

# **INSTRUMENTAL METHODS OF ANALYSIS FOR THE PROCESS AND QUALITY CONTROL IN IRON AND STEEL INDUSTRY**

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## **INTRODUCTION**

Analytical control of the various processes in iron and steel production has long been recognised as essential to successful operation and is in daily practice throughout the industry.

To meet the close specifications of chemical composition and physical properties demanded by the customer, rigorous control over raw materials, intermediate products and the finished steel is exercised to an increasing extent in the chemical and metallurgical laboratories of the iron and steel works.

Apart from quality control of the final products, analytical data, coupled with physical tests in some instances, provide vital information for the steel maker in the attainment of increased production and trouble free-operation. In other words analytical data is essential to ensure product quality as well as for process control by ensuring maximum economy of materials and minimum wear on furnace refractories.

In addition to quality control and process control, the analytical data is of great importance in the commercial field also. The acceptability and prices of many materials, ranging from iron ore and coal to rolled steel depend on the major and minor element contents. The

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rigorous checking of all incoming supplies also prevents inferior material from entering the works.

Control over an increasing range of ancillary materials is also necessary. These include water supplies, waste products, lubricants and non-ferrous materials.

Works investigations by metallurgists and engineers invariably lead to the receipt of miscellaneous 'deposits', refractory substances and other materials for complete analysis. In fact, the analyst may expect to deal with anything and everything.

Finally, the development, examination and introduction of new analytical techniques and procedures, on an individual or co-operative basis, is an essential function of any large modern analytical laboratory. Investigation of this type lead to the adoption of more rapid, accurate and economical methods and systems.

**Types of samples :** The important materials which are received in an iron and steel works laboratory may be classified by process as follows <sup>[1]</sup> :

**Coal carbonisation :** Coal coke, ammonia liquor, wash oil, benzole, tar, coke oven gas, ammonium sulphate etc.

**Iron making :** Iron ore, pyrites, sinter, limestone, coke, blast furnace slag, blast furnace gas and various tap-hole and furnace lining refractories.

**Steel making :** Pig iron, scrap, iron ore, scale, lime, limestone, dolomite, fluorspar, aluminium alloys, graphite, ferro-alloys, mixer iron and slag, fuel oil and fuel gas, steel and slag, various refractories and fluxes.

**Rolling** : Fuels, Lubricants (oil and greases), steel product, soaking pit refractories and pickling bath samples.

**Ancillaries** : Boiler feed and circulation water for major areas of plant, raw water supplies, coke-oven and miscellaneous effluents, atmospheric pollutants, lubricants and non-ferrous alloys.

**Works investigations** : Deposits, slurries, refractories welding rods, fluxes etc. Laboratory investigational work obviously involves the material relevant to the exercise.

Those substances connected with more than one operation are included under each heading.

## **TECHNIQUES**

In recent years the introduction of more rapid steel making techniques has made imperative the development and application of speedier means of analytical control. At the same time the tighter specifications on principal and residual element contents demanded by the customer have implied more stringent systems of examination and greater degree of accuracy. This has affected all aspects of laboratory work so that, today, the sheer volume of work in the chemical laboratory has tended to make the older classical methods irrelevant. These challenges can be met only by adopting the modern instrumental methods of analysis in place of conventional wet chemical techniques. The advantages of instrumental techniques are :

- i) Much faster than the conventional wet chemical methods
- ii) Very highly reproducible
- iii) Scope for human errors is less due to less operator intervention
- iv) Accuracy comparable to chemical methods (Most of these methods are relative methods and therefore the ultimate achievable accuracy is limited by that of the standards used for calibrations).



