# X-ray Fluorescence Spectrometry in the Iron and Steel Industry

*Didier Bonvin*

# X-ray Fluorescence Spectrometry in the Iron and Steel Industry

**Didier Bonvin**
*ARL Applied Research Laboratories, Ecublens, Switzerland*

*In reviewing the current status of wavelength-dispersive X-ray fluorescence (WDXRF) spectrometry in the iron and steel industry, attention is given to aspects such as sampling and specimen preparation, calibration requirements and analytical demands for the various material types and the choice of instrument configuration.*

## 1 INTRODUCTION

WDXRF spectrometry is well established as an analytical technique in the iron and steel industry. WDXRF is routinely used for the analysis of raw materials, sinters, slags and coupled with optical emission spectrometry (OES) for determination of the elemental composition of cast iron and steels (Figure 1).

One of the great advantages of WDXRF is its ability to analyze both conducting and nonconducting solids and liquids, whereas OES is used mainly for the analysis of metals. Both techniques are really complementary in the iron and steel industry:

- Elements such as boron, carbon and nitrogen at levels down to parts per million (ppm) cannot be measured by X-ray fluorescence (XRF) spectrometry but OES allows the quick reporting of their composition in metals, which is essential in this industry.

- All other elements required (except hydrogen) can be measured both by XRF and OES. The latter technique is superior at low concentration levels and WDXRF allows better precision at high concentration levels, e.g. nickel and chromium in high-alloy steels, leading to substantial gains in the amount of expensive alloying elements that are added to make a given alloy grade.

- Analysis of nonconductive materials, such as slags and sinters, is done very effectively and quickly by WDXRF.

For the analysis of metals, this complementarity means that very often the same specimen is used for both analysis techniques.

The demands for lower limits of detection, improved reliability of trace element analysis and tight control of alloy compositions have been steadily increasing in recent years. In addition, there is a trend within the iron and steel industry to place the analytical capability closer to the process that uses the analysis values so as to facilitate and speed up any corrective actions during production. These demands have led manufacturers of WDXRF instrumentation to design instruments that are more sensitive, have greater flexibility and which can be easily incorporated into automated laboratories. In this industry, energy-dispersive X-ray fluorescence (EDXRF) spectrometry is generally not selected because of its poor
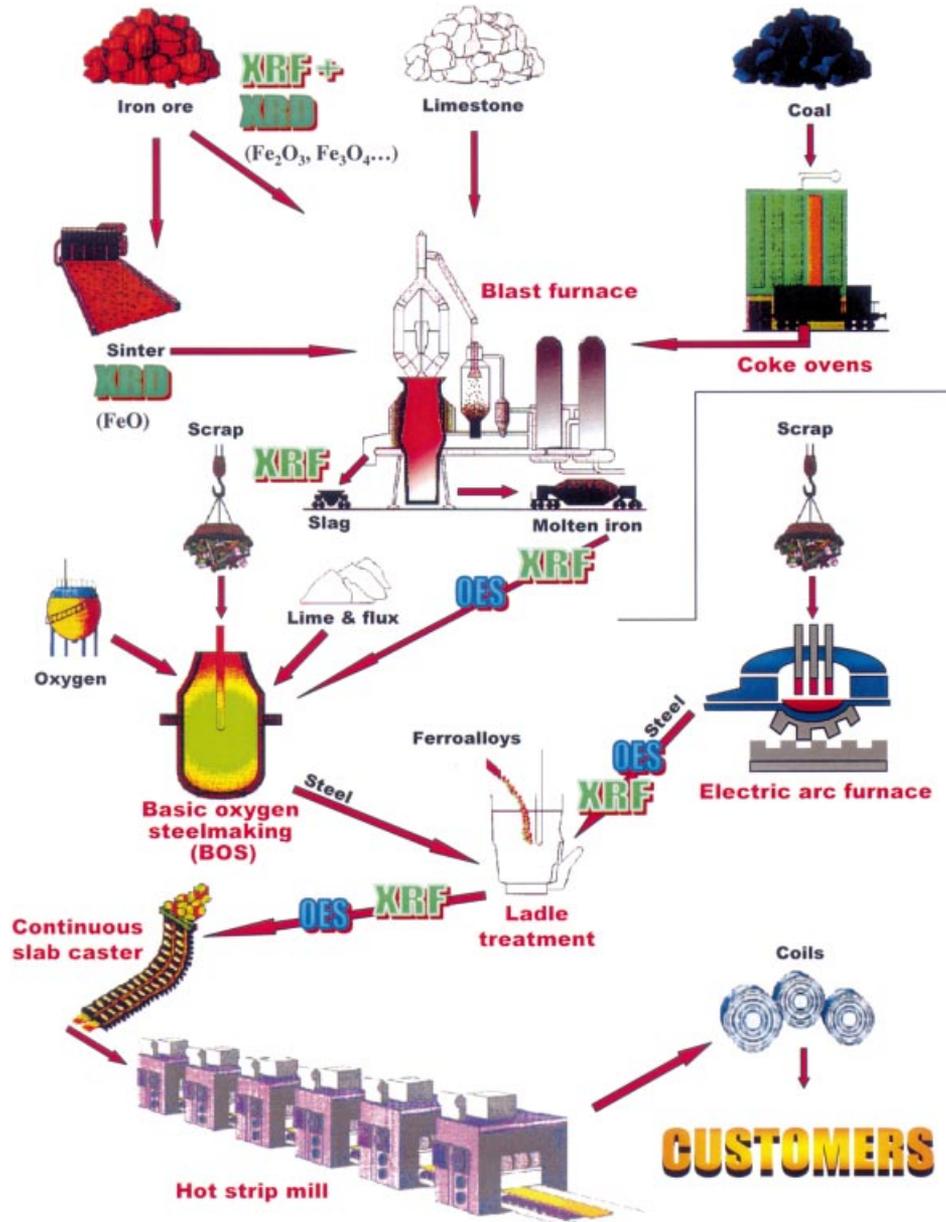
**Figure 1** Processes in the iron and steel industry with various demands on analysis.

resolution and low performance with light elements (Na to Cl and particularly Mg, Al, Si and S) and its insufficient precision for major element analyses.

## 2 SAMPLING

It is well known that the analytical result is only as good as the sample submitted for analysis. All too often the taking of a representative sample is neglected while at the same time emphasis is placed on producing the most accurate analytical result using the most sensitive procedure or instrumentation. The effort put into achieving high-quality results is, of course, totally misplaced if an equivalent effort is not applied to sampling.

