is washed off, allowed to settle, and the liquid decanted into another beaker; the residue washed by decantation with hot dilute HCl and the washings added to the rest of the tin solution, which is again reduced before titration. The precipitated Sb and Cu are heated with a few c.c. of strong H_2SO_4 until solution is complete and white fumes evolved. Then cooled, diluted, and titrated with $KMnO_4$.

$Fe_2 = Sb$.

K.—Titration of Sb_2O_3 in alkaline bicarbonate solution with iodine. (Mohr's method.) This is a useful assay in the absence of Cu, and is fully described in Sutton's "Volumetric Analysis."

L.—SOLUTION OF PRECIPITATED ANTIMONY IN $FeCl_3$ AND TITRATION WITH $K_2Cr_2O_7$ OR $KMnO_4$.

This method may be useful as an adjunct of the iodine tin assay as in H, and is useful for *type metal* and *solder* in the absence of copper. The precipitated Sb is dissolved in a small basin in a few c.c. of $FeCl_3$ and HCl (free from $FeCl_2$), and the solution titrated with bichromate until all the $FeCl_2$ is peroxidised, using spots of ferricyanide indicator on a plate.

$$3\ FeCl_3 + Sb = SbCl_3 + 3\ FeCl_2$$
$$3\ FeCl_2 + 3\ HCl + O1\tfrac{1}{2} = 3\ FeCl_3 + 1\tfrac{1}{2}\ H_2O.$$
$$SbCl_3 + 2\ HCl + O = SbCl_5 + H_2O$$

That is to say, when dissolving antimony in $FeCl_3$ and titrating with $K_2Cr_2O_7$, Sb requires altogether $2\frac{1}{2}$ O, or is equivalent to 5 Fe in terms of the strength of the bichromate solution when standardised by titrating FeO to Fe_2O_3.

Although $FeCl_3$ does not oxidise $SbCl_3$, yet the $SbCl_3$ is all oxidised by the Bic. *before* the $FeCl_2$; before the disappearance of the $FeCl_2$ is shown by the spot indications which is taken as the finish of the titration. The development of the colour is, however, slow towards the finish. $SbCl_3$ will reduce the brown solution obtained by mixing $FeCl_3$ and K_3FeCy_6 with formation of Prussian blue. Indeed, $SbCl_3$ may be thus titrated with Bic., using ferric ferricyanide solution as an outside indicator, or $FeCl_2$ as an inside indicator and K_3FeCy_6 as outside indicator. When $KMnO_4$ is used, the $SbCl_3$ is also oxidised in the titration as well as the $FeCl_2$. The above method is not to be recommended except for rough purposes, as it is hard to wash pptd Sb (by iron) free from $FeCl_2$ without redissolving some Sb by aerial oxidation.

M.—DRY ASSAY OF ANTIMONY.

1.—Antimonial litharge.

(*a*) 50 litharge roughly pounded,
10—15 soda ash, 10—15 charcoal,
5 borax, and a little fluor.
or (*b*) 50 litharge,
50—100 cyanide,
10 argol.

In either case fuse in a clay crucible at a moderate heat, and assay the button for *Sb*.

2.—Sulphide Ore.—This if mixed with much gangue should be concentrated by liquating 1,000 grams in a double luted crucible.

Fuse 25 grms. ore, 5 soda,
12 grms. iron filings, 5 borax,
in an E crucible, and assay the button, which should contain Fe, for antimony.

3.—Type Ashes—usually carbonaceous.—Fuse with 15 to 20 per cent. soda ash and a little ferrocyanide and borax. Melt the button away from iron shots in a ladle, and pour into a hemispherical mould. Assay the metal for tin and antimony.

N.—ASSAY OF ANTIMONY IN PRESENCE OF ARSENIC AND TIN (without separation).

We have seen that Sb may be estimated with $SnCl_2$ in presence of $SnCl_4$ and As_2O_5 by titrating the iodine liberated from KI in HCl solution and deducting the equivalent of the As_2O_5 present. It is, however, possible to estimate Sb by direct titration with $SnCl_2$ in a fairly strong and hot, but not too strong HCl solution; in such a solution arsenic acid is not affected at all until all the $SbCl_5$, $FeCl_3$, and $CuCl_2$ have been reduced, and therefore if we titrate until the colour goes we have the measure of the Sb + Fe + Cu. This method may be applied to type metals, which contain only traces of Fe, and usually under 1 per cent. Cu. The Cu must be known and deducted for, but it serves the purpose of an internal colour indicator. The method is beautifully simple and rapid, as the Cu may be estimated with sufficient accuracy in type metals and most anti-friction metals in a few minutes. In the case of solders, which are, as a rule, free from Cu or Fe, a drop of $FeCl_3$ is added to the assay as an indicator. With regard to the accuracy of the method, there can be no doubt that it is sufficiently accurate for most commercial purposes.

N 1.——RAPID DETERMINATION OF ARSENIC, ANTIMONY, AND TIN in alloys, or when separated together as sulphides.

