

the same ore, each scorifier containing 50 to 100 grains of ore and the resulting buttons of lead placed in one scorifier and re-scorified until the lead is reduced to a sufficiently small bulk for cupellation. The quantity of lead required varies with the nature of the gangue. Argentiferous and auriferous lead ores only require five times their weight of lead, while arsenical and pyritic ores require fifteen or sixteen times their weight. The following table may be used as a guide:—

Quartzose, - - - - -	8
Basic (oxides), - - - - -	8
Lead ores, - - - - -	5
Arsenical and antimonial, - - - - -	16
Fahl ore, - - - - -	12 - 16
Pyritic ores, } - - - - -	10 - 15
Blende, }	

The borax must be used very sparingly, in just sufficient amount to form a liquid slag, or it may form a crust over the ore and lead, preventing oxidation. It is better to add a few grains at first, and the remainder at intervals as the process advances.

#### ASSAY OF TIN ORES, Etc.

§ 142. The tin of commerce is obtained from its oxide, known as cassiterite or tin-stone, which may generally be recognised by its appearance and high specific gravity which varies from 6.3 to 7.1 in good specimens. When pure, it contains 78.62 per cent. of tin. Tin pyrites is of a yellowish grey colour with strong metallic lustre, having a specific gravity of 4.35, but does not occur in sufficient quantities to be used for extracting the metal on the large scale. It is chiefly found mixed with other sulphides. The following analyses show the composition of good specimens of tin ores:—

Cassiterite.		Tin pyrites.	
Tin, - - - - -	77.50	Tin, - - - - -	27.55
Oxygen, - - - - -	21.50	Copper, - - - - -	29.39
Ferric oxide, - - - - -	0.25	Iron, - - - - -	12.44
Silica, - - - - -	0.75	Sulphur, - - - - -	29.64

Tin ore as taken from the lode contains from 2 to 5 per cent. of cassiterite, which is often associated with one or more of the following bodies:—Quartz felspar, chlorite, schorl, and other stony minerals, mispickel, iron and copper pyrites, iron oxide and wolfram. Cassiterite, having a high specific gravity, is separated from its gangue by a series of washings, which remove the lighter materials. The mispickel and pyrites are converted into oxides by roasting and removed by a subsequent washing. The concentrated product is known as "black tin" (varying from 60 to 72 per cent. of pure tin), and the common impurities are silica, copper and iron oxides, and wolfram. In certain stream tin ores there may be as much as 7 per cent. of titaniferous iron ore.

(a) Before any variety of tin ore is assayed it is necessary to separate the oxide from its associated gangue, which is very skilfully accomplished by an experienced person on a "vanning shovel" (Fig. 23). For this purpose the ore is very finely crushed and sifted so as to obtain all the particles of the same size. The amount of ore taken for the purpose varies with the richness. With poor ores an ounce or 250 grains may be taken; with rich ores half or even a quarter of this amount is used. The weighed portion of ore is placed on a vanning shovel. The vanner stands in front of a tub of water, and allows a little water to run on to the ore. He then raises the shovel a little above the surface of the water, and, holding it nearly horizontal, imparts to it a circular motion until the whole is brought to the centre: by this motion, too, the lighter portions will travel to the top and the



heavier ore pass to the bottom. The top finer mud is then run off. This is repeated until the water standing for a moment is tolerably clear. Water is again added, and the shovel is rotated, the workman imparting to it an elliptical motion at the front and back positions. Besides the elliptical motion, at certain points a jerk is added in one direction throwing the earthy matter forward and the heavier minerals backwards. This jerk is produced just as the wave of water is returning so that it carries forward the lighter matter, whilst the heavier portions at the bottom are hardly affected by it, but the jerks gradually throw them backwards. When the washing is complete the residue is dried on the shovel, then transferred to a hot crucible and roasted till free from sulphur. The roasted mass is then put on the shovel again, the hard particles rubbed to powder by a clean flat hammer-head, the adhering particles washed from the hammer, and the vanning repeated until everything except the tin oxide is, as far as possible, removed. The cleaned ore is dried, freed from particles of iron by a magnet, and weighed. By this means a close approximation to the real amount of tin present in the ore can be ascertained. A complete set of appliances for vanning purposes will include a shovel (Fig. 23) having a bent deal handle, 3 feet long; a bruising hammer weighing  $2\frac{1}{2}$  pounds; two sets of scales and weights, one for heavy weights, the other for weighing the "black tin"; a furnace such as shown in Fig. 1; and a water box, 4 feet long, 2 feet 6 inches wide, and 8 inches deep.