In the iron and steel industry, the samples submitted to the laboratory are intended to be representative of a shipload of iron ore, a stockpile of raw materials, intermediate and final products from the steel plant. This represents an enormous reduction in size to derive a laboratory-size sample of about 5 kg from many thousands of tons of original material. It is important that a sampling procedure is implemented which will

minimize the errors associated with sampling these large volumes of material. If possible, samples should be taken from moving streams using automatic cutters that remove samples from the conveyor belt in a controlled and regular manner.

The volume of material collected at the belt must be reduced in a systematic way so that the sample that ultimately reaches the laboratory is homogeneous and fully representative of the original sample.

Tests have shown that a totally automated system that takes and prepares the sample is capable of a precision that is typically twice as good as that of a manual system. The results of an automatic sampling system are compared with a manual system in Table 1.[1] Included in the comparison is the analytical precision obtainable by preparing and analyzing 10 replicate fusion beads. The results emphasize the point that sampling is the limiting factor in the achievement of precise analytical data when analyzing large sample volumes.

The quality of sampling being of the utmost importance with a view to obtaining representative results, International Standardization Organization (ISO) norms have been produced, e.g. ISO 3081, 3082 and 3083 for sampling

and sample preparation of iron ores and ISO 14284 for sampling and preparation of steel and iron.

For processed final products such as cast iron and steel, a dip sample is usually taken from the molten

**Table 1** Sampling precision trials on iron ores. (Reproduced by permission of Dr Ulrich Senff.)

| Component | Average (%) | Automatic SD[a] ($2\sigma$) (%) | Manual SD[a] ($2\sigma$) (%) | Analytical precision SD[a] ($2\sigma$) (%) |
|---|---|---|---|---|
| Fe | 66.12 | 0.54 | 1.1 | 0.2 |
| $SiO_2$ | 2.68 | 0.52 | 1.22 | 0.02 |
| $Al_2O_3$ | 1.04 | 0.2 | 0.44 | 0.01 |
| Mn | 0.12 | 0.06 | 0.16 | 0.01 |
| MgO | 0.09 | 0.04 | 0.08 | 0.01 |
| CaO | 0.08 | 0.08 | 0.12 | 0.01 |
| $TiO_2$ | 0.05 | 0.02 | 0.02 | 0.01 |
| P | 0.036 | 0.004 | 0.01 | 0.002 |
| $K_2O$ | 0.018 | 0.008 | 0.022 | 0.001 |
| Zn | 0.002 | 0.002 | 0.002 | 0.001 |
| LOI[b] | 1.16 | 0.16 | 0.32 | 0.06 |

[a] SD, standard deviation.
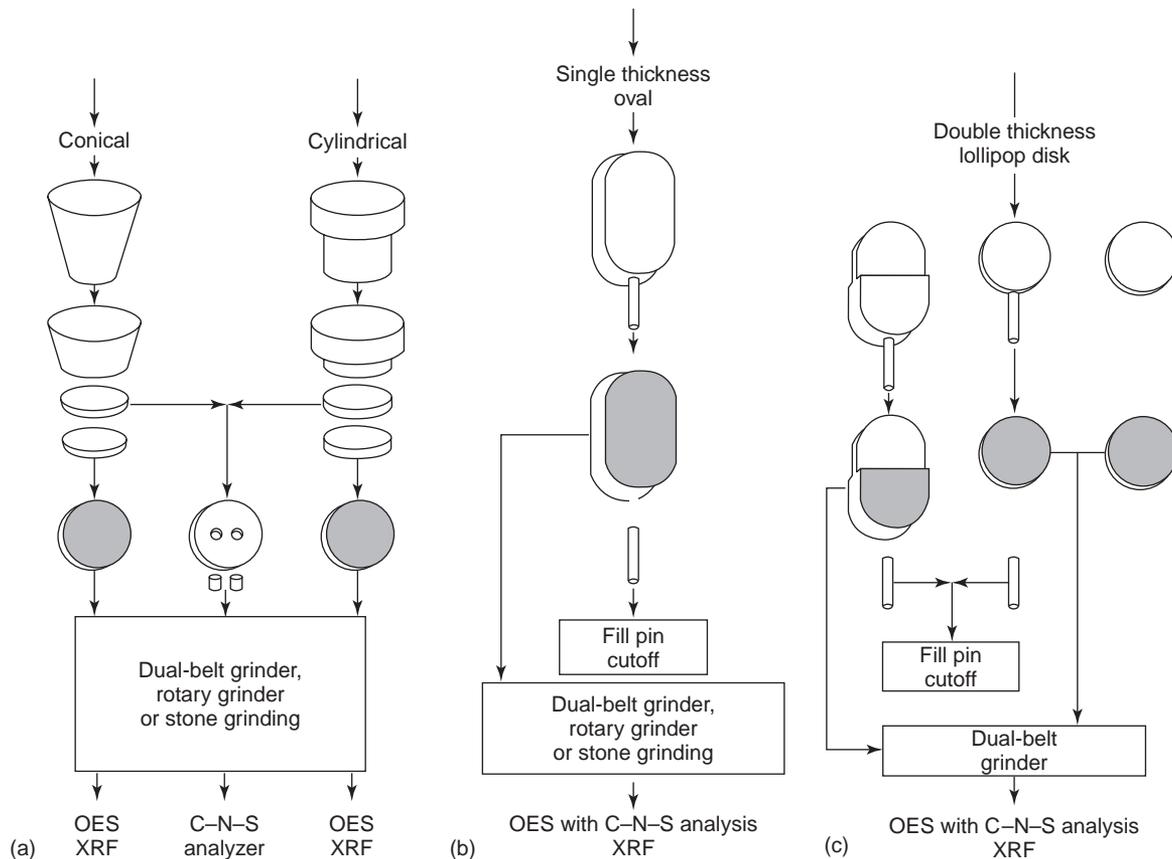[b] LOI, loss on ignition.



**Figure 2** Typical sample shapes used for metal analysis in the iron and steel industry. (Reproduced by permission of Herzog Maschinenfabrik GmbH.)

mass. An appropriate sampling device is used and the molten material is cast into a mold that provides rapid solidification (see **Metal Analysis, Sampling and Sample Preparation in**). The aim of the exercise is to produce a homogeneous and representative sample through a methodology which will ensure as high a reproducibility as possible and promote the formation of a fine-grained metallographic structure of the specimen. For these reasons, the mold casting has nowadays been largely replaced by immersion probes, which allow better control and reproducibility of the conditions in which the samples are taken. The most popular type of immersion probes produce the so-called lollipop, in either oval or disk form, as shown in Figure 2(a–c). They produce samples which will fit into the sample holders of all modern WDXRF spectrometers (maximum diameter 52–60 mm) and which present a flat surface of at least 30 mm diameter as the aperture of the holder for presentation of the sample to the WDXRF spectrometer is typically 28–30 mm in diameter.

