

For silver,	{	Cover the work with sulphuric acid, and add nitre from time to time in small quantities. Used hot.
Do.,	{	Sulphuric acid, 10 measures; nitric acid, 1 measure. Used cold. Work must be dry before being dipped in this liquid.

All deposits may be stripped from work by making the articles the anode in a suitable liquid.

PART II.

ASSAYING BY DRY METHODS.

§ 90. Assaying (Fr. *essayer*; Lat. *exigo*, to examine, to weigh) was a term originally used to denote the estimation of a particular metal in an ore, alloy or other metallic compound by the dry way. At the present time the word has a far more extended signification, and assaying has become so identified with chemical analysis that the two terms are often used synonymously, and it is not unusual to call the determination of an *organic* constituent of a mixture 'an assay.' It should further be borne in mind, that analysis contemplates the determination of every constituent, while an assay only involves the estimation of one or more.

§ 91. Practical assaying may be conveniently classified under two heads, viz.—"Dry" and "Wet."

In the former, the operator effects the isolation of the metal by the agency of heat, generally following the methods, and even the sequence of the methods carried out on the large scale in the works, by which means he considers he will be able to discover the amount of metal a given ore will yield when treated in quantity. But the amount of metal obtained will often differ according to the plan pursued and the kind of apparatus used. Improvements now follow each other so rapidly that a larger yield is obtained from the same compound than formerly, so that many *dry* methods of assaying have been superseded by the more accurate although often tedious *wet* processes.

In the latter, advantage is taken of the strong chemical affinities of those liquids which easily dissolve metals and their compounds (sometimes at the ordinary temperature), and of those re-agents which form insoluble compounds with different elements by which means they are precipitated and separated in a weighable form. In some cases, minerals are first acted on by gaseous agents such as chlorine and sulphurous acid, the metal being afterwards separated by solution and precipitation. In others, a metal in solution is displaced by the addition of another metal whose chemical affinities are greater, such as copper by iron, silver by copper, etc.

Under the head of *wet* methods may be included those operations in which a component is isolated by the agency of electricity, although in some cases solution is not necessary, the compound being simply melted and maintained in a state of fusion while the current passes through it.

§ 92. Wet assays may very conveniently be divided into two classes—

1. *Gravimetric*, which aims at transforming the known components of a body into their elementary state, or some combinations which will admit of exact determinations by weight, and of which the composition is accurately known.

2. *Volumetric*, or analysis by volume. This admits of a more rapid estimation than by weighing, and consists of the determination of that volume of a re-agent of definite strength which is required to effect a certain change in the liquid to be analysed. For example, if we wish to know the amount of copper in a solution of its nitrate which has been rendered blue by ammonia, it may be ascertained by running into that liquid from a graduated burette a sufficient quantity of potassium

cyanide to exactly decolourise such solution; the potassium cyanide having been previously standardised by observing how much of it is required to decolourise a solution containing a known quantity of pure copper. The standard solution having been accurately determined, the balance will only be required to weigh out the samples to be tested.

PRELIMINARY OPERATIONS.

§ 93. *Sampling*. In determining the quantity of any constituent of an ore or metallurgical product, it is absolutely essential that the portion of the substance taken for assay corresponds to the average quality of the ore or product. This is best done by taking a large quantity, thoroughly mixing, and removing small portions, about $\frac{1}{20}$ th of the whole, from different parts of the heap, which must also be thoroughly mixed together. This is again repeated on the reduced quantity till a sample of about $\frac{1}{2}$ lb. is obtained.

If the sample is a liquid it is sufficient to shake up the bottle containing it, and take a measured quantity. If the liquid contain solid matter in suspension, measure the whole, filter, well wash the residue, make up to original bulk, and assay the liquid and solid portions separately.

If the sample is a metal or alloy, it should be cleaned and a hole drilled through it, the borings being used for the assay. Soft metals may be cut with a knife instead of boring.

§ 94. *Drying*. If the returns are required on a dried sample, the substance must first be crushed to a fine powder, and carefully dried at a temperature of 100° C., so as to remove all the moisture which has been mechanically absorbed. This can only be done when the body

under examination does not yield its combined water or otherwise decompose at that temperature. When it is unsafe to heat at 100°, a lower temperature may be obtained by immersing the vessel containing the powder in a liquid which has a lower boiling point than water; or the drying may be partly effected by pressing between blotting paper; or placing in a dish in a desiccator, which latter is kept dry by means of sulphuric acid, or chloride of calcium. If the substance persistently retains water at 100°, then the air bath (Fig. 52) may be employed, the temperature of which is regulated with the aid of a thermometer.

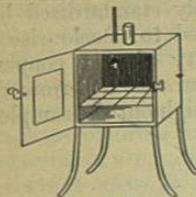


Fig. 52.

§ 95. *Mechanical subdivision.* The facility with which a body may be dissolved or acted on by fluxes is largely influenced by the state of division of the particles; the finer these are, the more perfect and more rapid will be the action. The crushing and grinding is performed in small quantities at a time, in mortars of various kinds made of cast iron, steel, gun-metal, porcelain, or agate. For moderately soft bodies porcelain is used, for ordinary ores and products the iron mortar. When it is necessary to avoid loss and the mineral is very hard, the steel mortar is indispensable. In cases where the substance requires to be reduced to an impalpable powder, it is effected by pulverising in small portions at a time in the agate mortar.

It sometimes happens as in the case of gold and silver ores that particles of metal are present, which, on account of their malleability, cannot be crushed to powder, and passed through the sieve. These "metallics" as they are termed are assayed separately, and the amount relative to the portion examined added to the final result.

After crushing and drying a given quantity, it should be put in a dry stoppered bottle for further use.

