

INSTRUMENTAL TECHNIQUES FOR CHEMICAL ANALYSIS OF FERRO-ALLOYS

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1.0 INTRODUCTION

Ferro-alloys are metallic addition agents used in iron and steel making to incorporate an alloying element into the molten material or to refine steel, for example by removal of oxygen and sulphur, in which case the alloying element is only to a minor extent incorporated in the steel. These additions are made to the ladle before the pouring into moulds. Most ferro-alloys are alloys of the main element (usually, 15-85%) with iron, hence the name. Sometimes ferro-alloy contain two or three alloying elements which act in different ways and there are also complex boron alloys in which titanium and aluminum can fix the oxygen and nitrogen in the steel bath so that the boron may enter solution and exert a metallurgical influence.

The increasing demand for ever narrowing tolerances in specification of the physical properties of iron and steel, and of chemical composition on which they depend, coupled with the introduction of much faster melting processes, emphasize the need for more accurate and rapid quality surveillance in which the analytical control of chemical composition at all stages of production is of major importance.

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 works, with the help of various instrumental analytical techniques. The commercial importance of the major elements in ferrous-alloys implies that standard or reference chemical procedures must be available for use.

Apart from quality control of the product, analytical data, coupled with physical tests in some instances, provide vital information for the plant manager in the attainment of increased production and trouble-free operation, with the maximum economy of materials and minimum wear on furnace refractories, mill bearings and so on.

In the commercial sense the prices of many materials, ranging from iron ore and coal to rolled steel, are governed by major and subsidiary element contents. For example, the price of ferro alloy ore is fixed on a sliding scale based mainly on iron content. Here the analyst's skills are required to determine chemical composition to an accepted degree of precision, using the available standard methods, thus providing an essential service to his employer, who may be the buyer or seller.

The determination of the concentration of a particular element in a sample irrespective of the chemical form of that element is part of the broad analytical field of "elemental analysis". For many years the procedure used in analytical chemistry were overwhelmingly dominated by reliance on the chemical reaction of the elements, and the fields of gravimetric, volumetric, and electrochemistry were widely used in this respect. Usually the methods were time consuming and needed meticulous attention. Because of the long lapse time involved, only the most essential analyses were performed on industrial products by the manufacturing company. Frequently, the methods could not be used for product control. Often by the time the analysis were completed, the product was already shipped. Analysts who were really artists in their own right carried out analysis by intuition. Colorimetric procedures were common in which the analyst dissolved the sample and developed a colour specific to the component being analyzed, held the solution upto the sky and came to a " go, no-go" decision on the quality of the sample (the "blue sky" technique). With time, less intuitive instrumental techniques were developed which could be successfully operated by much less skilled operators.

The introduction of more rapid steel making techniques has made imperative the development and application of speedier means of analytical control. This has affected all aspects of laboratory work so that, today the sheer volume of work in the specialist area of the chemical laboratory has tended to make the older classical procedures irrelevant. In the last couple of decades there has been a steady drift away from the classical methods of analysis and a score of instrumental analytical techniques have gained acceptance for quality control and certification of analysis for a wide range of ferrous alloys.

The object of this article is to try and present, particularly to a non-analyst, the range of instrumental techniques which have been most commonly used for the determination of elements, and some of the criteria which have to be considered when choosing an analytical technique for a particular application.

2.0 STANDARD REFERENCE SAMPLE

The quantitative determination by instrumental methods of analysis is a relative method, while the chemical analysis is an absolute method. On the basis of the fact that there is a certain relation between the amount of analytical element and its spectrum intensity the analysis is done by comparison with a standard sample whose content of element has been already known. Standard reference alloys are essential for establishing the validity of a method and providing a sound basis for the determination of precision and accuracy. The general requirements for the standard sample are as follows:

- (i) The concentration of each element should be covered the analytical range
- (ii) The chemical structure and the metallurgical history should be similar to those of the unknown samples to be analyzed
- (iii) The concentration has been authorized by a reliable chemical method
- (iv) It should be a homogeneous sample free from the crystalline segregations
- (v) The concentration of the major components should not be far away from that in the unknown sample
- (vi) The number of standard samples should be enough to make a calibration curve

A few laboratories, are able to establish their own standards using alternative techniques on material of known homogeneity, but for most, it becomes necessary to employ the commercially available standard materials. Despite the fact that there are many certifying agencies around the world that issue metal standards, the picture for the immediate future is not especially bright.