# 3 SPECIMEN PREPARATION

Specimen preparation involves the procedure for preparing the sample in a form that is acceptable for introduction into the XRF spectrometer. It is clear that here again a high reproducibility of the preparation method is essential in order finally to ensure high precision and accuracy of the analyses. As seen above, a minimum flat diameter of 30 mm is generally desired for the analysis.

## 3.1 Metals

Metal samples include pig irons, cast irons, carbon steels, stainless steels and tool steels. Samples taken at the production point are usually of the correct size and consequently only require surface preparation. Only in the presence of visible defects such as air bubbles, nonmetallic inclusions or cracks will the operator have to take a decision about the validity of the sample.

The surface preparation procedures generally involve the use of abrasive paper either on a rotary grinder or on a belt linisher. Polishing striations give rise to a shielding effect, which results in a decrease in fluorescence intensities, especially for lighter elements, depending on the orientation of the sample. As expected, the decrease in intensity is more important when the XRF analytical devices view the sample perpendicularly to the striations than when they look at the sample parallel to them. For this reason, modern spectrometers are equipped with spinning of the sample holders to smooth out the influence of sample orientation, resulting in reproducible intensities on samples and standards.

Surface preparation is often started with a coarse alumina paper, e.g. 30–80 grit. The final surface finish is obtained by using finer grits, e.g. 120–180 grit, but this additional fine grinding is not practised everywhere. Grinding with alumina paper will, of course, contaminate the surface of the specimen with aluminum. Therefore, accurate aluminum content is generally determined by the OES technique, for which the depth of analysis is larger. Alternatively, silicon carbide abrasive paper can be used, but this will give a similar problem with silicon. Other types of abrasive paper such as zirconium oxide have been shown always to contain some alumina and therefore cannot solve the problem entirely. An interesting alternative is being applied in France on stainless steels where lathe preparation is used, which produces a good quality of surface without contamination.

## 3.2 Pressed Powders

Pressed powders offer the quickest and simplest form of sample preparation for WDXRF analysis. There are, however, limitations to the procedure and as long as these are recognized the method can be used for the preparation of most of the oxides and ferroalloys associated with the iron and steel industry.

The most serious disadvantages of the pressed powder procedure are particle size effects and mineralogical effects. Particle size effects are most significant in the determination of light elements where long-wavelength XRF radiation is emitted from the upper layers of the specimen and is influenced by differences in particle size. To minimize these effects, the particle size for pressed powders should be <50 μm. This is achievable with vibro-rotatory milling equipment. Care should be taken in the choice of mill vessel as contamination of the sample occurs during the milling process. In the iron and steel industry, vessels made of chrome steel are generally used because they are stronger and less expensive than the tungsten carbide (WC) versions. However, being less hard, they will wear quicker and also will contaminate the specimen with iron and chromium. This is why in cases where only minimum contamination can be tolerated WC should be chosen.

When the binding characteristics of the powder are not sufficient, a suitable binder/grinding aid must be added to the sample before milling the mixture. Generally a dilution of one part of binder to nine parts of sample is used. The powder can then be pressed into an aluminum cup or a steel ring.

One of the difficulties in carrying out an XRF calibration for pressed powders is that generally certified

reference materials (CRMs) cannot be used efficiently owing to mineralogical effects. The use of in-house standards of the same material types as those requiring analysis is recommended in order to produce calibration curves which will fit with the production samples.

### 3.3 Fused Beads

#### 3.3.1 Introduction

Preparation of oxide materials as fused beads based on the original method of Fernand Claisse[2] is the best method of obtaining accurate results. Essentially, the fusion procedure consists of heating a mixture of sample and flux at high temperature ($800-1200\,^\circ$C) with a borate so that the flux melts and dissolves the sample. The overall composition and cooling conditions must be such that the end product after cooling is a one-phase glass. Heating of the sample–flux mixture is usually done in platinum alloy crucibles (e.g. Pt–5% Au), but graphite may also be used when conditions permit. Both particle size effects and mineralogical effects are removed as the original structure of the sample is completely destroyed by the fusion at high temperature and the elements are then embedded in a truly homogeneous matrix. Thus improvement in reproducibility and accuracy can be achieved with this method compared with the pressed pellets method, as shown in Table 2.[1]

#### 3.3.2 Advantages of the Fusion Technique

The fusion technique also has additional advantages:

- Possibility of high or low specimen dilution: the dilution level is often dictated by the ability of the given oxide to be fused completely and without segregation. Lower dilution allows better limits of detection and decreases the preparation errors as a larger amount of sample is weighed.

- Possibility of adding compounds such as heavy absorbers or internal standards to decrease or compensate for matrix effects.

- Standards of desired composition can be prepared from pure oxide materials in order to generate calibration curves.

- CRMs can be used without restriction to generate calibration curves.

- Possibility of obtaining very large calibration ranges within the same calibration curve when the proper matrix corrections are used (Table 3).[3]

Figure 3 shows an example of such a calibration curve for Ca covering a concentration range from 200 ppm to 94%.

**Table 3** Calibration ranges achievable with a general calibration for oxides prepared as glass beads (data for ignited samples): the standard error of estimate (SEE) gives a measure of the accuracy achieved with such wide range calibration for oxides. (Reproduced by permission of ARL/Applied Research Laboratories SA.)

| Element | Range (%) | Typical SEE (%) |
|---|---|---|
| CaO | 0.02–94.4 | 0.21 |
| $SiO_2$ | 0.35–99.7 | 0.17 |
| $Fe_2O_3$ | 0.025–94.0 | 0.15 |
| MgO | 0.01–97.3 | 0.10 |
| $Al_2O_3$ | 0.16–89.2 | 0.11 |
| $K_2O$ | 0.006–15.4 | 0.05 |
| MnO | 0.005–8.0 | 0.04 |
| $Cr_2O_3$ | 0.002–17.4 | 0.03 |
| $TiO_2$ | 0.011–3.8 | 0.03 |
| $P_2O_5$ | 0.014–1.0 | 0.04 |
| $SO_3$ | 0.015–3.7 | 0.05 |
| $Na_2O$ | 0.045–10.4 | 0.05 |

**Table 2** Comparison of repeatability with blast furnace slag for pressed powder and fusion bead preparation: 10 specimens prepared from the same sample. (Reproduced by permission of Dr Ulrich Senff.)

