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Sampling, Solution and Precipitation

1.0 IMPORTANCE OF METALLURGICAL ANALYSIS

Metallurgical analysis is indispensable for chemical control of production in the metallurgical industries. It is also required for chemical investigation of soil, fertilisers, chemicals, agricultural products, minerals etc. In almost every scientific research, dealing with chemical phenomena, the methods of chemical analysis are used.

Now-a-days, a thrust has been given to total quality in every industry. The stimulus for Indian industry to look towards total quality management, comes from the need to step up export efforts. In the present competitive market, chemical analysis plays a vital role in achieving total quality of metallurgical products. In this book, different methods of chemical analysis have been described in a systematic manner.

1.0.1 Scope of Metallurgical Analysis

Metallurgical analysis basically involves the qualitative as well as quantitative analysis of various raw materials, metals, alloys, by-products and other materials. Qualitative analysis deals with the identification and separation of substances and the chemical principles involved in the procedures. The qualitative analysis in metallurgical fields is particularly essential prior to quantitative analysis of unknown substances. Quantitative analysis is concerned with the determination of the amount of an element or chemical substance present either alone or in a mixture of other substances. Metallurgical analysis actually consists of four major steps :

(i) sampling, that is selection of a representative sample of the material to be analysed,

(ii) conversion of the desired constituents into a form suitable for measurement,

(iii) measurement, and

(iv) calculation and interpretation of the measurement.

1.0.2 Importance of Chemical Analysis in Metallurgical Industries

In our modern society chemical analysis of different materials holds an important position. A knowledge of various procedures of chemical analysis has become essential in practically all fields of science and technology. Chemical analysis is of particular importance in metallurgical industries because the quality of finished products cannot be maintained without a knowledge of the correct composition of raw materials used as well as of finished products. The discovery of new alloys and other materials would not be possible without the correct analysis of various materials at different stages of processing. Chemical analysis is such an important part of our industrial structure and advancing science that without it our present-day economy could not exist.

The last six decades have witnessed an increasing interest in the problems and methods of chemical analysis which is mainly due to (i) the great increase in industrial production, (ii) the great number and variety of products, and (iii) the more careful control required in the manufacture of various products.

During the last few decades a great increase has been recorded in the variety and number of analyses needed to solve the problems in engineering, metallurgy, manufacturing and many other fields. Thousands of chemical analyses are performed yearly in monitoring the processes and materials of metallurgical industries in the world.

It is often necessary to determine traces of elements in the metals and alloys required for specific applications such as metals in nuclear metallurgy and semiconductor grade metals. The properties of common metals, aluminium, iron, copper, zinc, lead etc. are greatly influenced by the presence of other elements which may be either added intentionally or which are present as impurities. Therefore, it becomes necessary to know the composition of these metals accurately.

The progress of most of the research problems in extraction of metals and production of alloys is greatly affected by the availability of suitable facilities for their chemical analysis.

1.0.3 Outline of Methods used in Metallurgical Analysis

In metallurgical industries, we perform the chemical analysis of raw materials, products and by-products. There are two types of analysis—qualitative analysis and quantitative analysis.

The former type of analysis is used to detect or identify elements or ions present in the substance, whereas the latter type of analysis is carried out to find the quantity or amount of constituents present in a substance or in a mixture of substances. Qualitative analysis usually precedes quantitative analysis.

Qualitative analysis for the estimation of important ores, fuels, fluxes, refractories, iron, steel, ferro-alloys, non-ferrous metals and alloys have been discussed in the preceding chapters. A brief outline of the methods of analysis is given here and will be followed by the classification of various methods used in metallurgical analysis in more details.

The first step of metallurgical analysis is sampling *i.e.*, to obtain a small portion of material from a bulk for analysis. During the analysis procedures, we require to make a suitable solution, its precipitation, filtration etc. In the second chapter, all these steps have been discussed briefly.

In Chapter 3, general principles and reactions of common cations and anions involved in qualitative analysis have been discussed. This type of analysis employs both dry and wet tests. In dry tests the sample and the suitable reagents are taken in the solid state and reaction is usually formed by heating them. In the wet tests, the sample and reagents are taken in solution and we usually observe the colour change or precipitate formed after the reaction.

In Chapter 8, physico-chemical methods of analysis have been discussed. The main physico-chemical methods of analysis are based on the principle of colorimetry and absorptiometry, electrolysis, potentiometric titration, polarography, spectroscopy etc.

Colorimetric analysis is based on the relationship between the colour intensity of the solution and the concentration of the coloured substance. The intensity of the colour may be matched either by the visual method or by using instruments called colorimeters. Instruments consisting of photo-electric cells are used to avoid error due to the human eye. The instrument is called photo-electric colorimeter or photoelectric comparators or absorptiometers. Absorptiometers are usually employed with the light contained

within a narrow range of wavelengths, furnished by pressing the white light through filters.

The principle of electrolysis is employed in the analysis of metals and alloys. In this method, the deposition of metal is carried out on a weighed cathode by the application of a sufficient high voltage across the electrodes. Various types of commercial apparatus for electrolysis are available now-a-days, for this type of analysis. Potentiometric titration is best suited for those cases, where the visual indicator method (in ordinary volumetric analysis) fails or is of limited accuracy. In this method, the change in potential of a suitable indicator electrode is observed as a function of the volume of added titrant. The apparatus consists of an electrode system, a potentiometer and a sensitive spot galvanometer of high resistance.

The polarographic method of analysis is a rapid and accurate technique. Here electrolysis of a solution is carried out between a dropping mercury cathode and a mercury pool anode. During electrolysis, a voltage which increases at a uniform rate is applied to the cell and a current-voltage curve is recorded. From the curve, which is known as a polarogram, the character and concentration of the substances in solution are determined.

In spectroscopy, we utilise the principle of definite wavelength by elements under a suitable excitation condition. The wavelengths and intensities of radiations of atoms or molecules are characterised by a spectroscope or spectrograph.

Physico-chemical methods of analysis are also called instrumental methods, since the measurements involved require instruments.