§ 96. *Weighing.*

See § 17. No exact rule can be given for the amount to be taken for analysis, which will differ according to the amount of the body present in the substance to be examined. In a sample of brass for example, 1 gramme or 15 grains would be a suitable amount; but in iron, containing a minute quantity of phosphorus or manganese, five to ten times this amount would be best to determine the amount of these elements. The greater the quantity taken the more accurate is the result likely to be, but the smaller the quantity the sooner will the assay be finished, so that if the operator avoids both extremes he will best combine accuracy with economy of time.

In weighing, the knife edges must not be allowed to fall suddenly on the agate planes. During the addition or removal of weights or other matter, the balance must be lifted off the agate planes. The pans must not swing during the weighing. The balance must be perfectly horizontal. The weights should not be lifted with the fingers, but manipulated with forceps. Both weights and pans should be scrupulously clean and a camel hair brush kept at hand for removal of dust, etc.

Bodies should never be weighed while hot, but first allowed to cool in a desiccator. Solid substances are generally weighed in watch glasses, or, if the substance be hygroscopic, it may be weighed in a stoppered bottle, then a portion turned out for analysis, and the bottle and its contents again weighed; the loss indicating the amount taken.

Sometimes a precipitate is decomposed by ignition; it then becomes necessary to weigh it on a tared filter paper, previously dried at 100°. This drying of the paper is repeated until the weight is constant. But as paper rapidly absorbs moisture on cooling, it must be

cooled and weighed in a stoppered bottle which has been accurately counterpoised. A pair of watch glasses with carefully ground edges, and a clip, may be substituted for the weighing bottle.

Liquids should always be weighed in stoppered bottles, as loss by evaporation is very likely to occur from open ones.

As the ashes of burnt filters are usually mixed with the ignited precipitates, the average weight of the ash, previously determined, must be subtracted from the weight obtained. This is assumed to be done in the following examples. The average weight is determined by burning a number of similar papers (say ten) until all carbonaceous matter is removed, in a weighed platinum crucible, cooling in a desiccator, carefully weighing and dividing by the number used.

§ 97. Estimation of Moisture.

In some cases it is desirable to estimate the amount of moisture in a given substance, as in fuel, for example. A portion, say 30 grains, is first weighed in a counterpoised pair of dry watch glasses. The top-glass having been removed, the whole is put into a water oven (Fig. 53), and maintained at 100° C. for an hour. The cover is then put on, being held in position by a clip, the whole is cooled in a desiccator, and weighed. The operation is repeated until the weight is constant.

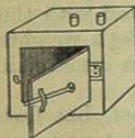


Fig. 53.

The mode of estimating combined water depends on the nature of the substance. When the body may be ignited, so as to remove the water, a platinum or porcelain crucible would be most convenient. When the body is decomposed at a red heat, but the water not removed at 100°, then the air bath (Fig. 52) may be employed.

§ 98. Solution.

Substances are generally dissolved in flasks, beakers,

or dishes; the solution being promoted, in most cases, by the agency of heat.

The most suitable beakers, especially where ebullition is necessary, are of a conical form, which may be conveniently closed with a small funnel. In cases where liquids require to be evaporated, the ordinary cylindrical shape is most suitable, as a greater surface is exposed, and solid matter readily washed out. The top should be covered with a clock glass, having a hole at one side for escape of vapours and for the introduction of a glass rod to stir the liquid, as bumping is to a large extent prevented, and solution or evaporation accelerated when continuous stirring is possible. Glass rods should be carefully rounded at the ends, and never left in a liquid when the latter is liable to bump. In cases where long continued ebullition is necessary, a flask with a long neck is commonly used, the liquid being less liable to loss, as the fluid which is spurted up is stopped by the sides and flows back again to the main liquid. These vessels however, are more difficult to clean than beakers. If alkalies have to be treated, glass is unsuitable, being acted upon by these bodies.

§ 99. Evaporation.

The simplest case is where the fluid merely requires to be concentrated, and is most rapidly performed in a large dish, generally of porcelain, which should never be more than two-thirds full, and the top loosely covered with a clock glass. The vessel should be heated on a sand or water bath (Fig. 54); and the operation will be much more safely performed if the liquid is kept just on the point of ebullition.

A convenient water bath may be made by placing the evaporating dish on the top of a beaker in which water



Fig. 54.

is kept boiling. When it is desirable to evaporate a liquid to dryness the action must be closely watched towards the conclusion, as small particles are projected upwards by the vapour. This may be avoided by supporting the dish or other vessel on an iron ring, 2 inches from the bottom plate, under which the burner is placed, the vessel being also surrounded by a case of sheet iron; in this way a uniform heat will be communicated to all the parts.

Some bodies have a tendency to creep up the sides and over the edge of a vessel during evaporation; in such cases, the inside edge should be slightly greased with tallow. Residues which are thick or gelatinous are dried more quickly, and spurting avoided, if agitated with a glass rod.

§ 100. Ignition.

This is generally effected in dishes and crucibles of platinum and porcelain, the greatest care being required to prevent loss by spurting and decrepitation. In all cases where platinum may be used, vessels of this metal are preferable on account of lightness, infrangibility, and the readiness with which they may be heated to redness. Sometimes patches of carbonaceous matter adhere tenaciously to the cover and sides of the crucible. These parts must be very strongly ignited to remove such stains before weighing. A gas muffle will be found exceedingly convenient for igniting precipitates, as the

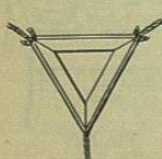


Fig. 55.

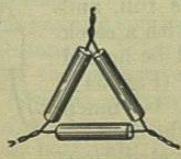


Fig. 56.