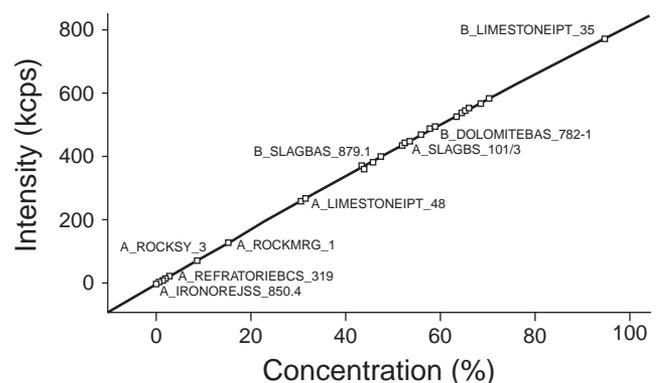| Component | Concentration (%) | SD ($2\sigma$) (%) | |
|---|---|---|---|
| | | Fused disk | Pressed powder |
| CaO | 40.7 | 0.12 | 0.22 |
| $SiO_2$ | 34.8 | 0.08 | 0.18 |
| $Al_2O_3$ | 14.2 | 0.06 | 0.08 |
| MgO | 7.2 | 0.08 | 0.1 |
| $TiO_2$ | 0.88 | 0.02 | 0.02 |
| S | 0.59 | 0.02 | 0.02 |
| $K_2O$ | 0.51 | 0.01 | 0.02 |
| MnO | 0.42 | 0.01 | 0.02 |
| FeO | 0.39 | 0.02 | 0.12 |
| P | 0.005 | 0.002 | 0.002 |



**Figure 3** Calibration curve for Ca in various oxide materials using the fused-bead preparation technique. (Reproduced by permission of ARL/Applied Research Laboratories SA.)

### 3.3.3 Variables in the Method

There are still many decisions that need to be made in order to achieve accurate analyses with the fusion bead procedure.

### 3.3.3.1 Choice of Flux

This is the most important aspect as the flux must be able to dissolve all the different material types that require analysis. Many preferences exist among the various laboratories engaged in major element analysis of oxide materials. The most frequently used fluxes are borates, namely lithium tetraborate, lithium metaborate and sodium tetraborate. Lithium tetraborate is widely used as it is suitable for many applications. Sometimes mixtures of these fluxes are more effective, e.g. fluxes with 12 parts of $Li_2B_4O_7$ to 22 parts of $LiBO_2$[4] or 65% $Li_2B_4O_7$–35% $LiBO_2$.[5]

Nonwetting additives are often used in order to reduce the retention of the melt in the crucible during pouring, reduce any sticking of the bead to the mold and therefore allow cooling without risks of cracking. Additives can be liquids such as solutions of HBr, $NH_4I$ or LiF or solids such as LiBr.

Oxidizing agents, e.g. $LiNO_3$ or $NaNO_3$, are added when some metallic particles occur in the sample in order to save the platinum ware and obtain a homogeneous bead.

Because of all these additions, accurate weighing is essential in order not to introduce serious errors.

### 3.3.3.2 Fusion Apparatus

Types of fusion apparatus range from simple gas burners or muffle furnaces to sophisticated automatic fusion machines with multiple burners or induction coils.

### 3.3.4 Disadvantages of the Method

The disadvantages of the method are relatively obvious and constitute the reason why pressed powders are still used in many instances:

- time of preparation;
- cost per specimen due to the consumables, e.g. flux, additives and platinum ware;
- loss of volatile elements during the fusion;
- possible errors when weighing flux and sample.

## 4 CALIBRATION OF THE X-RAY FLUORESCENCE INSTRUMENT

### 4.1 Introduction

In order to obtain the concentrations of the various elements present in the sample, the XRF spectrometer must be calibrated. This is done by measuring reference materials, either a CRM or a secondary reference material (SRM).

*Overlap corrections* are necessary when a spectral line of an element interferes with the analyte line. The contribution from the interference line to the intensity of the analyte line must be corrected. Such a correction depends on the sensitivity of the instrument for the given analysis lines, and therefore they have to be determined experimentally, for example by running binary standards.

In addition, it is essential that *matrix corrections* be used in order to achieve the desired accuracy. The correction coefficients can be determined experimentally with a large number of reference materials. However, the common practice nowadays is to generate theoretical $\alpha$ factors through specific software programs which take into account the conditions of excitation (anode type, kV, mA), the geometry of the instrument and the matrix considered. Finally, matrix correction must be applied to the intensities obtained on the XRF instrument through a multivariable regression program in order to obtain the corrected calibration curves.

### 4.2 Setting-up Samples and Control Samples

In order to maintain the calibration over time, a number of stable samples representing the high and low intensities (not the concentrations) found in the various calibration curves are chosen. They are called setting-up samples. The drift correction, also called recalibration or standardization, needs to be performed at given intervals. Modern high-power WDXRF instruments are very stable in the long term and standardization is often practised with intervals of 1 week or more. Procedures are now used in order to determine at which time the standardization must take place. On-line statistical process control (SPC) software performs the statistical analysis as a background task as soon as a stable control sample has been run. In case of nonstatistical behavior of a given analysis channel, an alarm appears on the instrument screen requesting a selective standardization. SPC allows guaranteeing of the precision and accuracy of the spectrometer, which is required by quality systems such as the ISO 9000 series of standards.

Small, low-power desktop XRF machines, in contrast, require a monitor sample (also called type standard) to be used generally before each analysis in order to correct for possible drift.

It is not necessary that the setting-up samples have the same matrix as the production samples, but it is essential that they are very stable and easy to clean. For example, for slags or sinters, flat, polished, glass–ceramic samples are very adequate whereas for calibration of iron or steel, diamond-polished metallic samples are selected.[6]

**Table 4** Metallic materials analyzed by XRF

| Type | Typical frequency | Typical response time (min) | Response time requested |
|---|---|---|---|
| Pig iron (blast furnace iron) | 90 per day | 3–15 | 3–5 min |
| Pig iron before desulfurization | 30 per day | 3–15 | Asap[a] |
| Pig iron after desulfurization | 30 per day | 3–15 | Asap |
| Steels | 150–300 per day | 3–6 | Asap |
| Ferroalloys (each type) | 1 per batch + 1 per week | 15–45 | Within the day |

[a] As soon as possible.