§ 143. *Assay of Tin Stone* (Cornish method).

For this purpose take 12,000 grains of washed ore as delivered by the miner; grind in an iron mortar, and pass through No. 60 sieve. Well mix; remove 5000 grains, and pass the whole of this through a sieve with 80 meshes to the inch.

(a) Weigh out 1000 grains of oxide, and 200 grains of

anthracite powder which has also been passed through No. 80 sieve; place in a plumbago crucible which should be smooth inside (those sold by Messrs. Morgan of Battersea are especially suitable for this purpose), and put well down in the furnace. Gradually raise the temperature as the operation proceeds; in about twenty minutes remove the crucible, and rub down the inside with a piece of wood to remove any adhering particles of metal or oxide, replace in the fire and heat strongly for another ten minutes; then withdraw, impart to the pot a circular motion to collect all the metal in one mass, scrape the excess of anthracite and slag to one side and pour the metal into a rectangular mould, Fig. 17g, by which means a strip is produced long enough to test its physical properties, such as the character of the "cry" when bent, its softness, malleability and fracture when broken. After pouring the metal, the residue must be thoroughly scraped out of the pot; the particles of carbon, etc., ground very fine in an iron mortar, and any particles of metallic tin picked out and added to the main portion. The residue is then sifted and vanned on a shovel, or it may be placed in a porcelain or similar dish, and a gentle stream of water allowed to run on, by which the carbon, etc. is washed away. The dry residue is mixed with an equal bulk of carbonate of soda, placed in a small clay crucible (not plumbago), and fused for ten minutes. Now pour into mould; powder the slag and pick out any shots of metal, which must be weighed with the main quantity obtained in the first smelting. The weight divided by ten gives the percentage of black tin. In Cornwall the results are generally expressed in cwt. per ton of ore. A small quantity of borax or fluor-spar is occasionally used to flux refractory slags.

(b) To get a better idea of the quality of black tin; it may be re-melted and allowed to remain in the pot after removing from the fire until the scraped surface ceases



to oxidise, then poured into a rectangular mould made of marble and allowed to cool undisturbed. If pure, the surface will be bright, smooth, rounded at the sides, and free from spots. (See § 25.) A frosted appearance indicates the presence of iron, copper, zinc, lead, antimony, etc. Low quality ores containing these metals, in combination with arsenic, sulphur, and oxygen, will give too high results, as they are reduced and alloy with the tin.

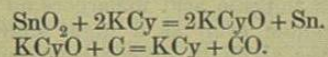
(c) A purer assay product from the above process may be obtained as follows:—Place 1000 grains of ore in a porcelain dish; moisten with hydrochloric acid, and add sufficient water to cover the powder. Heat gently for half an hour; fill up with hot water; filter; wash once or twice; dry the residue; mix it with anthracite, and smelt as before. If wolfram be present in the ore it increases the apparent amount of tin. It may be removed by boiling the assay sample in aqua-regia and dissolving out the tungstic acid, which has been liberated, by means of ammonia.

§ 144. *Assay of Tin Ores containing Silica, as Tin Slags.*

This assay is conducted on the principle, that iron displaces tin from its combination with silica, forming silicate of iron and metallic tin. If, however, the iron be in excess, an alloy of tin and iron will be formed, but the slag will be free from tin. Take 500 grains of ore, 200 grains of forge scales or hematite, 100 grains fluor-spar, and 100 grains of anthracite powder, place in crucible and cover with lid. Heat for half an hour moderately, then for another half hour at the highest temperature of the furnace; remove crucible from fire; allow to cool; break open the pot; remove slag, and clean the button of tin. The amount of pure tin in the button can only be obtained by a wet method.

§ 145. *Assay of Tin Oxide by fusion with Potassium Cyanide.*

This re-agent is expensive when pure, and very objectionable from its poisonous nature, and the obnoxious fumes liberated when it is heated. The common variety is more effective as a reducing agent because it contains potassium carbonate. When used alone, 100 grains of oxide require 500 to 600 grains of the cyanide, so that the following mixture may be substituted with economy and good results: 100 grains ore, 200 grains common cyanide, 30 grains charcoal. It is well to place a little cyanide in the bottom of a small clay crucible, then add the ore mixture (the cyanide need not be crushed to powder); place in a fire at low red heat for ten minutes, then increase the temperature for another five minutes; remove from furnace and pour into a half-round mould. Allow to cool; detach the button of tin; wash away any adhering slag, and weigh. The following equations show the reactions:—