(2) The ignited precipitates must really be the bodies

temperature is uniform and may be easily regulated. With regard to this subject, Fresenius lays stress on the following four points:—

(1) No loss of substance must be incurred.

they are represented to be in the calculation of the results. (3) The incineration of the paper must be complete. (4) The crucibles must not be attacked.

Crucibles are usually supported on triangles of platinum or pipe-clay (Figs. 55 and 56).

§ 101. *Precipitation.* Cylindrical glass beakers, in all cases where glass is admissible, are preferred on account of the facility with which the precipitate may be washed on to the filter, and the last traces removed. Sometimes the precipitation is effected by means of a gas such as sulphuretted hydrogen; in that case the beaker should be covered with a glass plate having a hole through which the glass tube conveying the gas may pass. That portion of the tube inside the beaker should be detachable, so that any precipitate may be removed from the inside. A large tube drawn out thus



will be found very convenient for cleaning. Precipitation is generally hastened by warming the solution, and by much stirring.

§ 102. *Filtration.* This operation is in the vast majority of cases performed by means of paper, which should be sufficiently close in texture to prevent the finest precipitate passing through; such paper should filter rapidly and be as free as possible from ash. The amount of ash is found by igniting a given number of papers of equal size in a platinum crucible till a perfectly white ash is left, cooling in a desiccator, weighing, and deducing the amount for each one.

(a) The funnels used should incline at an angle of 60°, the ribbed form being preferred for rapidity. The paper should never protrude beyond the funnel, and should, in fact, be a little less. The funnel is supported either in the mouth of a beaker or flask, or on a suitable wooden

stand. The stem of the funnel should be allowed to touch the side of the beaker, so that the liquid may run quietly down the side and not splash. Whenever possible, a liquid should be filtered hot, as it runs through much more quickly, and for the same reason the precipitate should be washed with hot water. A liquid should never be poured directly into the centre of the filter, but poured cautiously down a glass rod, so as to run on to the sides. In order to prevent a liquid creeping over the edge of a beaker and running down the outside after pouring on to a filter, the edge may be greased with a little tallow smeared on the outer edge at the part where the pouring is effected.

(b) In cases where a precipitate or insoluble residue is not required for weighing, a plug of cotton wool may be inserted into the neck of the funnel and used as a filter. Sometimes asbestos is substituted for paper where strong acids would attack paper, being especially useful where a precipitate has to be dried at a certain temperature and weighed. For this purpose a glass tube is drawn out at one end, and the asbestos loosely plugged into the narrowed part.

(c) To remove the last traces of a precipitate from the containing vessel, a glass rod having one end covered with a bit of India-rubber tubing is employed to rub the sides of the beaker, or a caoutchouc finger stall may be used. If the precipitate has been filtered from a flask, then a long feather, from which all the plumules have been stripped except a tuft at the end, is used.

(d) It is generally advisable to allow a precipitate to completely settle before filtering, so that the supernatant liquid may be poured through the paper first, and the precipitate washed two or three times before the main body is swilled on to the filter by a jet of water projected from a wash bottle. To ascertain whether a precipitate is properly washed, the last few drops may be evaporated on platinum foil, when no residue should be left.

RE-AGENTS.

By the term re-agents is meant substances used by the chemist to ascertain the nature of the body being examined. One class is used to separate the bodies into different groups, another to recognise the special members of a group.

§ 103. (a) General Re-agents.

Acetic Acid, - - -	$\text{HC}_2\text{H}_3\text{O}_2$	1 part water to 1 acid.
Ammonium oxalate, - -	$\text{Am}_2\text{C}_2\text{O}_4$	20 parts " " 1 salt.
" chloride, - - -	AmCl	Saturated solution.
" carbonate, - - -	Am_2CO_3	4 parts water, 1 part salt, and 1 part ammonia.
" sulphide, - - -	Am_2S	Saturate 3 parts of ammonia with sulphuretted hydrogen, and add 2 parts of ammonia.
Ammonia solution, - -	AmHO	Used strong and dilute.
Ammonium sulphate, - -	Am_2SO_4	Saturated solution.
Silver nitrate, - - -	AgNO_3	20 parts water to 1 of salt.
Barium chloride, - - -	BaCl_2	10 " " " 1 " "
" nitrate, - - -	Ba_2NO_3	15 " " " 1 " "
Calcium chloride, - - -	CaCl_2	5 " " " 1 " "
Cobalt nitrate, - - -	Co_2NO_3	10 " " " 1 " "
Calcium hydrate, - - -	CaH_2O_2	Saturated solution.
Ferric chloride, - - -	Fe_2Cl_6	2 of water to 1 of salt.
Hydrochloric acid, - - -	HCl	3 " " " 1 " acid.
Nitric acid, - - -	HNO_3	2 " " " 1 " "
Lead acetate, - - -	$\text{PbH}_2\text{C}_4\text{O}_4$	10 " " " 1 " salt.
Sodium hydrate, - - -	NaHO	10 " " " 1 " hydrate.
" phosphate, - - -	Na_2HPO_4	10 of water to 1 of salt.
" carbonate, - - -	Na_2CO_3	Saturated solution.
Potassium cyanide, - -	KC_y	6 of water to 1 of salt.
" ferrocyanide, - - -	K_4FeCy_6	12 " " " 1 " "
Sulphuretted hydrogen, -	H_2S	Saturated solution.
Sulphuric acid, - - -	H_2SO_4	5 of water to 1 of acid.