3.0 SAMPLING

Most ferroalloys are hard, abrasive, or tough; some components may also be brittle. Crushers, pulverizers, and other sampling equipment must be such that the minimum contamination from iron and other metals is ensured. Manganese steel or properly hardened alloy steel, and hardened and tempered chromium steel are commonly employed. Another reason for great care in sample preparation is that many ferroalloys are high in price.

3.1 SAMPLING FROM LIQUID METAL

a. Sampling Procedure:

Two or more spoon samples shall be taken during the pouring of each cast or ladle, preferably during the first third and last third of the teeming. The spoon samples so obtained shall be poured into suitable metal moulds. Alternatively, the moulds may be filled directly from the metal stream. Liquid sampling is not suitable for ferro-alloys subject to segregation in the liquid states.

b. Sample Preparation:

The samples shall be prepared by one of the following methods

- (i) where drilling is possible (e.g low carbon, low silicon, ferro chromium), drill the test ingot at a point one third of its height from the bottom, from the out side to the centre or cut off and discard the bottom third of the test ingot. Mill across the whole exposed face of the remaining sample after grinding off the outer skin.

Drillings or millings shall be as fine as possible, and if necessary may be further reduced in a hardened steel percussion mortar to pass a 425 um sieve.

- (ii) where drilling is not possible, the test ingot shall be broken on a suitable 'anvil' and the pieces crushed in a hardened steel percussion mortar until the whole passes a 425 um sieve. Reduce the sample if necessary to the final quantity required by repeated coning and quartering. Crush in a hardened steel percussion mortar to pass the mesh as specified below, mix divide if necessary, and bottle for analysis

Ferro boron)	Ferro vanadium	355 um
Ferro molybdenum)		
Ferro tungsten)	Low carbon Ferro manganese	425 um

High carbon Ferro chromium)
High carbon Ferro manganese)
Ferro niobium) (212 um
Ferro titanium)
Ferro silicon)

3.2 SAMPLING FROM SOLID METAL

Ferro-boron, ferro-molybdenum, ferro-niobium, ferro-titanium, ferro-tungsten and ferro-vanadium are made in relatively small casts or buttons, and as they tend to segregate to an appreciable extent, a large number of pieces should be taken to obtain a representative sample.

Break down the gross lot, and blend thoroughly by repeated coning. Fill the containers by means of a scoop or shovel, placing every tenth scoopful or shovelful in the sample container. Where automatic loading is employed obtain the sample by diverting the stream of pieces at least once during the filling of each container. The content of the sample container shall amount to at least one-tenth of the gross lot.

Crush the total contents of the sample drum in a jaw crusher to less than 12.5 mm, the reduce by coning and quartering until 45 Kg of sample remains. Sieve on a 6.7 mm sieve, and return the oversize to a jaw crusher set to crush the pieces to pass the sieve. Cone and quarter this sample until 5 Kg remains. Sieve on a 1.7 mm sieve, and crush the oversize in a hardened steel percussion mortar until all of the sample passes the sieve.

Reduce the 5 Kg sample to 1.5 Kg by coning and quartering then sieve on a 710 um sieve and crush the oversize in a hardened steel percussion mortar until all of the sample passes the sieve. Reduce the 1.5 Kg sample if necessary to the final quantity required by repeated coning and quartering. Crush in a hardened steel percussion mortar to pass the mesh as specified below, mix, divide if necessary, and bottle for analysis

Ferro boron	150 um	Ferro niobium	212 um
Ferro molybdenum	150 um	Ferro titanium	212 um
Ferro tungsten	150 um	Ferro vanadium	355 um

4.0 REPARATION OF SAMPLES AND SOLUTIONS FOR ANALYSIS

The precision attainable in the analysis of ferrous alloys depends upon the care and attention given to the initial preparation and dissolution of the sample, and the consideration given to the removal of major alloying or interfering elements. All ferrous materials are relatively passive to strong nitric acid; solutions 50% (v/v) nitric acid can not be used to dissolve samples. Ferrous alloys will not dissolve in strong sulphuric acid or perchloric acid, and solutions greater than 33% (v/v) should not be used as initial attacking acids.

4.1 SOME PROBLEMS POSED DURING SOLUTION

Silicon in most ferrous alloys ranges from 0.001-5% and partly precipitates as gelatinous silica during solution techniques which do not include a dehydration step. Silicates in solution can precipitate in the atomization chamber and can cause severe depressive effects in the flame. The precision and accuracy of many determinations can be improved by removal of silica either by dehydration or by volatilization with hydrofluoric acid during the solution process. Precipitated silica can co-precipitate or co-absorb some of the elements being sought, and during method development this possibility should be assessed. Some workers combine the gravimetric determination of silicon with the solution preparation for the subsequent determination of other elements.