A purer button of tin may be obtained by a previous digestion with dilute hydrochloric acid as in § 143 (c). The results obtained by this method are accurate and the assays rapidly performed, but the quantity of tin obtained is too small to test its physical properties, which are such reliable guides to the operator as to the quality of the tin. A Cornish sample of oxide of tin was submitted to assay by the anthracite method and by the cyanide method with the following results:—

	Tin.	Tin.
With anthracite, and 1000 grains ore,	71·0%	71·5%
With cyanide and carbon, and 100 grains of ore,	72·0%	72·0%

The former method after treatment of ore with dilute



hydrochloric acid yielded 71.0 per cent. of tin, and the latter method, 72 per cent. It will be seen by these results that with good tin oxide the cyanide method yields a higher result, especially as the button is free from oxide, while the ingot obtained from the anthracite method is covered with a black scale of oxide.

§ 146. *Assay of Ores containing Tungsten, Arsenic, and Sulphur.*

(a) When tungsten is absent, the ore, after crushing very fine, is roasted in a clay dish, with frequent stirring, until all volatile matter is removed, by which means the arsenic and sulphur are largely removed and the tin left as oxide, which can then be assayed by one of the foregoing methods.

(b) Tungsten is present. Weigh out 200 grains and roast until as free as possible from sulphur and arsenic. Place in a crucible and reduce by the potassium cyanide method. The tungstic acid undergoes no reduction by potassium cyanide even at a high temperature, but unites with the alkali to form a compound soluble in water. The amount of tungstic acid may then be estimated by a wet method.

The following is an example of the composition of "black tin."

Tungstic oxide, - - -	1.5
Tin oxide, - - -	72.1
Silica, - - -	4.6
Titanium oxide, - - -	.8
Copper oxide, - - -	1.0
Ferric oxide, - - -	18.6
Sulphur, - - -	.6
Arsenic, - - -	.3
	<hr/>
	99.5

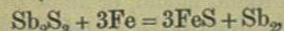
ASSAY OF ANTIMONY ORES.

§ 147. For the purposes of assay, the ores may be divided into two classes, viz., those which contain sulphur and those free from sulphur, such as oxides. The former are by far the most abundant and are generally associated with iron, lead, zinc, silver, quartz, and sulphate of barium. They have a lead grey colour and give a similarly coloured streak. The formula of the pure sulphide is  $Sb_2S_3$ .

§ 148. *1st Class.—Sulphides.*

(a) These may be assayed by roasting to oxide and reducing with carbonate of soda and carbon, or by direct reduction with metallic iron as in the case of galena. The roasting must be conducted at a low red heat, otherwise the ore will fuse and sublime, and with constant stirring to prevent the particles clotting together. The operation takes about three quarters of an hour, being complete when no further odour of sulphur-dioxide is perceived.

(b) The direct method is preferable to the foregoing, both on account of economy of time and the less liability to loss, but a series difficulty will arise if certain precautions are not attended to. When sulphide of antimony is heated with iron in amount according to the following equation,



the whole of the antimony is set free, but if the iron be in excess, an alloy of antimony and iron will be formed. Now sulphide of iron has a density only a little less than that of antimony, so that complete separation of the two bodies can only take place by keeping the contents of the crucible for a considerable time in a state of fusion, by



which means the white crystalline button of antimony remains at the bottom, covered with the bluish-yellow iron regulus. It is better to let the crucible cool and then break to remove the metal from the slag button.

Assuming the ore to be pure sulphide of antimony, 50 grains of iron will be required for each 100 grains, producing theoretically 71.43 grains of antimony; but 60 to 65 grains is about the amount practically obtained, the loss being due to volatilisation.

(c) A rough estimate of the amount of sulphide of antimony in stibnite may be obtained by liquating it from the earthy and siliceous gangue with which it is associated. Place the lid of a clay crucible or the side of a broken crucible in an inclined position on a tripod stand, and on the top, 100 grains of ore. Heat from beneath by means of a large Bunsen burner and allow the fused sulphide to flow into a weighed vessel, then cool and weigh the liquated sulphide. Instead of the above, the apparatus Fig. 47 may be employed.

(d) Suppose 50 per cent. of sulphide present, then the following mixture may be used for the assay:—

200 grains ore, 35 grains clean iron filings or thin iron wire cut up very small, 50 grains carbonate of soda, and 10 grains charcoal. Place in a black lead or a brasqued crucible; cover with lid or a piece of coke and heat moderately for fifteen minutes, then raise the temperature for another quarter of an hour; remove from fire and pour into a half-round mould, or allow to cool and break the pot as before described. Carefully detach slag and regulus, and weigh the white crystalline button of metallic antimony.