# 5 MATERIAL TYPES AND ANALYTICAL REQUIREMENTS

In the iron and steel industry, analyses on materials and products are carried out for two very distinct purposes: control of the process and control of incoming material for invoicing purposes. Analysis requirements are generally expressed in term of limits of detection, of precision at given concentration levels and of accuracy. In view of the high performance of modern WDXRF instruments, accuracy depends more on the quality and number of standard samples used for the calibration and on the matrix and overlap corrections than on the intrinsic qualities of the instrument. This is why instrument manufacturers nowadays utilize numerous CRMs and are able to deliver instruments that are fully factory calibrated.

The materials that are analyzed by WDXRF in the iron and steel industry are metallic (Table 4) or nonmetallic (Table 5). A third category can be defined for the various coatings and other miscellaneous materials (Table 6).

Two parameters allow rating of the importance of a given material within a plant, its frequency of analysis and the desired reporting time. The response time varies as a function of the distance that the specimen has to travel to reach the analytical equipment, the degree of automation involved and the type of XRF spectrometer (sequential, simultaneous or simultaneous/sequential).

**Table 5** Nonmetallic materials analyzed by XRF

| Type | Typical frequency | Typical response time (min) | Response time requested |
|---|---|---|---|
| Iron ores | 5–10 per day | 10–30 | 2–4 h |
| Sinters | Every 2–4 h | 10–60 | 2–4 h |
| Blast furnace slags | 20–40 per day | 6–30 | Asap[a] |
| Converter slags | 20–40 per day | 6–30 | Asap |
| BOS slags[b] | 30–50 per day[c] | 6–30 | Asap |
| Ladle slags | 20–40 per day | 6–30 | Asap |

[a] As soon as possible.
[b] BOS, basic oxygen steelmaking.
[c] Depending on the process, sometimes none.

**Table 6** Miscellaneous material analyzed by XRF

| Type | Typical frequency | Response time requested |
|---|---|---|
| Bauxite, olivine, limestone, dolomite, serpentine, calcium hydroxide, ilmenite, casting fluxes, mold powder | 2 per week | Within the day |
| Coke ash, coal ash | 1 per incoming batch + 10 per day | 2–4 h |
| Refractories | Occasionally | Within the day |
| Coatings (Zn–Al, Zn–Ni, Zn–Fe, Sn, Cr, plastic) | 1 per hour | 30 min |

## 5.1 Analysis of Iron Ores

Producing steel from natural material is achieved through reduction of iron ores in a blast furnace or a direct reduced iron (DRI) process as opposed to the alternative method using steel scraps fused in an electric furnace (Figure 1).

Two procedures are available for the preparation of iron ores in a suitable form to allow XRF analysis. The preparation through fusion into glass beads (section 3.3) opens up the possibility of having a standardized method and is described in ISO 9516.[7]

Pressed powder briquettes of iron ore are employed in cases where ultimate accuracy in not required, when the number of samples to be tested is large,[8] when trace elements must be determined or when an additional X-ray diffraction (XRD) analysis is intended on the same specimen.

The XRD technique permits the determination of the compounds or phases present in a sample. However, only limited use has been made of quantitative XRD in process control as such instruments are usually housed in the Central Research Laboratory, well away from the process.

The latest instrumentation incorporating an XRD device into a conventional WDXRF instrument permits

the determination of both the elemental and phase composition of specimens.[9] The determination of the relative proportions of hematite ($Fe_2O_3$) and magnetite ($Fe_3O_4$) in iron ore, for example, results in better utilization and optimization of the available mineral resources. This kind of instrument can replace the time-consuming wet chemical methods employed up to now to determine these different phases.

More details on the analysis of iron ores can be found in **Iron Ore, Sample Preparation and Analysis of**.

## 5.2 Analysis of Sinters

Sinters represent the majority of the ferrous products charged into the blast furnace (around 75% or more). They are made of iron ores, coke and limestone heated to 1200 °C and sintered by aspiration of air through the mixture. This allows substitution of the raw iron ores by a man-made material with desired specifications and keeps the fluctuations of the firing conditions in the furnace as small as possible.[10]

The XRF technique only determines the presence and amount of elements. In the case of sinters and other oxidic materials, some elements are to be reported as oxides rather than elements, e.g. $SiO_2$, $Al_2O_3$. Hence the calibration of the XRF instrument for these elements is based on the oxide concentrations so as to obtain the desired oxidic reporting.

Determination of the oxides/elements (Table 7) is carried out by XRF after preparation either as pressed pellets[11] or as fused beads in the same manner as for iron ores.

The pressed pellet method is also desired when using low-power desktop XRF equipment installed at the sinter plant, so as to have a quick and simple preparation. In such a case an analysis is performed every hour and a

**Table 7** Typical elements or oxides determined in sinters, their concentration ranges and the typical reproducibility of analysis over 20 days using a high-power instrument with X-ray tube settings of 50 kV, 40 mA.[11] (Copyright ASTM. Reprinted with permission.)

| Element/oxide | Typical range (%) | Concentration (%) | SD (%) |
|---|---|---|---|
| Fe | 30–70 | 35.71 | 0.2 |
| CaO | 3–35 | 27.73 | 0.23 |
| MgO | 0.1–15 | 8.52 | 0.12 |
| $SiO_2$ | 3–10 | 7.74 | 0.19 |
| Mn | 0.1–6 | 1.91 | 0.01 |
| $Al_2O_3$ | 0.5–5 | 1.6 | 0.12 |
| $K_2O$ | 0.01–1.0 | 0.1 | 0.003 |
| P | 0.01–1.0 | 0.15 | 0.006 |
| $Na_2O$ | 0.01–1.0 | 0.03 | 0.002 |
| S | 0.01–1.0 | 0.07 | 0.006 |
| Zn | 0.01–0.1 | Not tested | |

moving average over three samples is taken, leading to acceptable results.[12]

One of the most important controls to be applied in sinter is the amount of FeO phase, which allows one to monitor the sintering process and to avoid problems in the blast furnace operation during oxide reduction. XRF does not allow a distinction between the various phases of iron oxide, i.e. $Fe_2O_3$, $Fe_3O_4$ and FeO; it only measures the total iron in the sample. Other methods are required for the FeO value, e.g. titration with potassium dichromate or XRD. A recent advance in instrumentation has been the integration of an XRD system into an XRF spectrometer, which allows both elemental and phase determination to be carried out on the same specimen.[9,13] The determination of FeO in sinter is possible with good precision with such an integrated XRD system with a counting time of <100 s.

## 5.3 Analysis of Slags

Slags originate from various stages in the iron and steel process, e.g. blast furnace, converter, basic oxygen furnace (BOF) (also called BOS), electric arc furnace or ladle.