(b) The following re-agents are used in the dry state:—

Borax, $\text{Na}_2\text{B}_4\text{O}_7$. Fusion Mixture, $\text{K}_2\text{CO}_3 + \text{Na}_2\text{CO}_3$. Nitre, KNO_3 . Potassic cyanide, KCy . Lime, CaO . Sodium carbonate, Na_2CO_3 .

(c) *Special Re-agents.*

Ammonium sulpho-cyanide,	AmSCy	10 parts water to 1 salt.
" acetate	$\text{AmC}_2\text{H}_3\text{O}_2$	10 " " " 1 "
" molybdate,	Am_2MO_4	
Alcohol,	$\text{C}_2\text{H}_5\text{O}$	
Barium hydrate,	BaH_2O_2	
Barium carbonate,	BaCO_3	In suspension in water.
Carbon disulphide,	CS_2	
Copper sulphate,	CuSO_4	10 of water to 1 salt.
Chlorine water,		
Calcium sulphate,	CaSO_4	Saturated solution.
Ether,	$\text{C}_2\text{H}_{10}\text{O}$	
Hydrochloric acid,	HCl	Concentrated.
Hydrofluosilicic acid,	$2\text{HF}, \text{SiF}_4$	
Mercuric chloride,	HgCl_2	20 of water to 1 salt.
Indigo solution,		
Magnesium sulphate,	MgSO_4	10 " " " 1 "
Methylated spirit,		
Magnesia mixture,		
Nitric acid,	HNO_3	Concentrated.
Platinum chloride,	PtCl_4	10 of water to 1 salt.
Potassium ferricyanide,	$\text{K}_3\text{Fe}_2\text{Cy}_{12}$	12 " " " 1 "
" chromate,	K_2CrO_4	10 " " " 1 "
" iodide,	KI	10 " " " 1 "
Sodium acetate,	$\text{NaC}_2\text{H}_3\text{O}_2$	10 " " " 1 "
" hypochlorite,	NaClO	By passing Cl gas into dilute solution of soda.
Hydrogen sodium sulphate,	NaHSO_4	5 of water to 1 salt.
Sodium thiosulphate,	$\text{Na}_2\text{S}_2\text{O}_3$	30 " " " 1 "

(d) *Solids.*

Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$; Hydrogen potassium sulphate, HKSO_4 ; Potassium chlorate, KClO_3 ; Microcosmic salt, HN_3AmPO_4 ; Barium hydrate, BaH_2O_2 ; Calcium chloride, CaCl_2 ; Calcium carbonate, CaCO_3 ; Ferrous sulphate, FeSO_4 ; Manganese dioxide, MnO_2 ; Starch; Sulphur; Iron Sulphide, FeS ; Iodine; Bromine; Sodium Chloride, NaCl ; Zinc; and copper.

CHARACTER AND USES OF RE-AGENTS WITH THEIR COMMON IMPURITIES.

§ 104. (a) *Acids.*

Sulphuric Acid is most likely to be contaminated with nitric acid, sulphate of lead, and arsenious acid. It is used as a solvent for liberating sulphuretted hydrogen, and for precipitating lead, barium, etc.

Hydrochloric Acid should be colourless and free from arsenic, sulphurous acid, chloride of iron, and free chlorine. It should leave no residue when evaporated on platinum foil. It is largely used as a solvent, being especially useful where it is not desirable to form insoluble compounds or to oxidise the body acted upon. It cannot be used in presence of silver, lead, or mercurous salts.

Nitric Acid is a good oxidising agent, and largely used as a solvent for metals and metallurgical products. Its commonest impurities are oxides of nitrogen, potassium and sodium sulphates, and chlorine.

Acetic Acid, if impure, is liable to contain sulphuric acid, hydrochloric acid, copper, lead, iron and calcium. It is employed in cases where a mineral acid is not admissible.

Tartaric Acid is used as a saturated solution, and also as a dilute solution. It may contain calcium and sulphuric acid.

Sulphuretted Hydrogen forms a most useful group re-agent as well as for special cases. It is decomposed by contact with air and should be prepared every two or

three days and kept in a black stoppered bottle. It is frequently used in the gaseous form.

(b) *Alkalies.*

Potash and Soda are most likely to be contaminated with silica, alumina, carbonic, sulphuric and hydrochloric acids, and oxide of lead. They are seldom perfectly pure, but good potash and soda should effervesce but slightly with acids, and their solutions should be kept in bottles of German glass which contain no lead. They are chiefly used for dissolving certain oxides, and thus separating them from insoluble ones.

Ammonia.—The solution is used both concentrated and dilute. It should be colourless, and leave no residue when evaporated on platinum foil. It may contain sulphate, chloride, and carbonate. This is one of the most frequently used re-agents, being employed to precipitate many oxides and to neutralise acids.

Barium Hydrate.—The crystals of this re-agent are dissolved in water and the insoluble matter filtered off. It is used to precipitate magnesia; also carbonic, sulphuric and phosphoric acids.

Calcium Hydrate Solution or lime water is used to separate magnesia, etc., from the alkalies, and for the detection of carbonic acid. It must be kept excluded from the air.

(c) *Salts of the Alkalies.*

Sodium Hydrogen Sulphite is a powerful reducing agent and used to reduce arsenic to arsenious acid, chromic acid to the sesquioxide, and ferric oxide to ferrous oxide, etc. Also used to separate sulphide of arsenic, in which it is soluble, from the sulphides of antimony and tin.

Hydrogen Sodium Phosphate, when in solution, must be kept in German glass bottles since it acts on glass containing lead. It precipitates the alkaline earths and all heavy metallic oxides. It is a special test for magnesia. The commercial salt may be purified by re-crystallisation.

Sodium Thiosulphate is used for precipitating many metals as sulphides, chiefly in separations, such as copper from zinc.