(e) Antimony sulphide may also be assayed by mixing 50 grains of ore with 200 grains of potassium cyanide and heating in a clay crucible. The reduction takes

place at a low temperature, so that by proper management very little antimony is lost by volatilisation.

§ 149. *2nd Class.—Oxides and Bodies nearly free from Sulphur.*

Oxide of antimony is readily reduced at a low temperature by heating it in a clay crucible with 6 to 8 per cent. of charcoal, but 5 to 6 per cent. of the metal is lost by volatilisation.

When the oxide is associated with earthy matter a suitable flux must be added. As the gangue is generally siliceous, 100 grains of ore may be fused with 100 grains carbonate of soda and 5 grains charcoal in a clay crucible. When the liquid mass remains tranquil, remove from fire, allow to cool, break crucible, and detach the button of antimony. The slag must be broken up carefully and any shots of metal picked out. When a little sulphur is present add 1 or 2 grains of iron wire to the ore mixture. When oxides of iron and other metals are present, they will also be reduced and alloy with the antimony.

#### ASSAY OF ZINC ORES, SLAGS, ETC.

§ 150. Zinc is generally found in nature associated either with oxygen, carbonic acid, silica or sulphur, and for the purposes of assaying may be divided into three classes:—

- (1) Oxides, including carbonates.
- (2) Silicates.
- (3) Sulphides, including all ores containing sulphur.

The dry assay is troublesome and uncertain, because the compounds require a high temperature for their reduction, and zinc being highly volatile can only be obtained by a process of distillation; also, the metal not being concentrated in the form of a button, is



contaminated with oxide and any volatile matters present in the ore.

§ 151. *Class I.—Oxides, etc.*

1000 grains of ore, previously crushed very fine and passed through a sieve with eighty holes to the linear inch, are mixed with 200 grains of finely powdered anthracite and introduced into a hot fire-clay retort, having a moderately wide neck, the body of which is placed in a hot furnace; the outer end of the neck is connected with a glass tube which is luted to make the joint air-tight. The reduction is by this means perfect, but the difficulty consists in recovering the metal from the neck of the retort, even when broken, and in ensuring the freedom of the powder from oxide and other impurities. The neck of the retort should be as smooth as possible and thoroughly blacklead, otherwise the reduced metal will cling very tenaciously to it. Moreover the proportion of oxide mixed with the reduced metal is larger the smaller the quantity of ore submitted to assay.

The charge having been introduced and the glass tube attached, the retort is placed in the fire and gradually raised to the highest temperature attainable, which should be a white heat inside. The reduction is then complete, and the reduced metal will be found nearer the bottom of the neck the higher the temperature employed. When the neck is narrow it is very liable to be choked up by the condensed metal, so that it must occasionally be opened by means of an iron rod to insure a free passage, or an explosion may take place.

When complete, the apparatus is allowed to cool, the neck broken off, and the zinc scraped out for weighing. The true amount of zinc may be obtained by digesting the deposit, and any pieces of the retort containing metal in hot nitric acid, which dissolves zinc and its oxide. The solution is then evaporated to dryness,

heated to redness, and the oxide weighed;  $\frac{1}{31}$ ths of which is oxygen, and  $\frac{2}{31}$ ths zinc, which approximately equals  $\frac{1}{15}$ ths.

§ 152. The amount of zinc in pure ores may be estimated by the difference in weight after strongly heating with carbon. 100 grains of finely sifted ore are well mixed with 20 grains of charcoal, also finely sifted, placed in a blacklead crucible, covered with a lid, and rapidly raised to a white heat. When zinc vapours cease to come off, the crucible is removed and the residue collected. The loss indicates the amount of zinc oxide; but, as some carbon remains, this residue must be roasted to remove it, and any residue weighed. The loss in weight multiplied by  $\frac{4}{5}$  gives the zinc.

§ 153. *Class 2.—Silicates.*

Silicates are reducible by carbon the same as oxides, but sufficient basic flux, such as lime, magnesia, and fluor-spar, must be added to unite with the silica. Take 500 grains ore, 100 anthracite, 25 lime, and 25 fluor-spar for the distillation method.