1.0.4 Classification of Various Methods Used in Metallurgical Analysis

Qualitative Analysis. The qualitative analysis of metallurgical raw materials and products can be performed by the usual methods used in identification of various elements and ions in analytical chemistry. The various tests performed for qualitative assessment include spot tests, dry tests and the usual solution tests. Spot tests are performed by placing one or two drops of the sample solution on a porcelain plate or absorbing paper and then reacting it with suitable reagents. Dry tests include the flame tests for alkali metals, borax bead test and other tests, where flame is used for fusion. Solution test being the most common, is performed in test-tubes using considerable amounts of test solution and reagents. In all the cases, the specific colour

developed, precipitate formed and similar other characteristics are the indications of specific substances present there.

Quantitative Analysis. The quantitative analytical methods are ordinarily classified according to the property that is observed in the final measurement. These methods may be broadly divided into two general groups :

Group I. It consists of those methods in which the final measurement of the substance or element sought is made by direct or indirect measurements of volume and weight after proper treatment of a measured quantity of the material to be analysed. The two most important classifications in this group are gravimetric methods and titration methods. The latter are often referred to as volumetric or titrimetric analysis.

In gravimetric methods, the analysis is carried out by a series of weighing operations. The most usual is the isolation of the required substance by direct precipitation of the substance or a suitable compound of it with subsequent purification, drying, ignition etc. before weighing.

In titrimetric methods, the substance sought is determined by a careful measurement of the volume of a solution of known concentration required to react with the solution to be analysed.

Upto about 1920 nearly all the analyses were based on the properties of mass and volume i.e. gravimetric and titrimetric respectively. As a consequence, gravimetric and volumetric analysis are known as classical methods of analysis.

Advantages of classical methods

- (i) Classical methods give the absolute data directly.
- (ii) These methods do not require costly equipments.
- (iii) In the classical analysis, one notices at an earlier stage if anything goes wrong.
- (iv) Classical methods are very suitable for the analysis of the major constituents as the per cent error is less.
- (v) The standard samples used for instrumental analysis are analysed only by classical methods.

Disadvantages of classical methods

- (i) Classical methods do not provide the information about the physical and combined state of the substance.
- (ii) The quantity of sample required is comparatively large. It is still more for the samples where the substances sought are present in small amounts.

(iii) The process is very slow and one person can hardly perform more than a few analyses in a day in most cases.

(iv) A small fraction of the sample, *e.g.*, the surface cannot be analysed.

Group II. This group consists of those methods in which the final measurement is made upon the system as a whole. Almost any physical measurement may be used in this group to give the desired analytical result. Comparison of the samples for analysis with the standard samples of known analysis is necessary in this group for measuring any physical property. Since suitable instruments are required, this group is referred to as instrumental analysis. This classification along with the physical property used is shown in Table 1.0.1.

Table 1.0.1 Classification of Instrumental Analysis with the Physical Property Employed

| <i>Physical property measured</i> | <i>Analytical methods</i> |
|-----------------------------------|---|
| (i) Absorption of radiation. | Spectrometry, colorimetry, atomic absorption, nuclear magnetic resonance, absorptiometry, and electron spin resonance spectroscopy. |
| (ii) Emission of radiation. | Emission spectroscopy, flame photometry, fluorescence, and radiochemical methods. |
| (iii) Scattering of radiation. | Turbidimetry. |
| (iv) Diffraction of radiation. | X-ray, electron diffraction methods. |
| (v) Electrical potential. | Potentiometry. |
| (vi) Electrical conductivity. | Conductimetry. |
| (vii) Electrical current. | Polarography, amperometric titrations. |
| (viii) Quantity of electricity. | Coulometry. |
| (ix) Mass-to-charge ratio. | Mass spectrometry. |
| (x) Thermal properties. | Thermal conductivity and enthalpy methods. |

Instrumental methods of analysis. The instrumental methods of analysis have both merits and demerits, which have been discussed in detail in the respective chapters.

Advantages of instrumental analysis

(i) Instrumental analysis may provide more information than classical methods. For example, X-ray techniques can give the crystal structure of the materials.

(ii) For estimation of components from a little material the instrumental techniques are superior to the classical procedures.

(iii) A small fraction of the sample can be analysed, for example, the surface layer of a metal or an alloy.

(iv) Speed of the analysis is very high. Instrumental methods often produce the results within a few minutes. This fact is very important for controlling a manufacturing process.

(v) Many instrumental techniques have much greater simplicity of manipulation. An analysis can be carried out in many cases by untrained personnel.

Disadvantages of instrumental analysis

(i) The instrumental methods do not give absolute data. A calibration with standard samples is required.

(ii) Due to the complicated nature of the instruments, they are often subject to interferences.

(iii) A result is always obtained even if it is erroneous. Regular checking of the electronic apparatus and the whole equipment by means of standard samples is, therefore, necessary.

(iv) Many times the results obtained are less accurate than obtained by classical methods. It is true particularly when the major constituents of material are to be determined.

(v) For many instruments the cost is quite high and may be beyond the reach of small laboratories.

1.0.5 Choice of Methods for an Analysis

There are very clear distinguishing features for instrumental methods and classical methods. Some instrumental techniques are more sensitive than classical techniques, but others are not. With certain combinations of elements or compounds an instrumental method may be more specific; with others a classical procedure is less subject to interference. Generalisations on the basis of accuracy, convenience, or expenditure of time are equally difficult to draw. It is not true that all instrumental procedures employ more sophisticated or more costly apparatus. In fact, use of a modern automatic balance in gravimetric analysis involves more complex and refined instrumentation than is required for many of the instrumental methods.

In order to make the choice of methods for an analytical problem, the following factors should be taken into consideration:

(i) Complexity of the material to be analysed.

- (ii) The concentration of species of interest.
- (iii) The number of samples to be analysed per day.
- (iv) Accuracy required.
- (v) The amount of money available.

The choice will then depend upon the knowledge of the basic principles underlying the various methods available and thus their advantages and limitations.

1.0.6 Sample Selection and Preparation of Various Metallurgical Raw Materials and Products

Purpose of Sampling. The basic purpose of sampling is to obtain a small fraction of a large quantity of material for laboratory analysis. This small fraction should represent the average composition of the bulk material from which it is taken. Sampling is of great significance in analysis as it will be of no use if the portion of material analysed does not represent the average composition of the bulk material. A sample may thus be defined as a small portion of relatively large mass containing the same ingredients in the same proportions that occur in that bulk material. The sample is the actual material which is directly used for the estimation of various constituents.