Some of important instrumental methods used in the iron and steel works laboratory and their application area is briefly described below.

i) ***Spark atomic emission spectrometry :***

This is by far the single most important technique for the analysis of metal in an iron and steel industry. The modern day instruments can determine as many as upto 64 elements simultaneously in less than 20 seconds. The only limitation of this technique is the analysis of gases in steel (oxygen, nitrogen and hydrogen). Though some of the modern day instruments provide nitrogen analysis, the reproducibility and detection limits are below the expectations of the steel makers.

ii) ***XRF Spectrometry***

A versatile technique available to the analytical chemist, can analyse both metals and non-metallic samples. Hence, it is extensively used for the analysis of metals, slags, ores, refractory samples etc. The main limitation of the technique is that it is not suitable for the analysis of the low atomic number elements. The high cost of the instrument is also a factor to be kept in mind.

iii) ***ICP Emission Spectrometry***

This is an analytical method of extra-ordinary capability <sup>[2]</sup>. However, it is less widely adopted in metals analysis, mainly due to the availability of rapid multielement techniques such as spark emission and XRF spectrometry. The need to dissolve the sample, sometimes a lengthy and skilled task, can also be a limiting factor. However, there are various cases where ICP-AES is well suited. These are (a) sample presented in forms which are not suitable for spark emission or XRF. (b) Where a single instrument is required to analyse a wide

range of materials and (c) where there is a lack of accredited solid standards and synthetic standards may be used.

iv) **Atomic Absorption Spectrometry (AAS) :**

With the introduction of ICP-AES, the importance of AAS seems to have reduced some what. This is because ICP-AES allows a wider range of elements to be determined. Also the wide dynamic range of ICP-AES is often the outstanding advantage over AAS. If utilised properly, time consuming dilutions may be minimised or eliminated, whereas multiple dilutions may be required for AAS. In practice the detection limits attainable for many elements are comparable to those of flame AAS, although Pb and Cd are often superior by AAS. In addition, the degree of ionisation of alkali metals in the high temperature of ICP is such that flame emission gives better results. The ICP gives lower limits for refractory elements such as Al, Zr, Mo, lanthanides and elements not usually analysed by AAS, such as B, P and S. For some of these ICP-AES may rival graphite furnace AAS. For single element determination AAS is clearly superior, whereas ICP-AES is oriented towards multiple element analysis.

v) **IR Spectrometry :**

Infrared spectrometry is mainly used for the analysis of C and S in samples which are not in suitable form to be analysed by spark emission. It is also used for the analysis of oxygen in metals.

vi) **Thermal conductivity methods :**

Instruments based <sup>on</sup> as the measurement of thermal conductivity are used for the determination of hydrogen and nitrogen in metals.

After discussing briefly some of the techniques available to the modern day chemist working in an iron and steel industry, we will now discuss a few problems which were encountered in the not so distant past and how they were overcome.

### ***Determination of Thermal characteristics of bottom pouring compounds :***

Certain grades of steel are processed through the boggle bottom pouring route, to achieve better quality and higher yield. The mould powder (boggle bottom pouring compound) is used in the mould to achieve the requisite properties. The requirements of bottom pouring compound are to ensure smooth ingot surface free from cracks and entrapment of nonmetallic intrusions. The other functions of this material are to prevent thermal loss from solidifying ingot top and to act as a barrier to the entry of atmospheric oxygen into liquid steel. So the important parameters are the thermal characteristics, viscosity and thermal conductivity. To determine the thermal characteristics, the critical temperature points to be observed are defined as follows<sup>[3]</sup>.

***Initial deformation temperature, IT :*** The temperature at which the first rounding of the apex of the cone occurs. Shrinkage or warping of the cone ignored if the tip remains sharp. In Fig-1, the first cone shown is an unheated one, the second cone IT is a typical cone at the initial deformation stage.

***Softening temperature, ST :*** The temperature at which the cone has fused down to a spherical lump in which the height is equal to the width at the base as shown by the third cone, ST, in Fig-1.

***Hemispherical temperature, HT :*** The temperature at which the cone has fused down to a hemispherical lump at which point the height is one half the width of the base as shown by the fourth cone, HT, in Fig-1.

***Fluid temperature, F.T :*** The temperature at which the fused mass has spread out in a nearly flat layer with a maximum height of 1/16 in (1.6mm) as shown by the fifth cone, FT, in Fig-1.