§ 154. *Class 3.—Sulphides, etc.*

Zinc blende, having the formula  $ZnS$ , contains 66.34 per cent. of zinc when pure, but it is generally associated with sulphide of iron, and often with galena. The sulphide of iron imparts to it a black colour, hence its name of "Black Jack." A sample examined by Berthier contained Zn 61.5, Fe 4, S 33, earthy matter 1.5. The ore is crushed very fine and sifted as usual. Then take 1000 grains and roast in a roasting dish placed in a hot muffle until all possible sulphur is expelled, finishing at a high temperature to decompose any sulphate. It requires about three quarters of an hour to roast sweet, but needs very little attention, except occasional stirring, as there is little tendency to clot unless an abnormal



amount of sulphide of lead is present. The oxide thus formed is then assayed by distillation in a retort as explained in § 151, or estimated by "difference."

§ 155. *Difference Method for Blende.*—Weigh out 100 grains of sifted ore, and roast sweet. Re-weigh; then mix with 20 grains of charcoal, and heat rapidly to whiteness in a covered blacklead crucible. When all zinc vapours cease to come off, remove from fire; cool, and extract the residue. Roast again for about fifteen minutes until all excess of carbon is burnt off and any reduced iron is oxidised; cool, and weigh the residue. The method of calculating result is as follows:—

Ore taken = 100.	After 1st roasting, 84 = oxides.	
	,, 2nd ,, 16	
	Loss of zinc oxide, 68	

Multiply by  $\frac{4}{5}$ ths.  $68 \times \frac{4}{5} = 54.4 = \text{zinc.}$

The above method can only be approximately correct with pure ores, and with mixed ores it is useless, except as a rough preliminary assay.

§ 156. The following modification is much more reliable and with many ores is as exact as the wet methods. The operation is performed in a brasqued crucible, precisely as in an iron assay.

Weigh out 100 grains of finely sifted ore as before, and roast sweet. Weigh the oxides formed, and note the weight. Mix with 5 grains lime and 5 grains powdered glass free from lead. Introduce the ore mixture into the lined crucible; close the hole with a charcoal plug, and lute on the lid with clay. Then fasten the crucible to a piece of brick; place in bottom of hot furnace; fill up with small coke, and heat strongly for an hour. Allow the fire to burn down; remove the crucible,

and when cool break it open to obtain the button of slag and iron. Both are then weighed, all shots of iron collected and weighed separately—the difference gives the slag. Then calculate the amount of oxygen the iron has lost and add it to the weight of iron obtained. The oxide of iron plus the slag is then deducted from the roasted substance, and the difference gives the oxide of zinc. Also, by deducting from the weight of slag the amount of flux added, the quantity of gangue and non-reducible oxides is ascertained.

The following experiment by Berthier shows the method of calculating the result:—

100 parts of ore after calcining,		= 83.3
10 ,, China clay,		= 10
4 ,, lime,		= 4
		97.3
Metal obtained, -	45.3	} = 61.3 } = 80.7
Slag, -	16.0	
Amount of oxygen, -	19.4	
		16.6
Fluxes added, -	-	14
Earthy matters, -	-	2.0

#### ASSAY OF MERCURY ORES.

§ 157. The principal ore of mercury is cinnabar (HgS). Considerable quantities of mercury occur native; also in combination with chlorine and iodine.

The dry assay of mercury ores somewhat resembles that of zinc, the metal being estimated by distillation, and in the case of fixed earthy matter, by difference. In all cases the substance must be reduced to a fine



state of division, and passed through a sieve with eighty holes to the inch.

§ 158. (1) *Method by Distillation.*

In the case of native mercury the metal is distilled by simply heating the raw substance in a clay or iron retort placed in a furnace, the outer end of which is connected with a glass tube drawn out fine at its extremity or passed into a glass flask, the outer side of which is kept cool by a current of water, or similar means of condensation. If small quantities, say 50 to 100 grains, are operated upon, then a closed hard glass tube about twelve inches long and of half inch bore, heated by gas, is most convenient.



(a) The substance is introduced at the end *b c*, which is afterwards drawn out with the blowpipe, as in the figure. The heat must be so regulated as to drive the whole of the metal from *a* into the part *b c*, which is cut off when cold and weighed. The mercury is then rinsed out, the tube dried, cooled, and again weighed. The difference between the two weighings gives the mercury.

(b) In the case of cinnabar the end *a* may be left open and fitted with a cork having a hole through which a small glass tube is passed. The contraction at *b* is loosely plugged with asbestos, so as to allow a free passage of vapour, while it prevents any solid matter passing into *b c*. Powdered quicklime is first introduced and pushed to the end *b* by means of a glass rod. Now mix 50 grains of the ore dried at 100°C. with slaked lime, and place in the middle of tube; then fill up with lime, and attach the cork and glass tube. Then connect this with a gas tap; pass a gentle stream of coal gas or dry hydrogen, and heat the tube by means of a gas or

charcoal furnace. The former is more convenient, as the end *b* can be warmed first, and the heat gradually carried to the ore mixture. As the temperature rises the mercury sulphide is decomposed, the metal being carried forward by the gas into the drawn out part *b c*, which is kept cool, and there condensed together with a little water; but the latter is carried out by the continual stream of gas. The tube is then allowed to cool, the end cut off and weighed as before. If any of the condensed mercury cannot be removed with water it must be treated with nitric acid, washed out clean with water, and the mercury estimated by the wet way.