Sodium Acetate is employed principally to precipitate phosphate of iron, and to separate oxide of iron from alumina. Its chief impurities are sulphates.

Sodium Carbonate.—The impurities of this salt are likely to be chlorides, phosphates, and silicates; it may be largely purified by re-crystallisation. It precipitates most metals as basic carbonates, and decomposes certain insoluble salts. It is frequently used for neutralising acid solutions where ammonia could not be employed.

Ammonium Carbonate acts in much the same way as carbonate of soda, being generally preferred because of its volatile character. It is chiefly used to precipitate barium, strontium, and calcium, so as to separate them from magnesia. If impure, it may contain lead, iron, sulphates, and chlorides.

Ammonium Chloride serves principally to retain certain oxides or salts in solution, when others are precipitated by ammonia or other re-agents. It should leave no residue when evaporated on platinum foil. Its most common impurity is iron.

Ammonium Molybdate.—This salt is used in the estimation of phosphorus, and prepared for that purpose by dissolving it in ammonia, and decanting the clear fluid

into strong nitric acid till the precipitate re-dissolves. The following proportions may be taken :—

60 grams. of ammonium molybdate.
500 c.c. of nitric acid (specific gravity 1.4).
400 c.c. of ammonia (specific gravity .96).
400 c.c. of water.

Ammonium Sulphide is a valuable group re-agent, as it effects the precipitation of several metals which are not thrown down by sulphurated hydrogen. It also dissolves the sulphides of tin, antimony, arsenic, etc., and thus separates them from lead, bismuth, etc.

Sodium Sulphide.—This re-agent is substituted for ammonium sulphide to dissolve sulphides of antimony, tin, etc., in separating them from sulphide of copper.

Potassium Sulphate is used to separate baryta and strontia; it is used in many cases in preference to sulphuric acid.

Potassium Nitrite is used in the separation of nickel and cobalt, and to liberate iodine from its compounds in the presence of free acid.

Potassium Bichromate is a valuable re-agent in the volumetric estimation of iron. Also a good test for lead.

Potassium Cyanide is of great importance in the separation of nickel and cobalt, and of copper sulphide from cadmium sulphide, the latter being insoluble in potassium cyanide.

(d) *Salts of Alkaline Earths.*

Barium Chloride serves to precipitate sulphuric acid

by which means the acid may be estimated, and thus, indirectly, the estimation of sulphur also.

Barium Nitrate is used for the same purpose as the chloride in cases where insoluble chlorides, such as silver, would be formed by barium chloride.

Barium Carbonate is useful in separating the sesquioxides of iron and alumina from zinc, manganese, etc., when sulphuric acid is absent.

Calcium Sulphate is chiefly employed in distinguishing between barium, strontium, and calcium. Also for the detection of oxalic acid.

Magnesium Sulphate is employed in the detection of phosphoric acid. The following mixture is used in quantitative estimations :—

Magnesia Mixture.—The preparation of this re-agent is described by Fresenius as follows :—

Dissolve 83 grammes of crystallised sulphate of magnesia in boiling water, add 5 c.c. of hydrochloric acid, then 82 grammes of crystallised barium chloride, previously dissolved in water; boil, decant, filter, and test whether dilute sulphuric acid gives any precipitate in the filtrate; if it does, add a little more sulphate of magnesia. Mix the filtrate and washings; concentrate by evaporation; allow to cool; transfer to a litre flask; add 165 grammes of pure ammonium chloride, 260 c.c. of ammonia, and then add water to the mark. Allow to stand a few days and filter, if necessary.

(e) *Salts of Heavy Metals.*

Ferrous Sulphate furnishes a most delicate test for nitric acid in virtue of its reducing character. It is also used to precipitate gold from its solutions.

Ferric Chloride serves to effect the decomposition of phosphates of the alkaline earths, and for the detection of hydroferrocyanic acid, with which it forms Prussian blue.

Copper Sulphate is used for the detection of arsenic, ferrocyanides, and in the estimation of hydriodic acid.

Stannous Chloride is a good test for mercury and gold.

Platinum Chloride is the best re-agent for estimating ammonium and potassium.

Silver Nitrate serves for the separation and detection of some acids.

ASSAYING BY DRY METHODS.

IRON ORES AND RICH IRON SLAGS.

§ 105. First roughly crush half a pound of the ore and dry it at a low temperature to expel the mechanically absorbed water, taking care that the portion selected is typical of the whole mass of ore. Then crush to a fine powder in a clean iron mortar, until the whole can be passed through a sieve with twenty meshes to the linear inch. Now take from this 1000 grains and reduce sufficiently to pass through a sieve of sixty to eighty meshes to the linear inch and place in a dry corked bottle for use. It sometimes happens with hard quartzose ores, that triturating or grinding rubs off portions of iron from the mortar and pestle, so that such ores should be powdered by a percussive action of the pestle. Soft ores, such as limonite, may be pulverised in Wedgwood-ware mortars.

The object of the dry assay is to obtain the iron as a compact button of cast iron, by reducing its oxide with carbon, and separating the earthy matter as slag by the agency of suitable fluxes, which will vary with the nature of the ore. This is often ascertained by inspection, or by repute. Thus hematites, both red and brown, are usually associated with silica, and require both lime and alumina. Spathic and calcareous ores, not containing clay, require sand, or an acid silicate such as glass, besides lime and alumina; while clay ironstones may be fluxed with lime alone.

§ 106. Iron ores may be conveniently arranged for assaying in the dry way, into five classes:—

1. Ores containing silica, lime, and another base, which are fusible, *per se*.

2. Ores in which silica predominates.
3. " " lime "
4. " " alumina "
5. Ores containing a large amount of magnesia ; these are most difficult to liquefy.