1.—The tin is determined in the usual way; solution in HCl and $KClO_3$, separation of Sb and As on iron wire, filtration, precipitation with zinc, solution in HCl, and titration with ferric chloride. Add 5 per cent. of the arsenic percentage.

2.—The antimony is determined by solution in HCl and $KClO_3$, boiling off the excess of chlorine, and titration of the hot solution with $SnCl_2$. In absence of Cu (the amount of which must be known and allowed for), add a drop of $FeCl_3$ as an indicator.

3.—The arsenic is determined by (*a*) distillation with $FeCl_3$ and $CaCl_2$ in HCl, and titration of the evolved arsenic with iodine in alkaline bicarbonate solution; (*b*) sulphides are dissolved in HCl and $KClO_3$, the solution concentrated and distilled with a ferric chloride mixture containing also ferrous chloride, the evolved arsenic being estimated as before by titration with iodine in an alkaline bicarbonate solution; (*c*) or the solution of sulphides in HCl and $KClO_3$, from which the free chlorine has been driven off, is boiled with copper foil, which, with the precipitated Sb and As is afterwards distilled with ferric chloride mixture. The determination of the three metals in an alloy should not take more than 2 hours by these methods.

3*a*.—Or, better, the fine filings are dissolved by slow digestion with HCl and $KClO_3$ in a warm place, keeping always present a slight excess of free chlorine. When solution is complete, add a little more chlorate, dilute, boil off the chlorine, cool, add KI and titrate with $SnCl_2 = As + Sb$.

APPENDIX.

At the suggestion of the Cornish Correspondent of "The Mining Journal," and with the permission of the Editor of that paper, we subjoin a table showing a series of analyses of Cornish tin ores. Part of the article which accompanied the table in question, and which appeared in "The Mining Journal" for August 19, 1905, is also given herewith. The analyses were done by the writer of this book:—

These analyses were carried out by Mr. L. Parry, A.R.S.M., Assayer and Consulting Metallurgist, of Union Bank Yard, Huddersfield.

The wet assay adopted for tin is the one given in Mr. Parry's book, "The Assay of Tin and Antimony"—viz., reduction in a current of coal gas combined with a volumetric estimate of the tin.

In the cyanide assays the ores were extracted with *aqua regia*, and the solutions were tested for tin. In one or two cases a little tin (under .25 per cent.), was found in these solutions, and is included in the results given. The cleaned residues were reduced with cyanide (98 per cent. Au*), in clay crucibles. The assays were done on 20 gram charges, and the buttons of metal obtained were assayed for tin by the same volumetric method employed in the wet assays. The net cyanide percentages thus obtained average 1½ per cent. under the wet assays.

It is possible, by adopting a different procedure, to arrive at results by the cyanide assay that will more closely approximate to the wet assay than those given above. The ores, either cleaned with *aqua regia* or not, are reduced with cyanide in porcelain crucibles in the muffle, 5-gram portions being taken for assay. When the fusion is complete, the assays are cooled, and the crucibles and contents are boiled in water until the cyanide and cyanate of potassium are dissolved out. The residue is then extracted with HCl, and the tin in the solution then determined volumetrically. Although rather better results are obtained, the assay is more tedious, and there is little saving of time over the wet assay, whilst there always remains the possibility of tin being lost as alkaline stannate. In cyanide

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* "98 per cent. Au" is the trade mark of the purest cyanide made, which is used for electro-plating, hence the "98 per cent. gold." This cyanide holds 98 per cent. of pure KCN.

assays the cyanide should be finely powdered and well mixed with the ore, otherwise some of the ore is liable to escape reduction.

The wet assays were done throughout in duplicate. The arsenic and antimony were estimated in the *aqua regia* extract, and the results thus obtained are likely to be somewhat under the actual contents. The iron, silica, and tungstic acid were merely determined approximately. The crop ores having already been roasted, were not assayed for sulphur, but the unroasted slimes, Nos. 2, 5, 7, 8, and 11, were all rather strongly attacked by HNO_3, and were, therefore, assayed for sulphur.

It has been necessary to detail the tests made for the simple reason that the majority of our mine managers, and others who control the industry—apart from the smelters—will now, for the first time, secure reliable data as to the actual constituents of the black tin they have so long handled, and sold on an assay (Cornish method), which, to put it mildly, affords only sufficient indication of values to keep the buyer from blundering. In this connexion, the necessity for assaying the buttons obtained, by the cyanide method, for tin—that is, for purity of metal—was amply demonstrated. Notwithstanding the cleaning with *aqua regia*, only seven out of nineteen buttons—viz., Nos. 1, 3, 4, 14, 15, 18, 19—were pure tin. The others varied from 96½ to 99 per cent. Sn, with the exception of Nos. 9, 10, and 11, which came out 90, 92½, and 93½ per cent. Sn, respectively. The balance of the buttons was iron, showing that it is not possible to extract all the FE_2O_3 from all ores direct by extraction with *aqua regia*. The percentage weight of the buttons was greater than the actual tin percentages shown by wet assay in the cases of Nos. 6, 8, 10, 11, and 12, which held 96½, 90, 92.5, 93.6, and 97.2 per cent. Sn respectively. In Cornwall the purity of the metal produced does not much trouble the seller of black tin. Later on the importance of paying some attention to this matter may be deemed worthy of the consideration of every mine manager in the county, and more especially of those whose products, as indicated by the above table, call for special treatment.