§ 159. (2) *Method by Difference.*—Cinnabar when in combination with fixed earthy matter may be roughly estimated by heating 100 grains of the dry ore in a covered crucible for fifteen minutes at a strong red heat; then remove from fire; allow to cool, and weigh the residue. The difference indicates the amount of mercury sulphide volatilised. HgS contains 86.25 per cent. of mercury.

#### ASSAY OF BISMUTH ORES.

§ 160. This metal occurs native, frequently containing small quantities of arsenic, and often associated with silver, sometimes with iron and other metals. It also accompanies various ores of silver, copper, lead, zinc, nickel, and cobalt.

The other ores of bismuth are the oxide, sulphide, silicate, and carbonate. It is also found in combination with tellurium ores.

§ 161. (1) *Native Bismuth.*

This assay is a simple liquation process, the metal being separated by raising the mixture to a little above



the melting point of bismuth, when the metal flows out and may be collected in a suitable receptacle.

(a) Weigh 200 grains of the crushed ore; place in a small crucible, the bottom of which is perforated with a number of small holes; cover with a clay lid, and lute it on with clay. Place this in another crucible which leaves sufficient space for the liquated bismuth to collect, and lute the two together. (Fig. 47.) Then raise the inner crucible to a red heat, when the molten metal will run through the perforations into the bottom crucible. Remove the source of heat; allow to cool, and weigh.

(b) In most cases the native metal is associated with oxide or sulphide, so that it is necessary to add a certain amount of flux and reducing agent, the nature and quantity of which will depend on the amount of bismuth compound and earthy matter present. The following proportions may be taken as a guide:—

200 grains of ore, 200 grains of carbonate of soda, 20 grains of tartar, and a little iron to reduce any bismuth sulphide. Place the mixture in a clay crucible; cover with a layer of carbonate of soda, and fuse at a moderate temperature for about fifteen minutes; pour into half-round mould; allow to cool; carefully detach the slag, and weigh the button of bismuth obtained.

§ 162. (2) *Bismuth in Copper Ores.*

The separation of bismuth from copper may be effected by taking advantage of the great affinity of copper for sulphur, by which a regulus is formed containing the whole of the copper, any iron passing into the slag, while bismuth is reduced to the metallic state.

In the case of copper pyrites, take 200 grains of ore, 150 grains of borax, 150 grains of powdered glass, 200 grains of lime, 200 grains of fluor-spar, 50 grains of

sulphur, and 30 grains of charcoal. Place the mixture in a large copper assay pot and fuse in furnace till tranquil; then pour into mould, cool, detach button of bismuth from regulus and slag, and weigh.

In the case of oxidised ores, take 100 grains of ore, 200 grains of sodium carbonate, 80 grains of sulphur, and 20 grains of charcoal. Well mix together; place in crucible, and cover with 80 grains of common salt. Fuse and pour as in former case.

The metal obtained by either of the above methods is very liable to be impure, and as some of the metal is lost by volatilisation, only approximate results can be obtained.

The pure metal has a reddish white colour and bright crystalline structure when fractured. Copper may be detected when present, as it does not alloy with bismuth. Antimony makes the lustre duller, and sulphur imparts a black tinge.

ASSAY OF NICKEL AND COBALT ORES.

§ 163. The ores of these metals are often of a very complex nature, being generally associated with ores of other metals. The most important compounds are those with arsenic and sulphur.

The assay of nickel and cobalt by the dry way is based on their affinities for arsenic, by which means they are first concentrated in the form of a speise, and the cobalt afterwards removed by the superior affinity of nickel for arsenic. This method has already been described in § 119 in dealing with the valuation of copper ores containing nickel and cobalt.

(a) First form nickel speise, containing nickel, cobalt and iron. Take 100 grains of ore crushed very fine and passed through No. 80 sieve and mix with 20



grains of arsenic, 100 grains of carbonate of soda, 80 grains of tartar, and 30 grains of borax glass. The mixture is then fused in a clay crucible for about fifteen minutes, and when tranquil poured into a half-round mould and allowed to cool. The speise must then be detached from the slag and weighed. This should be repeated with a second portion of ore. The following results were obtained from two experiments:—

1st, - - - - -	66.310 grains.
2nd, - - - - -	65.630 grains.