The cones are made in a cone mold shown in Fig-2. The samples are first ashed and the cones are prepared from the ash. A binder may be used for the preparation of the cones. The dried cones are tested for various critical temperatures.

To determine these temperatures, we have recently procured one ash fusibility determinator. This instrument has an automated cone monitoring system employing a sophisticated electronic video system. The cones are heated in a furnace and the height and width of the cones are monitored and the various critical temperatures are automatically recorded.

#### ***Determination of diffusible and total hydrogen in steel :***

Hydrogen in steel is present not by design but because its complete elimination is scarcely possible. It is the cause of a number of steel defects and cases of failure. These defects are caused when hydrogen atoms pair to form the stable higher volume molecule  $H_2$ . The incidence of defects is increased by increased hydrogen content. The common types of defects due to hydrogen are<sup>[4]</sup>, the formation of flakes, fish eyes, blowholes and pin holes and longitudinal surface cracks. The common sources of hydrogen are, atmospheric moisture, flux additions, slag, vessel lining, alloy addition etc. Most of the hydrogen present in the liquid steel diffuses out during solidification and causes damage to the steel. Therefore, the determination of the hydrogen content in the solid product, which is usually low, is not very important. What is important is to know the hydrogen content in liquid steel before it starts solidifying. This is effected by collecting the sample of liquid steel in special sample tube (see Fig.3). The diffused hydrogen collected in the tube is analysed first and the residual hydrogen analysis is done on the solidified pin sample. By this the total hydrogen in liquid steel (diffusible & residual) can be determined.

### ***Determination of soluble aluminium***

From the metallurgical point of view, it is important to know the acid-soluble and acid-insoluble aluminium content of steel. This is because the acid-soluble aluminium will be in solid solution in steel whereas acid-insoluble aluminium will be in the form of oxide inclusions. The conventional method of determining the acid soluble aluminium is to dissolve the sample, separate the insoluble portions by filtration and determining the soluble aluminium by AAS or ICP techniques. This method, though gives accurate results is time consuming. Therefore, attempts have been made to determine the soluble aluminium by spark emission technique<sup>[5]</sup>. The spectrometric determination of dissolved and insoluble portions of elements in steel is based on the assumption that each inclusion in the crater volume of a discharge is an enrichment which at the beginning of sparking causes the excessive rise of intensity time curve (burn off curve). By measuring this peak and the intensity in the stationary state one can reach conclusion regarding the dissolved and insoluble portion. This procedure needs only additional software and no additional analytical time. However, it should be remembered that this is only an empirical method and the results should be regularly cross checked with other authentic methods.

### ***Determination of soluble boron :***

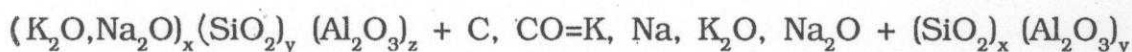
Boron in steel may be present as solid solution, acid soluble precipitates such as  $\text{Fe}_{23}(\text{CB})_6$  and  $\text{Fe}_2\text{B}$  and acid insoluble precipitates such as boron carbide and boron nitride. The determination of the acid soluble boron is important since it is a measure of the metallurgically effective boron in low-alloy steels. The methods available for the determination of soluble boron are all wet chemical methods with spectrophotometric detection. They are all time consuming methods and need a high degree of skill to get accurate, reproducible results. AAS cannot be used due to the low sensitivity of boron in



AAS. With the introduction of the ICP technique, it is now possible to determine soluble boron, fairly rapidly and with accuracy and reproducibility comparable to that of wet chemical methods.

### ***Managing the alkali problem in iron making <sup>[6]</sup> :***

Sodium and potassium generally exist in raw materials in the form of complex, aluminosilicates. These are stable compounds and no chemical reaction take place until high temperatures and strong reducing conditions are reached. Such conditions prevail in the high temperature zone of blast furnaces (near tuyers). The alkali compounds break according to



Sodium, potassium and their oxides move up with ascending gas stream and get absorbed by the down coming cooler materials like coke, ore and sinter. A part of this absorbed alkali is again vapourised to generate a recirculating load within the furnace. The rest of it is absorbed by the slag and leaves the furnace.