§ 107. In case the nature of the ore is unknown, and cannot be ascertained by inspection, the following preliminary investigation, devised by Berthier, will be found useful.

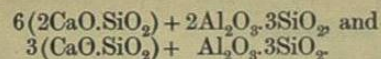
(a) Weigh out 100 grains of the ore ; heat to redness in a porcelain crucible ; cool and weigh. The loss represents the amount of carbonic acid, water, and other volatile matters ; except when the ore contains ferrous oxide, which is thus oxidised to the ferric condition with a proportionate increase in weight.

(b) Weigh out another 100 grains, and heat with very dilute nitric acid, which dissolves out the calcium and magnesium carbonates ; filter, wash the residue, dry and weigh. This insoluble portion consists of oxide of iron, quartz, and clay ; the difference gives the amount of earthy carbonates.

(c) Weigh out another 100 grains, and digest with strong hydrochloric acid, which dissolves both the earthy carbonates and the oxide of iron, while the clay and silica remain insoluble ; these are weighed, and the difference gives the amount of the carbonates of lime, magnesia, and oxide of iron. Now, the amount of these earthy carbonates having been previously determined, the quantity of oxide of iron present is easily computed.

§ 108. Having thus roughly ascertained the composition

of the ore, the nature and proportion of the fluxes can be calculated so as to produce a fusible slag. The following are suitable slags to aim for :—



—the former consists of 38 silica, 15 alumina, and 47 lime ; while the latter contains 30 lime, 14 alumina, and 56 silica. But the temperature of an ordinary assay furnace is barely sufficient to melt the second of these slags, without the addition of a little borax and fluor-spar. Borax, however, is not desirable when it may be dispensed with, as it takes up a portion of the iron oxide, which would then escape reduction, causing a loss on the assay. Good blast furnace slag, obtained from a furnace producing grey iron, if carefully freed from shots of metal, may be used as a flux for rich ores containing but little foreign matter.

§ 109. The readiest way of determining the proper amount and kind of flux for a given ore is to make three trial assays, which may be all done at the same time, by using the small brasqued crucibles (Fig. 34). The best proportion will yield the highest result. See § 111.

The following mixtures of fluxes will be found suitable for 100 grains of the ordinary ores of iron :—

<i>a</i>	<i>b</i>	<i>c</i>
White Sand, 10	Lime, - - 25	Fireclay, - 30
China Clay, 20	Glass, - - 25	Lime, - - 25
Lime, - - 25		

The weight of fluxes in most cases is about one half that of the ore used.

	Lime.	Fluor Spar.	Clay.
PLATNER recommends:—			
For magnetic ore, - - - - -	10	25	—
For specular ore, - - - - -	5	25	—
For earthy and siliceous hematites, } clay ironstone, and limonite, - - - - }	25	25	—
For forge cinders, - - - - -	20	20	—
For spathic ores, - - - - -	—	20	10

With the above proportions 100 grains of ore would be used.

§ 110. (a) The assay may be conducted in a clay or blacklead crucible, or the former lined with charcoal paste; the author has always found the lined crucible to give the best results. In naked crucibles 25 per cent. of charcoal must be added to the charge, so as to reduce the oxide of iron. Moreover, the assayer gains valuable information from the character of the slag, which, in a naked pot, clings so tenaciously to it, that the slag cannot be detached with any degree of accuracy; the slag, moreover, dissolves a quantity of argillaceous matter from the clay of the crucible, which alters its character, and increases its weight. Lined crucibles withstand the fire better than plain ones, because the lining supports the sides when they soften; they require no carbon to be added for reduction; the button of slag and iron can be readily removed, and each of these may be weighed, if desired.

(b) When the assay mixture has been introduced into the cavity, the hole is stopped with a charcoal plug, the lid of crucible luted on with clay, and the pot fixed on a piece of a brick, so as to retain it in an upright position

in the furnace. The brick is then placed on the bars of a hot furnace; small coke, packed carefully round the sides and top so as to fill up the furnace to the level of the draught hole, and the fire urged to its full extent by opening the damper. In about half an hour a fresh charge of fuel should be added, and the fire allowed to burn down, when the crucible may be removed, broken open, and the assay extracted. If the operation has been successful, the iron will be found as a rounded button covered with a mass of well melted slag, which can be easily separated. Sometimes the slag will contain small shots of metal; it must then be crushed to powder, the metal extracted with a magnet and weighed with the main button.

(c) The character of the slag may be judged according to the following considerations:—If perfectly transparent and of a green tint, silica is in excess; if a light grey or bluish enamel or translucent glass be found, then the earthy bases, lime and alumina, are in proper proportion; if stony and rough, or crystalline and dull in lustre, it is too basic. If the materials have only fritted and not melted, containing the iron as a grey powder, silica and alumina are deficient, lime and magnesia in excess. A vesicular slag with the iron interspersed in malleable scales indicates the presence in the ore of iron and manganese silicates, or an excess of silica which react on the carbide of iron, producing malleable iron and carbonic acid, which latter escaping, produces the spongy texture. This may be corrected by adding more lime to the fluxes used.

Manganese in small quantity imparts an amethystine tint; but in larger quantity a yellow green or brown colour. Titanium produces either a black scoria, sometimes much wrinkled on the outside, or a vitreous scoria of a blue tint. On the surface there may be particles of the red cyano-nitride of titanium. Chromium produces

a black resinous slag, sometimes surrounded by a thin metallic covering.