The relative ease of sampling varies greatly for different materials. Homogeneous materials do not offer any problem as every portion (large or small) contains its constituents in the same proportion, whereas the sampling of heterogeneous materials is quite complex. In actual practice, most of the materials requiring analysis, are heterogeneous in nature. The constituents—ores, fluxes, fuels and metallurgical products are unevenly distributed and it is quite difficult to obtain the same proportion of the various constituents in a small sample selected for analysis.

The purpose of sampling may be any one of the following:

- (i) For judging acceptability of the material.
- (ii) For detecting contamination.
- (iii) For identification of material.

1.0.7 Sampling of Solid Raw Materials (Ores, Fluxes, Coal, Coke, etc.)

The raw materials used in metallurgical industries vary greatly in their constituents, and therefore, sampling of these materials is quite complicated. Particularly when only 0.5—1 gm sample required for analysis has to be taken to represent as much

as 50-250 tons of material, the problem can be well realised. Sampling of solid raw materials usually consists of three main operations, *i.e.*, size reduction, mixing, and cutting a fraction. These operations have to be repeated as many times as possible for obtaining a truly representative sample.

Minimum Amount of Increment

The solid raw materials such as ore, limestone, coal etc. have so many different sizes that sampling by selection of individual pieces would be impracticable as well as unwise, because the sampler has no way of knowing the relative proportions of the various size pieces in the lot. The practical procedure of sampling of mixed sizes is taking off the increments or portions from the lot by means of a shovel or scoop or by diverting the moving stream of material for a short period at regular intervals.

The minimum amount of increment taken should be sufficiently large so that all particles, regardless of size, get the chance of being included in the increment taken. To achieve this objective, the following two rules may be used:

(i) When sampling from a moving stream by a collecting container, the inlet opening of the container must be at least three times the size of the largest piece in the lot to be sampled.

(ii) When sampling from the static beds or at rest (from a bin), the minimum weight of increment in kilogram must be 0.05 times the top particle size measured in millimeters.

1.1 SAMPLING OF ORES, METALS, ALLOYS AND OTHER PRODUCTS OF METALLURGICAL IMPORTANCE

Sampling is the process of obtaining a small portion from a large quantity of material and should be so carried out as to truly represent the composition of the whole lot.

The process is of great significance since the time and labour spent on analysis will be of no avail unless it is certain that the sample analysed is truly representative of the whole lot of the material.

In the case of homogeneous materials, there is no difficulty in sampling as every portion, whether large or small, contains the ingredients in the same proportion. However, in actual practice, such a condition is seldom found. Practically all metallurgical

products are heterogeneous in nature and sampling must be carried out with great care. The method will vary with the nature of the product.

1.1.1 Sampling of Ores and Similar Materials

Sampling of ores is probably the most complicated of all materials because of the great variety of constituents present and the large variations in their distribution throughout the mass. When it is considered that the final sample for chemical analysis usually weighs only half a gram (for fire assay somewhat less than 15 g) and that each must truly represent 1-5 car loads of ore weighing 50 to 250 tonnes, the enormous problem of sampling may be very well appreciated.

Sampling usually consists of three distinct operations, repeated as many times as necessary. These are crushing, mixing and cutting. By repeating the three operations, a sample may be reduced to the desired weight.

1.1.2 Relation of Maximum Particle Size to the Amount of Sample

Proper sampling depends primarily on a correct knowledge of the relation between the maximum size of the particles and the weight of the sample to be taken. The size of the ore particles usually depends on the value and uniformity of composition of the material. The more uniform it is, the smaller may be the sample taken after crushing to any particular size. A safe rule is that the weight of the sample should vary as the cube of the diameter of the largest particle. In other words, if the sample has been crushed in such a way that the size of its largest particle has been halved, then one-eighth of the sample weight should be taken for the next stage.

In certain ores, however, different minerals are not entirely detached from one another, but this condition is approached more and more closely as the size of the ore is reduced. Hence, a fixed number of particles of the fine ore is less likely to be a true average of the whole than the same number of particles of the ore before it was broken. Therefore, as the size of the ore particles is reduced, larger and larger number of particles should be taken for the sample. To conform to this condition, a rule has been proposed in that the weight of the sample taken should be proportional to the square of the diameter of the largest particle.

1.1.3 Sampling Practice

Ores and similar materials, unless already fine enough, are broken or crushed to a proper size. The size depends on the value and uniformity of the ore and the precision desired. However, the aim is always to minimize crushing, thus saving in cost and keeping down the dust content. Machines for crushing should be rapid in action and easy to clean. Jaw crushers (Fig. 1.1) and roll crushers fulfil these requirements.

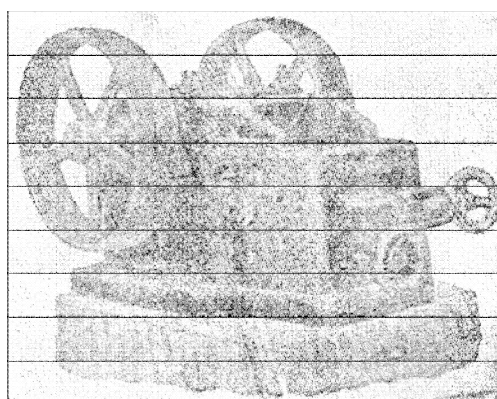


Fig. 1.1 Jaw crusher.

Various methods are available for sampling ores and similar products. 'Coning and quartering' is a well-known process of ore sampling. This is a hand-cutting method. The crushed material is shovelled into a conical pile, each shovelful being thrown upon the apex of the cone so that it will run down evenly all around. A slight damping of the ore is said to allow better mixing by coning. When the cone is completed, it is worked down into the form of a flat truncated cone by men who walk around, drawing their shovels from centre to periphery, or starting at the apex work the shovel up and down in the path of a spiral. Care should be taken not to disturb the radial distribution of the coarse and fine particles. After flattening, the cone is divided into four quarters by means of a sharp-edged board, or better, by a steel bladed quarterer. Two opposite quarters are removed and rejected, and the remaining two are taken for sampling. The sample may again be mixed by coning and quartering or it may be crushed, if necessary, and then coned and quartered. These operations are repeated until a sample is obtained which may conveniently be reduced to the degree of fineness required for analysis.