(b) *Treatment of the Speise.*

The action is based on the fact that when an arsenide of iron, cobalt, and nickel is heated in a muffle in contact with air and borax, the cobalt and nickel remain unaffected until the whole of the iron is oxidised and passed into the slag. Then in the same way, the nickel does not leave the speise until the cobalt has been scorified.

A piece of about 10 grains must be accurately weighed and the exact weight noted. An inverted crucible lid, Fig. 34, may be used as a scorifier; a very hot muffle being employed. Then 15 grains of borax glass wrapped in tissue paper is added to the scorifier, and when fused the button of speise is added, also wrapped in paper. The temperature must be sufficiently high to melt the speise at once, or some of the nickel and cobalt will oxidise and pass into the slag. In a short time the surface brightens; allow it to remain until the action stops, then lift out the scorifier and quench gradually in water. If all the iron has been removed, and the operation stopped at the right stage, the slag will be slightly coloured blue, showing that the cobalt was beginning to scorify. Remove the bead from the slag and place it in a small brasqued crucible; cover with lid, and heat until no odour of arsenic is perceived. Allow to cool and weigh.

(c) Repeat the above operation in another scorifier

with the weighed nickel and cobalt speise, using several scorifiers if necessary and less borax. When the whole of the cobalt has passed into the slag, a green cap will appear, indicating that the nickel is beginning to scorify; then quench in water as before, and weigh the bead which contains nickel arsenide only. ( $\text{Ni}_2\text{As}$ .)

The loss between this and the last weighing gives the amount of  $\text{Co}_2\text{As}$ .

(d) The following results were obtained from one of the samples of nickel speise mentioned in § 163 (a):—

Speise.	Nickel, per cent.	Cobalt, per cent.
1. 11.37 grains yielded	31.75	—
2. 10.326 " "	31.76	—
3. 11.159 " "	31.80 and	8.28
4. 11.396 " "	31.80 "	8.01

The method of calculation is as follows:—

$$\begin{aligned} & \text{Weight of speise taken} = 11.37 \text{ grains.} \\ & \quad \quad \quad \text{Ni}_2\text{As} = 5.914 \text{ "} \\ \text{Then as } 11.37 : 100 & :: 5.914 : 52.014 \text{ (Ni}_2\text{As).} \\ \text{Ni}_2 & = 117.52 \quad (\text{Ni} = 58.8) \\ \text{As} & = 75 \quad (\text{As} = 75) \end{aligned}$$

192.52

$$\begin{aligned} \text{As } 192.52 : 117.52 & :: 52.014 : 31.75 \text{ Ni.} \\ \text{Co}_2\text{As in No. 3} & = 1.516 \quad (\text{Co} = 58.8) \\ \text{" in No. 4} & = 1.494 \quad (\text{As} = 75) \end{aligned}$$

§ 164. *Assay of Speise containing Nickel, Cobalt, Copper, and Iron.*

(a) Take 100 grains of speise and mix with 100 grains carbonate of soda, 30 grains borax, 80 grains tartar, and 30 grains arsenic. Fuse in crucible; pour and detach speise as before, and weigh. Weigh accurately a piece of about 10 grains, and scorify the iron and cobalt as before, when a speise is left containing nickel and copper. Weigh, and



then wrap the bead in paper with ten times its weight of fine gold, and place the mixture in a hot scorifier containing molten borax, when the nickel gradually oxidises and passes into the slag. The operation is repeated until the slag ceases to be coloured with nickel oxide. Then remove the gold-copper alloy, which must be malleable; weigh and cupel with 35 times its weight of lead. The loss in weight gives the copper.

The first weighing after removing iron gives the combined weight of  $\text{Co}_2\text{As}$ , and  $\text{Cu}_3\text{As}$ .

The second weighing gives the amounts of  $\text{Ni}_2\text{As}$  and  $\text{Cu}_3\text{As}$ , and the difference between the first and second gives the  $\text{Co}_2\text{As}$ .

The third weighing gives the gold and copper.

The fourth weighing gives the gold, and the copper by difference between third and fourth.

The quantity of copper being found, the amount of arsenic originally associated with it may be computed. Then the difference between the  $\text{Cu}_3\text{As}$  and the second weighing gives the amount of  $\text{Ni}_2\text{As}$ .