Tungsten in ferrous alloys ranges from traces to 25% and hydrolyzes rapidly in oxidizing conditions and slowly with reducing conditions; the hydrolyzed product can occlude a portion of most of the elements in ferrous alloys. For some determinations the hydrolyzed tungstic acid can be removed by filtration and washed; the tungstic acid is then dissolved by washing with ammonium hydroxide or sodium hydroxide, the alkaline filtrate discarded, and the previously occluded elements recovered from the filter paper. An alternative approach is the use of hydrofluoric or phosphoric acids to complex the tungsten during the initial solution of the alloy. Molybdenum can hydrolyze under oxidizing conditions, but the effect is much less severe than for tungsten; the above recommended techniques for tungsten can be applied for molybdenum.

5.0 INSTRUMENTAL TECHNIQUES FOR CHEMICAL ANALYSIS OF FERRO-ALLOYS

The most commonly employed analytical techniques are flame atomic absorption spectrometry (Flame-AAS), optical emission spectrometry (OES) and X-Ray fluorescence (XRF).

5.1 ATOMIC ABSORPTION SPECTROMETRY

In recent years, atomic absorption spectrometry has become an increasingly important tool in the analysis of ferro-alloys. Almost every known metallic element can be determined by means of this tool.

Flame atomic absorption involves aspiration of the solution into an acetylene flame supported by either an air or nitrous-oxide oxidant gas. Light from a special lamp (either a hollow cathode or an electrodeless discharge lamp) that contains the element of interest and emits its characteristic spectrum is directed through the flame. As minute droplets of the sample liquid are vaporized, a steady state cloud of ground state sample atoms is formed in the flame. The analyte-element atoms absorb some of the characteristic light energy from the lamp, and a monochromator and detector system is used to measure the diminution in energy, which is proportional to the concentration of the analyte.

Atomic-absorption spectroscopy is generally free from spectral interference, but other types of interference may occur. In chemical interference, the number of free atoms may be reduced by formation of thermally stable compounds in the flame and hence atomic absorption.

Various means of countering this are (a) use of hotter flames (b) addition of 'releasing agent' which will form a still more stable compound with the interfering ion. Matrix or background effects are common in the analysis of ferrous alloys. If the matrix causes chemical interference it may be necessary to add a releasing agent as well as equalizing the matrix concentrations in standard and sample solutions. If the effect is severe, separation of the matrix from the metal concerned, by extraction or ion-exchange methods, may be necessary.

Even though other analytical techniques perform an extremely important role in the analysis of metals, atomic absorption spectrometric methods have become the "work horse" of the modern analytical laboratories because of their speed, ease of operation and low cost.

5.1.1 SOURCES OF DIFFICULTIES IN FERROUS ANALYSES

When test solutions with the maximum recommended concentration are being used, the burner may become clogged by salts which cause flame instability and memory effects between samples. These conditions can be minimized by using a wash solution with the same solvent concentration as the test solutions, rather than water, and by keeping the aspiration time for test solutions at a minimum. The technique of turning the burner to reduce the absorption path for higher concentration solutions can lead to lower precision. The most precise readings are normally obtained by dilution of the higher concentration samples and comparison with similarly diluted samples or by the use of less sensitive wavelengths.

Where the matrix or the percentage of the element sought are not fully compatible with available standards, appropriate quantities of standards should be mixed or very high purity metals used to assist the matrix matching.

5.2 OPTICAL-EMISSION SPECTROSCOPY

Optical-emission spectroscopy is a broad term nowadays. It covers techniques that employ a wide variety of excitation sources ranging from various forms of arc and spark electrical discharges to plasma-source techniques. In all instances, however, the technique is characterized by the measurement of atomic-emission spectral lines caused by the energy transitions of valence or outer-shell electrons.

In metal industry emission spectrochemical techniques, using arc or spark as light sources, has become an indispensable analysis method for on line control of chemical composition. From a viewpoint of the basic principle, this device is not different from the analysis method using a spectrograph, the method conventionally employed in wide application range. The only difference is replacement of the conventional photographic plate with the exit slit and the photomultiplier tube. This method is to cause spark to be discharged between a sample and a counter electrode, to photoelectrically measure intensity of emission spectra emitted therefrom, and to quantitatively determine the element contained.