This method may be made to yield fairly accurate results when properly carried out, but it is a slow and tedious process, requiring most conscientious work on the part of the labourers to ensure correct results. Now this is replaced, whenever possible, by machine cutting which is a cheaper process and gives more accurate results. A large number of machines have been devised for ore sampling. All these machines take the sample from a stream of falling ore. The machines may be classified as continuous or intermittent. The continuous samplers take part of the stream all the time by placing a partition in the falling stream of ore. The intermittent samplers, as the name implies, deflect the entire stream at intervals to make the sample. This is accomplished by passing a sample cutter directly across the stream.

If the quantity of ore is of the order of 50 kg or less, mixing may be accomplished by a method known as 'tabling'. The finely divided material is spread on the centre of a large sheet of an oil-cloth or a similar material. Each corner is pulled in succession over its diagonal partner, the lifting being reduced to a minimum. The particles are thus caused to roll over and over on themselves and lower portions are constantly brought to the top of the mass which ensures thorough mixing. The sample may then be rolled to the centre of the cloth, spread out and quartered as before. The process is repeated until a sufficiently small sample is obtained.

To expedite the process of quartering in the hand-cutting method, riffle samplers are now commonly employed. The riffle splitter (Fig. 1.2) or split shovel consists of a number of parallel troughs with open spaces between them, the spaces usually being of the same width as the troughs. These troughs are rigidly fastened together and either provided with a handle to make a split shovel, or set up at an angle of 45° which make an inclined riffle. These may be made in different sizes, but are useful only for small scale work. The ore is taken in a flat shovel (Fig. 1.3) or a special pan and spread over the troughs, care being taken not to heap the ore above the troughs. The ore which falls either in the troughs or in the spaces between them may be taken as a sample. The cutting may be repeated as many times as is deemed desirable.

In selecting a split shovel or a riffle cutter for any particular sampling operation, care should be taken that the distance between the riffles is at least four times the diameter of the biggest particle in the sample. It is found that a slight bridging action may occur if this precaution is not observed.

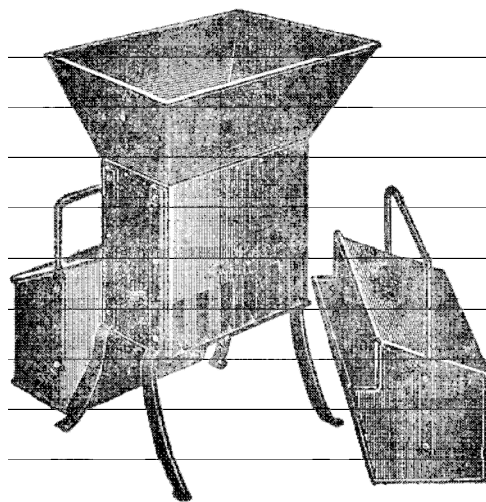


Fig. 1.2 Splitter.

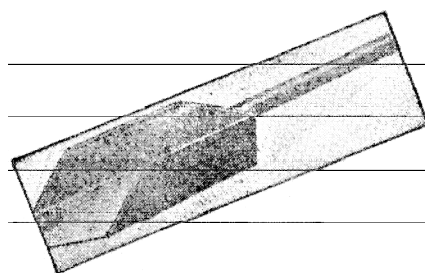


Fig. 1.3 Flat shovel.

1.1.4 Moisture Samples

Assays and chemical analyses are always made on dry samples and the value of a lot is always given on the moisture-free basis. Unless the entire lot is dried, it is necessary to take a sample for determining the moisture content. This sample is taken as soon as the ore is received in the laboratory. The method of sampling consists of taking a small shovelful from a definite point in the car or vessel as the material is being unloaded. The method is obviously both rapid and inexpensive. Moisture determinations are made in duplicate on samples weighing 1 to 2 kg. These are weighed into porcelain or enamelled iron dishes and dried at 105°C . The loss in weight gives the moisture content.

1.1.5 Ores Containing Metallics

When ores containing native gold, silver, copper as well as other malleable minerals are crushed, they are left on the sieve as flat scales, cylinders or spheres. When such ores are sampled, great care should be taken, firstly, to watch for the metallics and see that they are saved and secondly, to conduct the grinding in such a way that they may be removed at every opportunity.

When an ore containing metallics is being sampled, the original sample must be carefully weighed, the particles found on each sieve separately preserved and then weighed. The pulp resulting from each sampling and sifting must also be weighed. Both the metallics (remaining on the sieve) and the pulp (fines passing through the sieve) are assayed for the same constituents.

Various rules and formulas have been suggested for calculating these results, but no simple formula can cover all cases. Each example should be considered individually with proper assumptions based on actual knowledge of the conditions and occurrences during sampling.

One such formula is given below :

Let M = weight of metallics;

P = total weight of pulp;

a = assay of metallics (in any unit);

p = assay of pulp (in the same unit) ; and

x = assay of the entire sample.

$$\text{Then } x = \frac{Ma + Pp}{M + P}.$$

1.1.6 Sampling of Metals and Alloys

Metals and alloys cannot be sampled by crushing, mixing and cutting as described earlier. Such products can best be sampled either by taking a sample in the molten condition or by milling or sawing which enables the material to be collected from the entire cross-section of the cast bar or ingot. In some cases, it may be impractical, uneconomic or undesirable to take millings or sawings and for these drillings may be suitable.

Sampling of molten metal. For taking samples from the molten metal, three spoonfuls should be taken at the beginning, middle and end of the tapping period, avoiding inclusion of dust and slag. These should be cast separately in heavily chilled moulds in convenient sizes, such as $150 \times 50 \times 6$ mm. If the metal has a

tendency to segregate heavily during solidification or if the ingot cannot be machined satisfactorily, a granulated sample or a splash sample may be prepared. The granulated sample may be obtained by pouring the molten metal into cold water, in a thin stream adjusting the diameter of stream in such a way as to produce granules. When a sufficient quantity of granules is obtained, they should be reduced in size by crushing through a jaw crusher or a roll crusher or broken in a mortar. The sample so obtained should be divided into three approximately equal parts, each of which is placed in separate packages for analysis.