In the blast furnace, slag is formed from the impurities in the iron ores (known as the gangue), the flux and the coke ashes. It is a complex silicate of aluminum, calcium and magnesium containing small quantities of oxides of manganese and iron and calcium sulfide.[10] Slag has a double role: it permits the removal of the gangue thanks to its fusibility and fluidity, and it allows reactions of exchange with the liquid metal and permits control of the process in order for the desirable elements to remain in the melt while the others are removed. As an example, in an electric arc furnace the slag formation process can be controlled by adding oxygen, carbon and slag formers to the melt. This will promote the formation of CO instead of MnO and FeO and help keep these elements in their metallic form in the melt. The basic slag formers such as lime (CaO) and magnesia (MgO) will help to neutralize the acidity of the slag in order to save the refractory bricks of the furnace.[14]

Slag samples are crushed and ground in a mill to obtain a small enough particle size. Magnetic separation of metallic residues is done on the milled fractions before further preparation. The pressed powder method is generally used for routine elemental determinations in slags, especially when fast reporting is important (converter and ladle slags). High-speed slag analysis is gaining importance as a shorter reporting time allows, for example, optimization of the desulfurization of steel.[15] However, when a certificate must be produced in order to sell the slags or if accuracy is more important than speed of response, the fusion bead method is used. The oxides of interest in the slags are shown in Table 8 with their

**Table 8** Typical analytes determined in blast furnace and BOF slags, their concentration ranges and typical performance (pressed pellets, fixed channels, 30-s counting time, 30 kV, 80 mA)

| Element/ oxide | Typical range (%) | Performance (%) | |
|---|---|---|---|
| | | Precision ($2\sigma$) | Accuracy |
| $Al_2O_3$ | 0.1–30 | 0.03–0.34 | 0.05–0.3 |
| CaO | 15–65 | 0.1–0.4 | 0.4–0.7 |
| FeO | 0.1–40 | 0.02–0.37 | 0.03–0.4 |
| MgO | 1–15 | 0.05–0.2 | 0.1–0.5 |
| MnO | 0.1–25 | 0.03–0.3 | 0.03–0.4 |
| $P_2O_5$ | 0.01–5 | 0.007–0.09 | 0.01–0.2 |
| $SiO_2$ | 0.2–40 | 0.06–0.3 | 0.04–0.4 |
| $TiO_2$ | 0.2–3 | 0.08–0.1 | 0.1–0.2 |

concentration ranges and typical precision and accuracy for pressed pellets.

Other elements oxides are determined in various types of slags are S up to 1.5%, V up to 5%, Ni up to 0.3%, $K_2O$ up to 10%, $Na_2O$ up to 5%, $Cr_2O_3$ up to 10%, Zn up to 0.1% and F up to 2%.

XRF calibration for slags is relatively straightforward with few interelement corrections to use, especially when a specific calibration is applied for each type of slag. With pressed powder preparation, SRMs originating from the process in question should be preferred. If slags are prepared as fused beads, CRMs and SRMs can be mixed and the same calibration can be used for iron ores, sinters and slags.

**5.4 Analysis of Irons**

Blast furnace iron, also called pig iron, is brought to the desulfurization station and then to the converter, where it is transformed into steel by oxidation of the excess carbon (Figure 1). At each of these stages samples are taken in order to control the quality of the product (Table 4).

Cast irons are iron–carbon base alloys containing various amounts of silicon, manganese, phosphorus, sulfur and trace elements. Wide variations in properties can be achieved by varying the balance between carbon and silicon, by alloying with various metallic or nonmetallic elements, and by varying casting and heat treatments.[16]

Two types of cast irons are to be considered in order to achieve good precision and accuracy of analysis: white irons and gray irons. Gray cast irons present an inhomogeneous structure with flakes of carbon, which will impair the results especially on phosphorus and sulfur. Therefore, it is recommended to obtain molds and cooling conditions which will produce a white cast iron structure. In addition, all CRMs for cast irons are prepared by chill casting, which promotes the formation of a white iron structure with finely dispersed iron

carbides. The sampling is often done with an immersion probe, which delivers a compact coin-like specimen (Figure 2c).[17,18] Obtaining a slag-free specimen is very important as slag would lead to incorrect results for sulfur and silicon.

A proper surface can be achieved with a surface grinder (belt or disk) using an aluminum oxide abrasive paper. Although some referenced methods specify abrasive size up to 240 grit,[19] in practice coarser papers (e.g. 60- or 120-grit) are often selected in a production environment owing to time constraints. Another very effective specimen preparation is by using a 37-grit alumina stone wheel on a horizontal grinder. The specimen is fixed magnetically. Coolant should be used at first when grinding off the casting crust. The final grinding is done without coolant.[17] Fine polishing is only necessary when carbon is to be determined. Diamond polish surface preparation allows the best results in terms of accuracy, but it is time-consuming and seldom used in production control.[1]

The main elements that are to be determined in irons are listed in Table 9. The ranges given correspond also to factory calibrations that XRF instrument manufacturers can typically propose.[6]

**Table 9** Typical elements, their analytical lines and their concentration ranges (%) as determined in various types of irons

| Element | XRF analytical line | Blast furnace iron (pig iron) | Cast iron, nodular iron | High-alloyed cast iron |
|---|---|---|---|---|
| C | K$\alpha$ | 4.0–4.5 | 2.0–4.4 | 1.3–3.7 |
| Si | K$\alpha$ | 0.3–5 | 0.4–3.8 | 0.3–1.8 |
| Mn | K$\alpha$ | 0.1–2 | 0.009–2 | 0.2–2.0 |
| P | K$\alpha$ | 0.01–0.1 | 0.009–1.0 | 0.03–0.4 |
| S | K$\alpha$ | 0.001–0.17 | 0.005–0.2 | 0.007–0.08 |
| Cr | K$\alpha$ | 0.001–1 | 0.02–2.5 | 12.0–32.0 |
| Mo | K$\alpha$ | 0.001–1 | 0.007–1.5 | 0.5–4.0 |
| Ni | K$\alpha$ | 0.1–1 | 0.025–3 | 0.2–16.0 |
| Al | K$\alpha$ | | 0.005–0.1 | |
| As | K$\beta$ | 0.001–0.025 | 0.003–0.17 | |
| Bi | L$\alpha$ | | 0.002–0.01 | |
| Ce | L$\beta$ | | 0.003–0.06 | |
| Co | K$\alpha$ | | 0.004–0.15 | |
| Cu | K$\alpha$ | 0.001–1 | 0.01–1.1 | 0.02–1.3 |
| Mg[a] | K$\alpha$ | | 0.003–0.1 | |
| Nb | K$\alpha$ | | 0.002–0.5 | |
| Pb | L$\alpha$ | | 0.003–0.04 | |
| Sb | K$\alpha$ | | 0.003–0.15 | |
| Sn | K$\alpha$ | | 0.003–0.42 | |
| Te | L$\alpha$ | | | |
| Ti | K$\alpha$ | 0.001–0.6 | 0.003–0.25 | |
| V | K$\alpha$ | | 0.002–0.6 | |
| W | L$\alpha$ | | 0.006–0.1 | |
| Zn | K$\alpha$ | | 0.002–0.06 | |

[a] Nodular iron only.