1		2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
No.	Description.	Tin Wet Assay %.	SnO₂. Equivalent to Wet Assay of Sn.	Tin Cyanide net—includes Wet Assay of Buttons for Sn.	Difference between Cyanide and Wet.	Cu %.	As %.	Sb %.	S %.	WO₃ %.	SiO₂ %.	Fe %.	Fe₂O₃. Calculated from % Fe less % Fe as FeS₂.	FeS₂. Calculated from % of S.	Total Sum of 3, 6, 7, 8, 10, 11, 13, 14.	Remarks.
1	Dolcoath No. 1 (Crop) ...	71.6	90.9	69.75	— 1.85	*t*	*t*	*s t*	*n t*	0	4½	2	2.9	...	98.3	Trace of Cobalt.
2	" 2 (Slimes) ...	60.5	76.7	58.65	— 1.85	.1	*t*	*s t*	.6	0	7	7½	10.0	1.1	94.9	Trace of Cobalt and Zinc. Unroasted Slimes.
3	Wheal Grenville A (Crop) ...	72.5	92.0	71.0	— 1.5	*t*	*t*	*s t*	*n t*	0	4½	1½	2.2	...	98.7	
4	" B (Crop) ...	71.25	90.4	70.25	— 1.0	.2	*t*	*s t*	*n t*	0	5	1¾	2.5	...	98.1	
5	" No. 2 (Slimes).	59.9	76.0	57.05	— 2.85	.5	*t*	*s t*	.9	0	12	6	7.5	1.7	97.6	Trace of Cobalt. Unroasted Slimes.
6	Carn Brea No. 1 (Crop) ...	65.1	82.6	63.75	— 1.35	.4	.2	*s t*	*n t*	2½	5	6	8.6	...	99.3	A little MnO.
7	" 2 (Slimes) ...	58.0	73.5	56.0	— 2.0	1.4	*n t*	*n t*	1.0	0	6½	12	15.7	1.9	99.0	Slimes Unroasted.
8	" 3 (Slimes) ...	58.5	74.2	55.6	— 2.9	1.5	1.2	.25	1.0	0	5	12	15.7	1.9	99.75	Slight trace of Cobalt. Unroasted Slimes.
9	Basset No. 1 (Crop)	71.6	90.8	70.4	— 1.2	.1	*t*	*s t*	*n t*	0	3	2¼	3.2	...	97.1	
10	" 2 (Slimes) ...	62.0	78.7	60.8	— 1.2	.15	*t*	*s t*	*n t*	0	6	7½	10.7	...	95.5	
11	" 3 (Slimes) ...	64.8	82.2	63.5	— 1.3	1.8	.2	*t*	1.2	0	4	7½	9.3	2.2	99.7	Unroasted Slimes.
12	East Pool A (Crop)	67.25	85.3	65.6	— 1.65	.2	.25	*t*	*n t*	1—2	6	3½	5.0	...	98–99%	A little MnO.
13	" B (Crop)	67.1	85.1	65.9	— 1.2	.2	.3	*t*	*n t*	5	6	1¾	2.5	...	99.1	A little MnO and slight trace of Cobalt.
14	Levant No. 1 (Crop)	73.1	92.7	72.0	— 1.1	.15	.1	*t*	*n t*	0	1¼	3½	4.4	...	98.6	Trace Zinc.
15	West Kitty (Crop)	72.4	91.8	71.2	— 1.2	.1	*t*	*s t*	*n t*	*t*	5½	¾	1.0	...	98.4	Trace Zinc.
16	South Wheal Crofty (Crop).	64.7	82.1	62.8	— 1.9	.3	.75	*s t*	*n t*	1—2	6	3½	4.4	...	95.5	Trace Cobalt, Zinc, Mn.
17	Clitters United (Crop) ...	68.25	86.6	67.5	— .75	.15	.2	...	*n t*	2½	3	2	2.9	...	95.5	A little MnO. Trace Zinc.
18	Commerce (Crop)	76.5	97.1	76.0	— .5	0	*t*	...	*n t*	*s t*	1½	½	.7	...	99.3	Very pure Ore.
19	Wheal Kitty (Crop)	71.75	91.0	70.75	— 1.0	*t*	*t*	...	*n t*	0	6	1¼	1.6	...	98.6	Trace Zinc.
	Average	67.2	85½	65.7	— 1.5	.34	...	...	...	...	5	4½	6	In Slimes. 2.0		

N.B.—*t* means "trace." *s t* "slight trace." *n t* "not tried." One or two of the Ores probably hold a little Alumina.

Average Tin in Crop, 70.2 % Average Tin in Slimes, 60.5 %. SnO_2 contains 78.8 % Sn.

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