To obtain splash samples, the three spoonfuls of molten metal, collected as discussed earlier, should be splashed separately on to a clear surface so as to produce a thin sheet, less than a millimetre thick. The sample may be prepared from the thin sheet by milling or drilling.

Sampling of solid metal. When solid metals are to be sampled by machining, the preferred procedure is to collect material from the whole cross-section of the metal. For this purpose, milling or sawing is recommended. In case milling or sawing is not practicable, drilling is carried out right through the central portion of the representative cast bar or ingot.

As difference of composition may exist in different parts of an alloy bar due to segregation of various elements during cooling, several holes are drilled across a plane at right angles to the longest axis. The drillings so obtained are either mixed or assayed separately.

Accidental impurities such as particles of slag should be removed and if grease is present, a wash with ether or benzene is desirable. Non-magnetic metals and alloys should be carefully treated with a strong magnet to remove any ferrous particles introduced during machining.

Samples that are to be stored over long periods or those oxidised readily or otherwise altered in composition under varying atmospheric conditions or those which may become seriously contaminated in contact with paper or cardboard should be kept in wide-mouthed and well stoppered glass bottles. In other cases, tight leak-proof paper envelopes or cardboard cartons may be used.

1.1.7 Sampling of Metal Scrap

Metal scrap usually consists of old castings, foundry risers, sheets, plates, tubes, wires, bars, etc. For sampling scraps, pieces

representing each type of material in the same proportion as present in the scrap should be selected. Proportionate quantities of drillings, sawings, millings or clippings taken from these selected pieces are charged into a preheated crucible and melted as rapidly as possible without over-heating. The use of flux, which might alter the composition by reacting with the melt, should be avoided. When non-ferrous metal scraps are mixed with ferrous materials, the latter should be removed by using a strong magnet and accounted for separately in the analysis.

1.2 METHODS OF SOLUTION

1.2.1 Standard Solution Processes

Naturally occurring minerals and ores, various alloys, etc. are usually treated with different reagents in order to bring them in solution. Acids and acid mixtures are commonly used for the dissolution of these materials. They are added according to the nature of the constituents present; no attempt at generalisation can therefore, be made. Each case must be considered on its merit. For example, the treatment of pig iron with HCl will lead to the loss of some silicon as volatile compounds, whereas this does not happen in the case of steel.

To carry out the analysis of minerals and ores, a weighed quantity of the sample is taken in a suitable flask or beaker. Use of Erlenmeyer flask is usually recommended, if solution is best obtained by warming. Suitable solvent is then added to the flask. For a siliceous ore, HCl is commonly used. After gentle warming for some time, about 5 ml conc. HNO_3 is added and the material is heated until nitrous fumes are given off. After dilution to about 50 ml, 5 ml of conc. H_2SO_4 is added and evaporation is carried out till dense white fumes of SO_3 come off freely. The solution is cooled and diluted with 50-100 ml of water. Further addition of 5 ml conc. HCl is made and boiling carried out for a few minutes. After thorough settling, filtering is done which is followed by washing with hot water or dil. HCl.

This treatment is usually sufficient to get all the silica as insoluble residue, but in many cases a complete removal of silica may best be obtained by boiling with H_2SO_4 until no further deposition of moisture is observed on the cold watch-glass held over the mouth of the flask. This indicates complete dehydration of silica.

For sulphide ores, conc. HNO_3 is added and after gentle heating, small quantities of bromine water or potassium chlorate

is introduced at a time to decompose the sulphide completely. The solution is evaporated to dryness, cooled and conc. HCl gradually added. It is then gently heated and evaporated to dryness to decompose all chlorides and nitrates. Finally, it is taken up with conc. HCl and water, boiled, settled and filtered. This process is usually recommended where sulphur has also to be determined.

For ores containing zinc, conc. HCl and conc. HNO_3 are added and the solution boiled to low bulk. After adding conc. HNO_3 and KClO_3 , the mass is evaporated to dryness. This is followed by the addition of NH_4Cl and NH_4OH in excess. After shaking and gentle boiling, bromine water is added depending on the amount of Mn present. It is then filtered and washed with hot dil. NH_4Cl and NH_4OH . This treatment serves to precipitate iron, aluminium, manganese and silica, leaving zinc and other metals completely in solution.

When ores contain lead, they are treated with conc. HCl and lead is precipitated as lead sulphate along with silica. Barium, if present, will also join the residue. Detailed procedure is similar to that described for siliceous ores.

Ores and alloys can either be completely brought into solution by treatment with an acid, or a small residue may be left and subsequently treated with other acids or by fusion. Aluminium and zinc alloys are treated with HCl for solution. Copper alloys are soluble in HNO_3 but sometimes leave a small residue. When alloys containing tin are evaporated with HNO_3 and the residue taken up with water or dil. HNO_3 , then tin remains as insoluble metastannic acid and other ingredients go into solution.

1.2.2 Standard Fusion Processes

Substances which are insoluble or only partially soluble in acids are brought into solution by fusion with an appropriate reagent. The fusion reagents are generally called fluxes. The most commonly used fluxes are anhydrous sodium and potassium carbonates. These are used alone or, less frequently, mixed with other fluxes like potassium nitrate, sodium peroxide, sodium or potassium pyrosulphate and sodium or potassium hydroxide. The flux employed will depend on the nature of the insoluble substances.

All siliceous materials are fused with a mixture of anhydrous sodium and potassium carbonates known as 'fusion mixture'. The mixture consists of 3 parts of Na_2CO_3 and 2 parts of K_2CO_3 . Usually, for 1 part by weight of an ore, 10 parts by weight of this mixture are used. Metallic crucible, preferably of platinum, is employed for

carrying out the fusion. A layer of the fusion mixture is placed at the bottom of the crucible and then an intimate mixture of the flux and the finely ground substance is added. The crucible is first heated gradually till all the moisture and greater part of CO_2 have been expelled and then at a red heat until the mass is completely fused. The crucible is grasped by means of a tong and gently rotated so that the molten material distributes itself around the walls of the container and solidifies there in a thin layer. This procedure greatly facilitates the subsequent detachment and solution of the fused mass. The crucible is allowed to cool, placed in water and warmed till the mass is completely dissolved. Acid is sometimes added to achieve solution.