Flames are also used for atomic emission, but in the last 15-20 years the increasing use of plasma sources have given emission spectroscopy rebirth. Today the solutions are most often analyzed directly by inductively coupled plasma (ICP). The plasma is, in fact, ionized argon gas

and its associated electrons, at a temperature approaching 10,000K, which is created and maintained by a high-frequency electromagnetic field. An argon-sheathed quartz torch contains the plasma and provides the means by which nebulized sample solution is introduced into the plasma the light energy released by the excited sample atoms then passes through a slit into a spectrometer; where it is dispersed and measured.

An important advantage of the plasma is that no special sources are necessary. The concentration range of the ICP usually spans three or four orders of magnitude. This is an important requirement for automated analyses. Flame AA spans only two orders of magnitude. The ICP advantage of a very wide linear analytical range makes it less necessary to redilute a sample that may have exceeded the range. Because of high temperatures achieved by ICP, it has been spoken as free of chemical interferences than flame AA. Spectral interferences are an important consideration for the ICP, and different lines are preferred for a specific element in different matrices. This sometimes requires that spectroscopic skills be used to solve some difficult analytical problems.

5.3 X-RAY FLUORESCENCE

There are other techniques other than spectroscopy that are used for the determination of metals both at major and at trace levels. For example X-Ray fluorescence spectrometry is a widely used, highly reproducible technique that excels at higher concentrations. Samples are used in the solid, powder and solution forms. In this technique, a primary X-Ray beam impinges on the solid sample surface, causing the ejection of inner-shell electrons from atoms in the first few monolayers. As outer-shell electrons fill the vacated shells, secondary X-Ray photons are released. Energy dispersive instruments which are lower in cost and accurate, use either an x-ray tube or a radiation source to excite the sample and a solid-state detector to directly measure the energy distribution of the emitted secondary x-rays. Wave length dispersive instruments, which always employ an x-ray tube to excite the sample, refract the secondary x-rays with a dispersing crystal and measure the dispersed lines with geiger, scintillation or flow counters. These instruments come in sequential scanning and direct-reading simultaneous versions that are analogous to optical-emission instruments.

5.3.1 COMPARISON OF OPTICAL EMISSION AND X-RAY FLUORESCENCE

- (a) X-ray spectra are generally simpler than optical spectra
- (b) Optical emission covers the range from ppm levels to ca.10%., XRF from ca. 0.01 to 100%
- (c) X-ray spectrometers analyse a surface ca. 25 mm square on the specimen whilst emission excites a point centre with a surrounding sputtered area 5 mm in diameter
- (d) Interelement effect in XRF are of lower magnitude and complexity
- (e) Given adequate counting time, XRF is the more accurate and precise
- (f) Emission is the more rapid and suitable for steel making control analysis but demands closer attention to operating conditions
- (g) XRF caters for a wider range of sample conditions, e.g non-conductive materials can be analysed by XRF but not by emission unless first briquetted with graphite, which is conducting.

- (h) For simultaneous multichannel systems similar programmes, XRF instrument will be atleast twice as expensive.

6.0 CARBON,SULPHUR ANALYSIS

Method: The analysis sample is combusted inside an HF furnace in an oxygen stream under positive pressure. Carbon, sulphur and their compounds react to form carbon dioxide and sulphur dioxide. Selective and quantitative evaluation of CO₂ and SO₂ is obtained by means of two channel infrared analyser. The oxidation products of CO₂ and SO₂ which are released on combustion are carried in the oxygen stream and pass through a metal filter and dust trap to remove metal oxides, and then a drying column into the infrared detector. The analysis gas flows first through SO₂ cell, then through an oxidation furnace and a SO₃ trap into the CO₂ analyser. The oxidation furnace ensures that any CO present is converted to CO₂. The SO₃ formed from SO₂ is absorbed on cellulose.

The analogue detector signals produced by IR absorption are amplified electronically. Blanks due to the crucible and the flux added for optimum combustion are deducted from the signal.

Range (for 0.5g sample)	0-4.0% C, 0-0.3% S
Accuracy	+ 2 ppm or +1% relative for C + 3 ppm or +2% relative for S
Resolution	0.1 ppm

7.0 CONCLUSIONS

In metallurgical analysis, the need is always for the best accuracy and best speed. Control analysis is usually carried out under rigidly standardized conditions which have been designed so that the result is available in the shortest possible time. Check analyses are performed with the utmost care under less hurried conditions. Atomic absorption may be considered in both contexts. It will not, of course compete in speed with the large direct-reading emission or X-ray spectrometers. But smaller operators who can not afford such equipment undoubtedly find a modified form of control with atomic absorption extremely valuable.

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