(b) The following example will make the method clearer:—

Weight of speise taken, - - - -	10.168 grains.
„ after removing iron and arsenic, -	6.845 „
„ „ $\text{Co}_2\text{As}$ , - - - -	3.378 „
Weight of $\text{Co}_2\text{As}$ , - - - -	3.467 „

	Grains.
Weight of gold added, - - - -	34.182
„ „ and copper after removing $\text{Ni}_2\text{As}$ , -	35.090
„ copper present, - - - -	.908

But the copper exists in the speise as  $\text{Cu}_3\text{As}$ :—

$\text{Cu}_3 = 189$	( $\text{Cu} = 63$ )
$\text{As} = 75$	( $\text{As} = 75$ )

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As 189 : 908 :: 75 : .36 arsenic. Therefore the  $\text{Cu}_3\text{As} = .908 + .36 = 1.268$  grains, and  $3.378 - 1.268 = 2.110$   $\text{Ni}_2\text{As}$ .

The 10.168 grains of speise contains:—

Iron and arsenic, - - -	3.323 grains.
$\text{Co}_2\text{As}$ , - - - -	3.467 „
$\text{Ni}_2\text{As}$ , - - - -	2.110 „
$\text{Cu}_3\text{As}$ , - - - -	1.268 „

#### § 165. Assay of Cobalt Speise.

Assuming the speise to consist of the following ingredients:—

30 grains of cobalt.
4 „ nickel.
10 „ iron.
56 „ arsenic.

Well mix the speise with 10 grains of arsenic, 100 grains of carbonate of soda, 80 grains of tartar, and 30 grains of borax glass. Place in fire, and fuse at a bright red heat; pour when tranquil; allow to cool; extract the speise and weigh.

The speise is then assayed in the same way as nickel speise. A very high temperature is required to start with, but as the cobalt scorifies off, a lower temperature will suffice. When a large amount of cobalt, as in the present case, is known to be present, a larger scorifier may be conveniently used, and a greater amount of borax.

#### DRY ASSAY OF PLATINUM ALLOYS.

§ 166. (a) Take 3 or 6 grains of alloy according to the quantity of platinum present; add three quarters the amount of pure silver, and wrap the whole in the requisite quantity of lead to remove base metals by cupellation, and cupel until the bead brightens. Weigh



the bead obtained. The loss gives the amount of base metal originally present.

(b) Flatten; anneal; roll out thin; again anneal; roll into a cornet as in gold bullion assay; place in a parting flask, and boil for fifteen minutes with strong sulphuric acid, which dissolves out the whole of the silver. Wash, dry, and weigh the residue. The loss equals the silver originally present, plus the amount of pure silver added for cupellation.

(c) Add to the cornet twelve times its weight of silver and cupel with lead as before. Flatten bead; anneal; roll out again; anneal; coil into a cornet, and boil for a few minutes in dilute nitric acid, then with stronger acid as in gold parting. Wash thoroughly, dry, and weigh the residue. The loss gives the platinum, plus the silver added. The undissolved portion may be gold and osmium.

Boil in aqua-regia, and weigh the residue if any, which is the osmium. The loss in weight gives the gold.

(d) In platinum alloys containing much platinum not more than 2 grains should be taken for assay as the difficulty in cupelling is increased with the size of the button. Platinum will be dissolved in the sulphuric acid if too much silver is added, which would otherwise facilitate the cupellation.

### PART III.

#### ASSAYING AND ANALYSIS BY WET METHODS.

##### ESTIMATION OF BASES AND ACIDS WITH METHODS OF SEPARATING THEM FROM EACH OTHER.

###### GROUP I.

*Containing Silver, Mercurous Oxide, Lead.*

*Note.*—In the following exercises, two portions of each substance should be worked as a check on each other.

###### § 167. *Silver.*

Take 5 grains of pure silver; introduce into a conical flask; add sufficient dilute nitric acid to dissolve it; close the mouth with a small funnel, and heat gently till all is dissolved. Dilute with hot water and transfer to half pint beaker; add hot water till about half full; boil on sand bath; remove and add dilute hydrochloric acid with constant stirring as long as a precipitate is produced. A large excess of the precipitant must be avoided. Heat nearly to boiling with frequent stirring till the precipitate settles; pour off the supernatant liquid through a filter of known ash; wash the silver chloride twice in the beaker with hot water; then transfer to filter, and wash with water containing a little nitric acid, then with pure water. Dry thoroughly in water oven, and transfer precipitate to a dry watch glass. Incinerate the paper in a weighed porcelain crucible; add a few drops of nitric acid to dissolve any reduced silver; heat; then add a little hydrochloric acid; evaporate carefully to dryness; add the