Frequently, after fusion only a portion of the melt is soluble in water, as in the case of ores containing BaSO_4 . In such cases, the insoluble portion (*e.g.*, BaCO_3) is filtered off and washed with water. Further treatment of the insolubles will depend entirely on the circumstances.

Materials containing sulphides or other oxidisable constituents, which are to be removed or rendered soluble, are fused with an alkaline oxidizing mixture containing Na_2CO_3 and KNO_3 . One part of the ore may be fused with a mixture of 5 parts of Na_2CO_3 and 5 parts of KNO_3 . Nickel or platinum crucibles are generally recommended for this fusion. An intimate mixture of the flux and finely ground material is prepared and transferred to the crucible. Usually, a portion of the flux is reserved and used as a cover during the process. The crucible is heated gradually at first and finally at a red heat, until the mass is completely fused. The melt is then extracted as described above.

For the treatment of tin and chrome ores and for oxidising silicon in the residue left after acid treatment of certain alloys, sodium peroxide fusion is especially useful. This is carried out at a much lower temperature than the preceding one. The amount of sodium peroxide to be used is generally about five times the weight of the ore taken. It is often preferred to fuse the peroxide first and then add the finely ground ore in small portions at a time, allowing each portion to fuse before adding another. Complete fusion thus takes about five to ten minutes. The melt is extracted with water. It is necessary to boil the solution to expel the liberated H_2O_2 , when an excess of peroxide is added.

When the use of alkali carbonates or oxidising mixture is not considered desirable, caustic alkalis are employed as fluxes.

For one part of the ore, ten to twenty parts of sodium or potassium hydroxide are used. Nickel, silver, iron and platinum crucibles are desirable to carry out the fusion. The flux is first fused separately, the ore is then introduced and all the water is driven off. In some cases, during fusion a little KNO_3 or Na_2O_2 is added to maintain an oxidising condition. In cases where reducing conditions are to be maintained, a little charcoal is added on the melt. The melt is extracted with water and treated as previously described. The extract is partly neutralised with a suitable acid before filtering.

When minerals contain iron, aluminium and certain other metals in such forms which resist ordinary acid treatment, they are fused with potassium bisulphate or pyrosulphate. This type of fusion is especially useful for the treatment of ores containing tungsten and titanium. The amount of flux to be used depends on the circumstances and may be as much as thirty times the weight of the ore. Porcelain or silica crucibles are considered suitable for this fusion but not the metallic ones, as they would be attacked by the H_2SO_4 evolved during the fusion. In this case, a very high temperature is not desirable, but prolonged fusion is required for complete decomposition. The melt is extracted with water and then treated as required.

It is important to note that in previous process where an alkali flux is used, the water extract contains silica, if any, in the form of a soluble silicate, whereas in the bisulphate or pyrosulphate fusion all or most of the silica is left in an insoluble form. If it is desired to remove this residue, it is filtered off, washed with hot water or dil. HCl, dried and ignited.

The ignited residue may be treated with conc. H_2SO_4 and HF to expel silica as SiF_4 . The operation is performed in a platinum crucible and repeated until no further loss of weight occurs. The residue, if any, may then be dissolved in HCl or H_2SO_4 or, if insoluble, fused with potassium bisulphate as described above.

1.3 PRECIPITATION, FILTRATION AND FILTERING MEDIA

1.3.1 Conditions of Precipitation

In gravimetric analysis, the constituent to be determined is precipitated from the solution in a form which is so slightly soluble that no appreciable loss occurs. The precipitate is then separated by filtration and weighed. The physical nature of the precipitate should be such that it is readily separated from the solution by

filtration and may be washed free of soluble impurities. The precipitate must be convertible into a pure substance of definite composition. This may be effected either by ignition or by a simple chemical operation, such as evaporation with a suitable liquid. Thus, magnesium is precipitated from a solution as magnesium ammonium phosphate, $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$, but is weighed after ignition as the pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$.

The above conditions of precipitation are not so easy to achieve in practice. Sometimes, the precipitate separated from the solution is not perfectly pure. It may contain varying amounts of impurities, depending on the nature of the precipitate and the conditions of precipitation. The precipitate may be contaminated with such substances as are normally soluble in the mother liquor. This is termed as co-precipitation. Appreciable error may also be introduced by post-precipitation which occurs on the surface of the first precipitate after its formation. The size of the particles of the precipitate should be such that they do not pass through the filtering medium and are unaffected by the washing process.

The influence of digestion should now be considered. This is usually carried out by allowing the precipitate to stand for 12 to 24 hours at room temperature or sometimes by warming the precipitate along with the liquid from which it was formed. The object is, of course, to obtain the precipitate in a form which can be readily filtered. During the process of digestion, at least two changes occur. The very small particles which have a greater solubility than the larger ones will, after precipitation has occurred, tend to pass into solution and will be ultimately re-deposited on the larger particles. The co-precipitation on the minute particles is thus eliminated and the total co-precipitation on the ultimate precipitate is reduced. The rapidly formed crystals are probably of irregular shape and possess a comparatively large internal surface. Upon digestion, these tend to become more regular in character, thus resulting in a decrease in the area of the internal surface and consequent reduction of adsorption. The net result of digestion is usually to reduce the extent of co-precipitation and to increase the size of the particles, rendering filtration easy.

Most of the precipitates are produced in the presence of one or more soluble compounds and, therefore, washing is adopted to remove these as completely as possible. A minimum amount of washing liquid should be used to remove the objectionable matters since no precipitate is absolutely insoluble. The ideal washing liquid should, as far as possible, satisfy the following conditions:

(i) it should have no solvent action on the precipitate and should dissolve foreign substances easily ;

(ii) it should form no volatile or insoluble product with the precipitate ;

(iii) it should be easily evaporated at the drying temperature of the precipitate ;

(iv) it should have no dispersive action on the precipitate ;

(v) it should not contain any substance which is likely to interfere the subsequent analysis of the filtrate.

Some precipitates tend to oxidise during washing. In such instances, the precipitate should not be allowed to run dry and special washing solutions are used to prevent oxidation. For example, acidulated hydrogen sulphide water is used to cover copper sulphide precipitate during filtration.