Calibration of the XRF equipment will require basically the same overlap and matrix corrections as are used for steel analysis (section 5.5).

Some qualities of steel require sulfur contents below 10 ppm and impose the use of iron with very low sulfur concentrations, typically around 20–30 ppm.[20] In that case, the WDXRF instrument must be especially accurate for low levels of sulfur. In addition, the analysis result is required within the shortest possible time, hence the use of simultaneous instruments fitted with fixed channels for the required elements.

The improved determination of carbon in cast iron by WDXRF has become possible as a result of several important developments. A superior light element analyzing crystal (synthetic multilayer structure),[21] better excitation of light elements using thinner X-ray tube windows, higher excitation conditions and closer tube to sample coupling have all contributed to the detection limit of carbon in steels being lowered to 50 ppm (in a 100-s counting time) in the most sensitive instruments. Significant improvements in the detection limits (Tables 18 and 19), as well as in terms of precision (Table 10) for all the other elements normally determined in iron and steel, have also been achieved as a result of these instrumental enhancements. Concerning the determination of carbon and other ultralight elements by XRF, it is important to understand that their characteristic XRF radiations are of low energy and can emerge only from a very thin layer at the surface of the specimen (0.03 μm for carbon in an iron matrix). Hence reproducibility of surface preparation is of the utmost importance in order to achieve a successful analysis of ultralight elements by XRF.

## 5.5 Analysis of Steels

Examination of the output of large steel companies reveals that they can be producing up to 1500 different steel qualities. Preparation of a specific steel quality takes between 3 and 5 h from initial receipt of the hot metal to final production of the steel quality. During this time, samples are taken at regular intervals to monitor the progress of the process. All these samples require as quick a chemical analysis as possible owing to the short residence times of given charges at each treatment station for cost reasons.[22]

Specimens from all the production stages are nowadays generally transported by a pneumatic tube system into the laboratory, where they are prepared and analyzed. To save costs and increase speed of response, full automation of the whole preparation and analysis is being implemented in many iron and steel plants. This is discussed in **Automation of Analytical Control in the Steel and Metals Industry**.

The analytical steps from sample preparation to transmission of the results must be performed as quickly

**Table 10** Typical instrumental precision obtained on a cast iron sample: 10 replicate analyses of 25 s without preparation of the specimen between runs (30 kV, 80 mA)

| Element | XRF analytical line | Concentration level in the specimen (%) (unless specified otherwise) | SD (1σ), 25-s analysis on monochromators (%) (unless specified otherwise) |
|---|---|---|---|
| C | Kα | 3.8 | 0.035 |
| Si | Kα | 0.362 | 0.0008 |
| Mn | Kα | 0.12 | 0.0002 |
| P | Kα | 150 ppm | 1.6 ppm |
| S | Kα | 250 ppm | 1.8 ppm |
| Cr | Kα | 0.28 | 0.0006 |
| Mo | Kα | 0.45 | 0.0002 |
| Ni | Kα | 0.155 | 0.0004 |
| Al | Kα | 0.22 | 0.0012 |
| Cu | Kα | 0.14 | 0.0004 |
| Nb | Kα | 0.55 | 0.0002 |
| Pb | Lα | 100 ppm | 3.6 ppm |
| Sb | Kα | 470 ppm | 3.6 ppm |
| Sn | Kα | 200 ppm | 3 ppm |
| Ti | Kα | 0.12 | 0.0004 |
| V | Kα | 0.24 | 0.0004 |

as possible. Specimens undergo grinding, cleaning and punching prior to analysis. Not more than 180-grit abrasive paper should be used for grinding the specimen surface otherwise variations from operator to operator become too large. During steel making, the carbon level must be controlled and adjusted down to parts per million levels. Low-level carbon, nitrogen and sulfur are measured by combustion analyzers on 1-g slugs, which are punched from the metal after fine grinding (Figure 2a). Alternatively, carbon determination can also be done by OES when the precision and limit of detection (LOD) that can be achieved by XRF are not sufficient. For some or all of the other elements which enter into the composition of the steels (Table 11), both the OES and XRF analysis results are often taken into account. Sometimes an average of the two determinations is used for accuracy at the expense of speed of analysis, as the specimen must be reprepared after having been burned by the spark of the OES spectrometer.

WDXRF is used extensively for the analysis of the high-alloy steels because of the very good precision achieved on major elements (Figure 4a and b). In addition to the elements listed in Table 11, cerium, magnesium, selenium and tellurium are sometimes determined. The typical LODs for two types of XRF instruments can be found in Tables 18 and 19, and precisions at various concentration levels are given in Table 12.

The typical precisions (Table 12) required by the steel industry for elemental determinations can be achieved with counting times ranging from 20 s on

**Table 11** Elements, their analytical lines and their concentration (%) range for XRF analysis in various types of steels

| Element | Line | Low-alloy steel (free cutting steel) | High-alloy steel | High-speed steel |
|---|---|---|---|---|
| C | OES[a,b] | | | 0.03–2.0 |
| Si | Kα | 0.002–1.7 | 0.09–4.5 | 0.1–0.5 |
| Mn | Kα | 0.002–2.0 | 0.25–20 | 0.08–0.5 |
| P | Kα | 0.001–0.1 | 0.002–0.04 | 0.01–0.05 |
| S | Kα[b] | 0.001–0.08 (0.3) | 0.001–0.04 | 0.002–0.05 |
| Cr | Kα | 0.001–5.15 | 6.6–32.0 | 2.0–5.0 |
| Mo | Kα | 0.001–1.5 | 0.06–7.0 | 0.15–9.0 |
| N | OES[a,b] | | | |
| Ni | Kα | 0.002–4.7 | 0.1–35.0 | 0.03–0.45 |
| Al | Kα | 0.002–1.2 | 0.002–1.5 | |
| As | Kβ | 0.003–0.17 | 0.003–0.01 | |
| B | OES[a] | | | |
| Ca | Kα | 0.001–0.01 | | |
| Ce | Lα | 0.003–0.1 | | |
| Co | Kα | 0.003–0.3 | 0.01–2.1 | 0.05–18.0 |
| Cu | Kα | 0.001–0.70 | 0.03–3.5 | 0.01–0.1 |
| Fe | Kα | Rest | | |
| N | OES[a,b] | | | |
| Nb | Kα | 0.001–0.6 | 0.005–2.0 | |
| O | OES[a,b] | | | |
| Pb | Lα | 0.002–0.02 (0.3) | | |
| Sb | Kα | 0.003–0.07 | 0.014–0.18 | |
| Sn | Kα | 0.003–0.15 | 0.003–0.01 | |
| Ta | Lβ | 0.003–0.2 | 0.003–0.05 | |
| Ti | Kα | 0.001–0.4 | 0.003–2.7 | |
| V | Kα | 0.001–0.95 | 0.03–1.5 | 0.45–3.3 |
| W | Lα | 0.003–0.3 | 0.02–3.1 | 2.0–22.0 |
| Zn | Kα | 0.002–0.025 | | |
| Zr | Kα | 0.001–0.2 | | |