(d) After weighing the button it should be broken, which is usually done by wrapping it in paper and striking it with a hammer on an anvil. The appearance of its fractured surface will afford indications of any foreign bodies which may be present. Thus, a hard, white, "cold-short" metal indicates the presence of phosphorus. A somewhat fine grained mottled metal, fairly malleable when cold, but "hot-short," indicates sulphur, dark patches often existing on the surface and partially so on the fractured part. Manganese in quantity produces a bright crystalline structure, but in smaller proportion the iron may be strongly mottled. Titanium produces a button smooth on the outside, with a deep grey fracture which is sometimes crystalline. It adheres tenaciously to the slag, and is sometimes covered with red cyanide of titanium. Chromium yields sometimes a well-fused button with a white crystalline fracture; sometimes a half-fused mass of a white or grey colour, according to the amount of chromium present. This alloy is often very hard. A dark grey graphitic iron indicates an easily reducible ore, or that a very high temperature has been employed in the furnace. The weight of metal obtained may be more than the iron contained in the ore, as the reduced metal absorbs a little carbon and other bodies. But a little iron is generally taken up in the slag, and the cast iron obtained will therefore very nearly represent the true amount of iron in the ore.

§ 111. The most convenient and rapid method of conducting a number of assays is that introduced into this country from Sweden. The weight of ore taken in each case is 10 grains, and the total fluxes 5 to 5½ grains. The small brasqued crucibles (Fig. 34), the making of which is described in § 18, are used. After introducing the ore

mixture into the charcoal cavity the hole is plugged with a bit of charcoal, shaped with a penknife to fit the same, and as four crucibles are fixed to the same piece of brick, it is advisable to mark each plug so that each assay may be recognised afterwards, especially in a preliminary trial. A convenient way of doing this is to mark the under side of the plug with a small cavity scooped out, or by a line filed across, or a double line, and so on, taking care to enter these marks opposite the corresponding assay in a note book. The lids are then to be luted on, the crucibles attached to the brick with clay, and placed in the fire. When finished and cool, the crucibles are detached, broken open, and the iron weighed and examined as in § 110 (d).

ASSAY OF COPPER ORES AND PRODUCTS.

§ 112. Ores of copper for the dry assay may be very conveniently divided into three classes, viz:—

(1) Rich oxidised ores and products, which may be fused direct for coarse copper, or after a preliminary roasting.

(2) Pyritic ores, commonly called "yellow" ores, which require a preliminary roasting, or the addition of nitre when fusing for regulus.

(3) Grey ores, which contain sulphide of copper and a little iron, and require the addition of iron pyrites to form a proper regulus.

§ 113. The fluxes and re-agents required are:—

(a) *Calcined Borax* to form a fusible compound with bases, such as lime and oxide of iron.

(b) *Glass* free from lead, which forms readily fusible

double silicates with metallic oxides. It may be easily reduced to powder by heating in a muffle, plunging into water and finally pounding in a clean mortar.

(c) *Lime*—to flux off silica and silicates.

(d) *Fluor-spar* (free from galena, blende, and copper pyrites), which acts as a flux for gypsum, heavy spar, phosphate of lime, and silica. It induces fluidity in a slag and causes it to disintegrate on cooling.

(e) *Nitre*.—This salt in the fused state is known as "sal prunella." It forms a powerful oxidising substance for sulphur and metals.

(f) *Common Salt*, which should be free from sulphate, is best used in the previously fused state to prevent decrepitation. It is employed to impart fluidity to the slag, and acts advantageously in forming volatile chlorides with antimony and arsenic, although a little copper is carried off with the vapours. Berthier found that by heating equal weights of sodium chloride and copper until the former was volatilised, 3 per cent. of the latter was lost. It also moderates the action of those bodies which produce violent ebullition. (See also § 23, No. 22.)

(g) *Carbonate of Soda* forms very fusible compounds with silica, etc., being basic in character. It should be used in the dried state. If mixed with carbonate of potash the action is much more powerful; and the combination melts at a lower temperature.

(h) *Tartar* (Hydrogen-potassium tartrate).—The common variety known as "argol" (containing tartrate of lime and other impurities) is preferred on account of its greater reducing power.

(i) *Sulphur*.—Both roll and flowers of sulphur are used

(j) *Carbon*.—Used in the form of powdered charcoal and anthracite.

(k) *Iron Pyrites*.—This agent must be free from copper pyrites; the variety obtained from the coal measures is preferred for this reason.

(l) *Ferrous Sulphide* may be substituted for iron pyrites.

(m) *Refining Flux*.—This is prepared by inserting a red hot iron rod into a mixture of—nitre, 3 parts; tartar, 2 parts; and common salt, 1 part; all by measure. The operation is very conveniently performed thus:—Put the mixture into a large crucible; place the pot in a cold assay furnace; then plunge the hot iron in and remove it as soon as deflagration commences; cover the furnace with the bricks and leave until all action ceases. When cold, the brownish white mass can be detached and put into a bottle for use. The product consists of potassium carbonate, undecomposed nitrate, potassium tartrate, and the impurities present in the tartar and common salt. Carbonate of potash and a little nitre may be used for refining instead of the above, but experienced assayers prefer the deflagrated compound.

§ 114. In dealing with copper ores, an experienced assayer will generally determine by inspection to which category a given sample belongs, and treat it accordingly. If the nature of the ore cannot be ascertained from its appearance, a portion is ground fine and washed by vanning on a shovel, or in a copper ladle designed for the purpose (Fig. 24), by which means the different constituents will separate according to their specific gravities, or into ore and earthy matter. If this is insufficient, a preliminary rough assay should be made by fusion in a pot, or by the blowpipe.

ASSAY OF OXIDISED ORES OR PRODUCTS
SUFFICIENTLY RICH TO BE FUSED FOR
COARSE COPPER DIRECT.