From the facts enumerated above, the following general rules for precipitation can be given :

(i) Precipitation is usually carried out in hot solutions, provided the solubility and the stability of the precipitate permit. At higher temperatures, the solubility is increased with consequent reduction in the degree of supersaturation (supersaturation is an unstable state and plays an important part in determining the particle size of a precipitate). The velocity of crystallisation also increases with temperature, thus leading to better formed crystals.

(ii) Precipitation should be carried out in dilute solutions, due regard being paid to the solubility of the precipitate, the time required for filtration and the subsequent operations to be carried out with the filtrate. This will minimise the errors due to co-precipitation.

(iii) The reagents should be added slowly and with thorough stirring. These assist in the growth of large crystals.

(iv) A slight excess of the reagent is all that is generally required; in exceptional cases, a large excess may be necessary. In some instances, the order of adding the reagents may be important, otherwise precipitation may be effected under conditions which increase the solubility of the precipitate, thus further reducing the degree of supersaturation.

(v) Crystalline precipitate should be digested for as long a period as possible, preferably overnight, except in those cases where post-precipitation may occur. Digestion on the steam bath is considered desirable. This, as stated earlier, decreases the effect of

co-precipitation and gives more readily filterable precipitates. Digestion has little effect on amorphous or gelatinous precipitates.

(vi) The precipitate should be washed with an appropriate solution. Water cannot, in general, be employed owing to the possibility of introducing small losses as a consequence of the slight solubility of the precipitate. A solution should possess a common ion with the precipitate in order to reduce solubility errors and should easily be volatilised in the preparation of the precipitate for weighing. For these reasons, ammonium salts, ammonia solution and dilute acids are commonly employed.

(vii) Sometimes the precipitate is dissolved in a suitable solvent and re-precipitated. This appreciably reduces contamination of the precipitate as a result of co-precipitation or some other reasons.

1.3.2 Filtration and Filtering Media

Filtration is carried out to get the precipitate and the filtering medium quantitatively free from the solution. The accuracy of chemical analysis to a certain extent depends on the successful filtration operation. The filtering media usually employed are : (a) filter papers ; (b) filter mats of purified asbestos (Gooch crucibles) ; and (c) porous fritted plates of resistance glass, *e.g.*, sintered glass crucibles, Vitreosil crucibles, or porous porcelain crucibles. The choice of a filtering medium will depend on the nature of the precipitate. Precipitates are either coarse-grained, fine-grained or gelatinous. Filter papers are especially suitable for gelatinous precipitates and for those which are heated to a very high temperature before weighing.

(a) *Filter papers* : Quantitative filter papers should have a very small ash content. The sizes generally used are 9, 11 and 12.5 cm diameter. The ash content of a 11 cm circle, which is widely employed, should not exceed 0.0001 g. If the ash content exceeds this value, it should be deducted from the weight of the ignited residue. Quantitative filter papers are made with various degrees of porosity. The filter paper used should be such that it can retain the smallest particles of the precipitate and yet permit rapid filtration. Hardened filter papers are also available, which have an extremely small ash content, a much greater mechanical strength when wet, and are more resistant to acids and alkalis. They are strongly recommended for quantitative work.

'Whatman' brand filter papers have been found very satisfactory for practical work. They are available in different

grades. For elementary work, filter paper Nos. 30-32 and 530-531 may be used. They are comparatively cheap. When precise quantitative work is needed, Nos. 40-42 or, preferably, the hardened variety (Nos. 540-542) should be employed. Nos. 41 and 541 are used for gelatinous and flocculent precipitates, and Nos. 40 and 540 for most other precipitates encountered in quantitative analysis. Nos. 42 and 542 are intended for finest precipitates and have very slow filtering rate ; for this reason they do not find wide application in routine quantitative analysis.

The size of the filter paper used is determined by the bulk of the precipitate and not by the volume of the liquid to be filtered. The entire precipitate should occupy about a third of the filter at the end of filtration. Filter papers of 9 cm and 11 cm diameter are most frequently used.

The funnel should match the filter paper in size. The paper on folding should be within 1-2 cm of the top of the funnel. The filter paper should be carefully fitted into the funnel so that the upper portion sits tightly against the glass wall.

The funnel stem should have a length of about 15 cm in order to promote rapid filtration. It should just touch the side of the beaker or the flask in which the filtrate is being received or collected. This will prevent splashing. The liquid to be filtered is poured down a glass rod into the filter, directing it against the side and not the apex of the filter. The lower end of the stirring rod should be very close to, but not quite touch, the filter paper on the side having three folds of the paper. The paper is never filled completely with the solution. The level of the liquid should be within 5-10 mm from the top of the paper. Any precipitate adhering to the side of the beaker or to the stirring rod may be removed with the help of a 'policeman'*.

Gelatinous slimy precipitates which tend to clog the pores of ordinary filter paper may be easily filtered and washed through a macerated filter paper. It is prepared by vigorously shaking an ordinary quantitative filter paper torn into small pieces with hot distilled water in a stoppered conical flask, until it is disintegrated to a pulp. Macerated filter paper is also useful when it is desired to filter a solution containing finely divided precipitate which is difficult to coagulate.

(b) *Filter mats (Gooch crucibles)* : Filter mats of purified asbestos which are supported inside a Gooch crucible, the bottom

*A glass rod fitted with a small piece of rubber tubing at one end.

of which is perforated with numerous small holes, are also employed for filtering precipitates. Gooch crucibles are made of porcelain, silica and platinum, but the porcelain type is the most widely used for routine work. These are used under suction and require holders and receivers that are strong enough to withstand a partial vacuum.

Gooch crucible is usually supported in a special holder, known as a Gooch funnel, by means of a wide rubber tube (Fig. 1.4). The Gooch funnel passes through a one-hole rubber bung into a large filter-flask of about 750 ml capacity. The filter-flask is coupled with another flask of similar capacity and the latter is connected with a water filter pump.