The effects of alkali on the raw materials is as follows. Coke and sinter suffer gross deterioration in high temperature properties after absorbing alkali. The carbon dioxide reactivity of the coke rises sharply. Naturally, the coke would lose carbon very fast with a drop in strength. It may even break into small pieces. Alkali has been found to influence reaction involving iron ore also. Sinters with high alkali content have very high reduction degradation index (RDI) High RDI implies high degree of fines generation and unfavourable gas distribution. The final result of alkali accumulation is drop in productivity and the quality of hot metal.

The approach to the alkali problem is two pronged i) the loading of alkali should be reduced to as the low levels as or possible and ii) accumulation inside the furnace has to be kept at zero level through close monitoring and quick corrective actions.

This makes it very important to know the alkali content of the input materials (coke and sinter) and the output (blast furnace slag). Therefore, it is essential to analyse the alkali content of this material on a regular basis. XRF instruments are used for this analysis. In places where XRF spectrometer is not available, AAS or other methods can also be used for this analysis.

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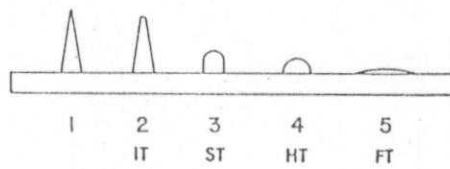
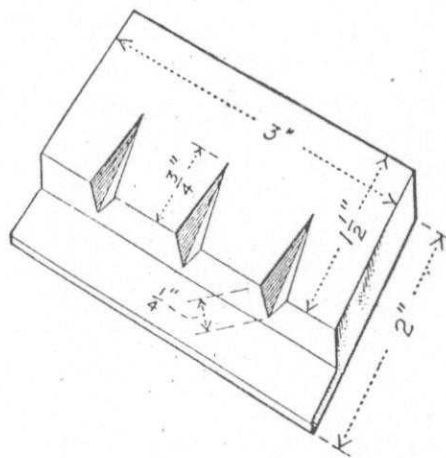


FIG. 1 Critical Temperature Points



Inch-pound Units, in.	SI Units, mm
1/4	6.4
3/4	19.1
1 1/2	38.1
2	50.2
3	76.2

FIG. 2 Brass Cone Mold



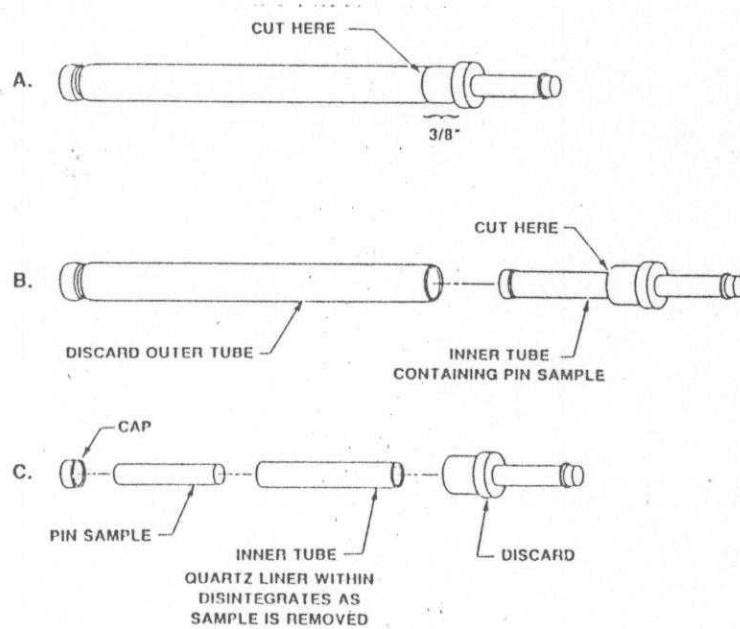


FIG.3 SAMPLE TUBE