§ 115. (a) *Fusion for Coarse Copper, with Oxidation and Scorification of Iron, etc.*

Take for this purpose,	200 grains of ore.
	160 " tartar.
	300 " carbonate of soda.
	60 " borax.
	60 " lime.

These proportions are only intended as a general guide, and will vary with the quantity and quality of the foreign matters to be slagged off. Thus if the ore contains lime, that body need not be added. Too much borax tends to cause copper to be retained in the slag. 15 to 20 grains of charcoal may be substituted for the tartar; the tartar must be regulated according to the quantity of copper present, as great excess would reduce the other oxides present, and produce an impure coarse copper. The crucibles known as "Cornish" are invariably used for copper assaying, being sold in nests of two; the larger size is called No. 1.

For 200 grains of ore and proportionate fluxes, No. 2 is sufficient (Fig. 36 a). Introduce the materials into the pot, and place in a moderately hot fire so surrounded with hot coke that all parts shall be uniformly heated to the same temperature: exclude the air as much as possible. When the surface remains tranquil, pour immediately into a dry and blackened half-round mould (Fig. 17 a). If the temperature be too high, and the operation prolonged after the copper oxide is reduced, iron and other oxides will be also reduced, and will become alloyed with

the copper: it will be impossible in refining to remove these impurities without loss of copper. However, iron in less quantity than 1 per cent. tends to free the accompanying slag from copper, and easily passes out in refining. When in much larger quantity, an irregularly shaped button with projecting points is obtained, and occasionally an imperfectly fused mass in consequence of the higher melting point of the iron-copper alloy. When the slag has set, it may be cooled by dipping into water (but must not be left in the water to cool), by which it is made brittle, and readily crushed to powder. After picking out any small shots of copper with a pair of brass forceps, the slag is cleaned by fusion to remove any copper remaining. If the assay be properly performed, the slag should be dark coloured, glassy, and free from red scales.

(b) *Cleaning the Slag by Reduction of the contained Copper.*

Mix the slag with 30 grains of carbonate of soda, 50 grains of tartar, and 5 grains of charcoal. Melt as before in the same crucible; pour into mould; cool; grind the slag in mortar, and pick out any shots of copper.

(c) *Refining the crude Copper by Oxidation and Scorification of Foreign Matter.*

The crucible used in the previous operations should be employed. Place it well down in the centre of the fire, so that the copper may be seen through the space between the two bricks which cover the furnace, and when a bright red heat has been attained, drop in the copper button and shots. The copper first melts, and is covered with a dull skin due to impurities; in a little time this coating of oxides clears off, leaving the metal bright, and emitting a bluish green light from its centre, termed the "eye." Now add about 100 grains of refining flux, close the furnace for a minute or two, then pour the contents of the crucible into a half-round mould. When set, partially cool as

before by dipping in water, so that the slag may be readily detached when cold. The refined button should be flat or only slightly depressed on its upper surface, with a thin film of an orange red colour; it should be soft, malleable, and tough; should break with difficulty and have a fine silky fracture. If impure, it has more or less the character of coarse copper.

(c) *Cleaning Refinery Slag to extract the Copper.*

Fuse the slag with 20 grains carbonate of lime, 30 of tartar and 10 of charcoal, and weigh the button of copper obtained with the refined button.

Refinery slag is either grey, flesh-coloured, pink, pale red, blue, or bluish green, from the presence of copper oxide, or deep red from the presence of cuprous oxide, which is probably due to the refining flux being too "sharp," *i.e.*, containing too much nitre.

The effect produced on copper by the presence of other metals may be seen by reference to § 26.

ASSAY OF YELLOW ORES OF COPPER.

§ 116. Pyritic ores are the most abundant ores of copper, and when pure may be represented by the formula $(\text{Cu}_2\text{S}, \text{Fe}_2\text{S}_3)$ containing 34.81 per cent. of copper.

The dry assay of copper ores by the Cornish method is intended to give the purchaser an idea of the quality and quantity of metal that can be obtained by smelting, but the loss is greater in the assay than in the smelting on the large scale. The loss of copper in the dry assay is shown by the table on the following page.

The Cornish assay comprises the following operations:—1. Fusion for regulus. 2. Roasting the regulus obtained. 3. Fusion for coarse copper. 4. Cleaning the slag from No. 3. 5. Refining the coarse copper. 6. Cleaning the refining slag.

Assuming the ore to contain from 10 to 20 per cent. of copper, the following fluxes may be taken as a general guide:—400 grains of ore, 300 borax, 300 glass, 400 lime, 400 fluor-spar, and 100 nitre.

Borax may be used alone in many cases, taking about 1200 grains instead of the above mixture. If the ore be a very poor one, then 500 to 600 grains should be taken; if rich, 200 grains will suffice.

Copper Present.	Dry Assay.	Margin.
35	33.25	1.75
30	28.5	1.5
25	23.5	1.5
20	18.5	1.5
18	16.5	1.5
16	14.5	1.5
14	12.75	1.25
12	10.75	1.25
10	8.75	1.25
8	7.0	1.0
6	5.0	1.0
5	4.0	1.0
4	3.0	1.0
3.5	2.6	.9
3	2.1	.9
2	1.3	.7

(a) *Fusion for Regulus.*

Use the copper assay pot (Fig. 36 b) which has been previously annealed by placing over a hot furnace in an inverted position. The ore and fluxes must be ground to a fine powder, and sifted if necessary, as a fine state of division greatly assists in the chemical reactions which occur between the components of the mixture. The ingredients should be well incorporated, placed in the pot, and the whole covered with about 50 grains of borax. Then place in a hot fire, using same precautions as given in § 115. Only a moderate draught should be