A Gooch crucible 4 cm in height, having a capacity of 25 ml and perforations of about 0.5—0.8 mm in diameter, is generally found suitable for most purposes. The crucible is first placed in the suction filtering apparatus and then filled half to two-thirds with a suspension of asbestos in water. This is allowed to stand for a few minutes in order to let the larger particles settle at the bottom and then the suction is gently applied. When the water passes through, the pump is turned on full and the mat sucked down tight. The thickness of the mat should be such that when looked through the crucible, the outline of the holes is barely visible. If the mat is too thin, more asbestos should be added and the process repeated. The asbestos mat is then thoroughly washed with distilled water under the maximum suction of the pump, until no fine fibres pass into the filtrate. The crucible is placed on a small ignition dish and dried to constant weight at a temperature which is subsequently used for drying the precipitate. Finally, the crucible is allowed to cool in a desiccator and weighed.

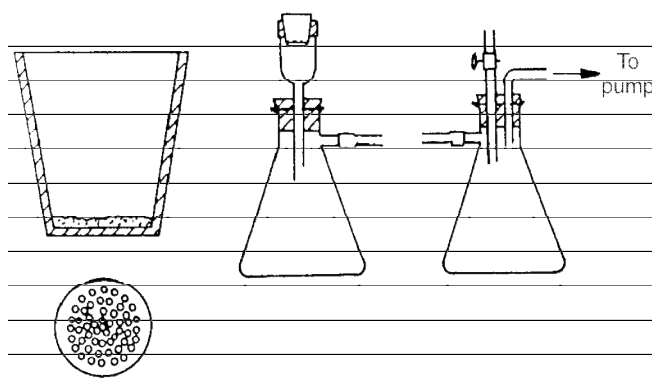


Fig. 1.4 Gooch crucible and filter flask.

Asbestos for the Gooch crucible should be carefully selected and prepared. Long-fibred, white silky asbestos is the most suitable. The fibres are cut into 1/2 cm long pieces and digested with conc. HCl in a boiling water bath. The asbestos is then filtered off on a Buchner funnel and washed with distilled water until free from chloride. A small quantity of the asbestos pulp is shaken vigorously with water in a flask and preserved.

It is observed that asbestos normally used for Gooch crucibles tends to lose weight above 288°C. Hence, it is recommended that precipitates which need heating above 280°C should not be filtered through Gooch crucibles. For such precipitates, porous fritted crucibles (*see below*) may be employed.

(c) *Porous fritted crucibles* : These crucibles now find wide application in the filtration operation. They are used exactly as Gooch crucibles. The best known ones are the sintered glass crucibles. They are usually made of Pyrex glass and have a porous disc of sintered ground glass fused into the body of the crucible. The fused in fritted filter disc is obtainable with various degrees of porosity ; the available grades are 1, 2, 3 and 4. No. 4 disc is suitable for very fine precipitates (such as barium sulphate) while No. 3 is used for precipitates of medium particle size. Two types of crucibles find wide application in quantitative analysis—the tall form and the low wide form. A crucible with a capacity of 30 ml is satisfactory for most purposes.

Sintered glass crucibles are resistant to most chemical reagents with the exception of hydrofluoric acid and hot concentrated alkalis. They are readily cleaned and dried to constant weight at 100-150°C. These crucibles can be heated upto 400°C (Pyrex glass softens at about 610°C and permanent strain may be introduced at temperatures above 430°C).

For temperatures above 200°C, usually Vitreosil filtering crucibles are employed. These are similar to the sintered glass crucibles, but are made of Vitreosil pure fused silica. They can be safely used up to 1000°C.

Another variety of crucible is the porous porcelain filter crucible. It is made of porcelain, glazed inside and outside, with a porous porcelain bottom. It is available in various sizes with an average pore diameter of 5—10 microns and meets most of the requirements of quantitative analysis. These crucibles may be heated to temperatures as high as 1000°C, but the temperature must be raised slowly as the joint between the porous disc and the

porcelain to which it is sealed may develop strain due to sudden heating.

Crucibles fitted with permanent porous plates are cleaned by shaking out as much of the solid as possible and then dissolving out the remainder with a suitable solvent. A hot 0.1 N solution of tetra-sodium salt of ethylenediamine tetra-acetic acid is an excellent solvent for many of the precipitates (except metallic sulphides and ferricyanides) encountered in analysis. The crucible may either be completely immersed in the hot reagent or the latter may be drawn through the crucible by suction.

1.3.3 Drying and Ignition of Precipitates

A precipitate obtained after filtering and washing is brought to a constant composition by drying and/or ignition before it is weighed. Though there is no definite temperature at which the precipitate should be dried or ignited, yet usually drying is accomplished below 250°C and ignition up to, say, 1200°C. Precipitates which are to be dried are collected in filter papers, or Gooch, sintered glass or porous porcelain crucibles. For ignition, precipitates should be collected in filter papers, porous porcelain crucibles, Vitreosil crucibles or, less commonly, in platinum Gooch. Ignition is affected by placing crucibles in an electrically heated muffle furnace which is equipped with a pyrometer and a temperature controlling device. Alternatively, the crucible may be placed in a special ignition dish or in a larger nickel or platinum crucible and heated with an appropriate burner.

The precipitates which are filtered through filter papers and are subsequently to be ignited require ignition either in contact or out of contact with the filter paper. The latter is employed in all those cases where ignited substance is reduced or changed by the burning paper, for example, barium sulphate, lead sulphate, silver chloride, etc. The funnel containing the precipitate is covered by a filter paper and dried at 105—110°C for 1—2 hours or until completely dry. The dried filter paper is removed from the funnel, the precipitate recovered from the paper as much as possible and allowed to drop in a watch glass resting on a glazed paper. Any small particles which may have fallen on the glazed paper are brushed into the watch glass with a small camel hair brush. The watch glass is carefully covered with a larger watch glass or a beaker. The filter paper is properly folded, placed inside a weighed porcelain or silica crucible and ignited. The crucible is allowed to cool and the filter ash is subjected to a suitable chemical treatment

in order to convert any reduced or changed material into the finally desired form. The precipitate from the watch glass is then transferred to the cold crucible and is brought to constant weight by heating to the proper temperature.

In other cases, both paper and precipitate are ignited together, care being taken to burn the paper slowly under oxidising conditions so that the carbon has completely disappeared. For most ignitions, a porcelain crucible may be used, but in cases where the residue is to be subsequently treated with HF, a platinum crucible should be used.