[a] Analysis done by OES for low levels of given element.
[b] Analysis done alternatively by combustion analyzer.

simultaneous instruments to 300 s on sequential machines (see Table 20).

**Table 12** Typical precision (%) required for XRF analysis of steels at different concentration levels

| Element | Concentration level (%) | | | | |
|---|---|---|---|---|---|
| | 0.01 | 0.1 | 1 | 5 | 20 |
| Si | 0.002 | 0.005 | | 0.03 | |
| Mn | 0.002 | 0.005 | | 0.03 | |
| P | 0.001 | 0.003 | | 0.02 | |
| S | 0.001 | 0.003 | | 0.02 | |
| Cr | 0.001 | 0.005 | | 0.02 | 0.04 |
| Mo | 0.001 | 0.005 | | 0.02 | |
| Ni | 0.001 | 0.005 | | 0.02 | 0.04 |
| Al | 0.001 | 0.004 | 0.01 | | |
| As | 0.002 | | | | |
| Ca | 0.001 | | | | |
| Co | 0.002 | 0.005 | | 0.03 | |
| Cu | 0.002 | 0.005 | | 0.03 | |
| Nb | 0.001 | 0.005 | 0.01 | | |
| Pb | 0.002 | | | | |
| Sb | 0.002 | | | | |
| Sn | 0.002 | 0.005 | | | |
| Ta | 0.002 | | | | |
| Ti | 0.001 | 0.003 | 0.01 | | |
| V | 0.001 | 0.004 | | 0.02 | |
| W | 0.002 | 0.003 | | 0.03 | |
| Zn | 0.001 | | | | |
| Zr | 0.001 | | | | |

Concerning the calibration of the XRF instrument, overlap corrections are necessary notably for the following interfering element–analyte pairs: Mo−P, Cu−P, Mo−S, Ti−V, V−Cr, Cr−Mn, Fe−Co, Ni−Cu, Cu−Zn, W−Zn, Mo−Zn, W−As, W−Ta, Ni−Ta, Cu−Ta, Ni−W and Sn−Pb. These corrections depend on the intrinsic sensitivity of the instrument to the given analytical line, therefore they are determined experimentally using binary standards. Note that iron being the matrix is not reported but is measured in order
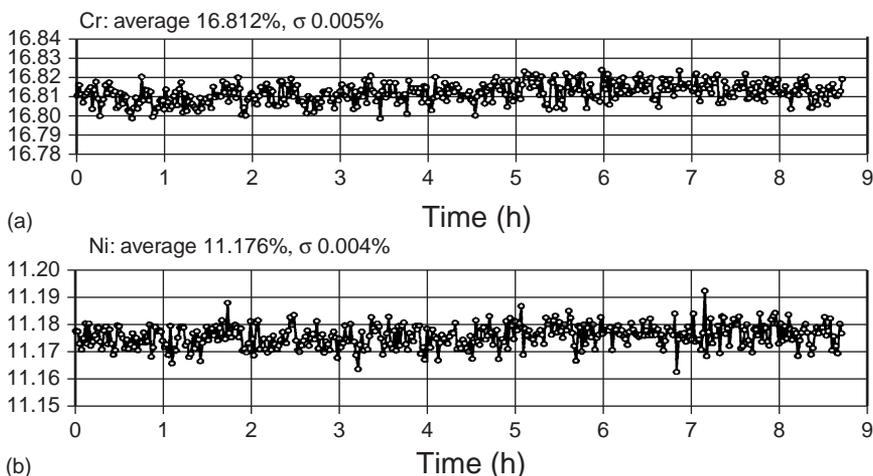


**Figure 4** Example of overnight repeatability for (a) Cr and (b) Ni in stainless steel using a state-of-the-art WDXRF instrument; 30-s counting time on fixed channels (monochromators). (Reproduced by permission of ARL/Applied Research Laboratories SA.)
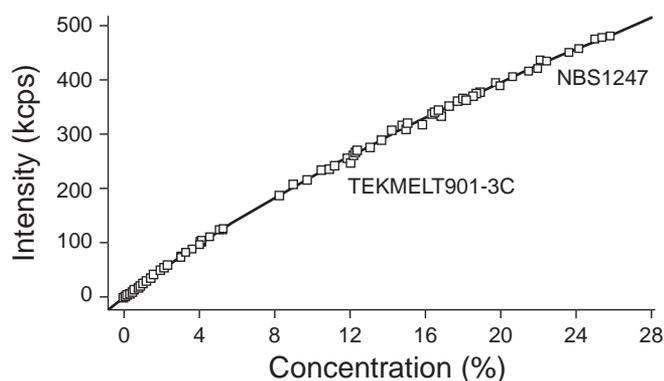
**Figure 5** Calibration curve for Cr in steel. A second-order curve is used in order to obtain a wide concentration range on the same curve (from 60 ppm to 25%). (Reproduced by permission of ARL/Applied Research Laboratories SA.)

to be able to make overlap corrections, notably on cobalt.

Matrix corrections are an essential part of the calibration in order to achieve the desired accuracy. The correction coefficients can be determined experimentally with a large number of reference materials (either CRMs or SRM). However, the common practice nowadays is to generate these $\alpha$ factors theoretically through specific software programs which take into account the conditions of excitation (anode, kV, mA), the geometry of the instrument and the matrix considered. With adequate matrix corrections, excellent accuracy over large concentration ranges can be achieved, as shown in Figure 5 in the case of chromium.

A correction for carbon on chromium improves the accuracy for the latter element. The carbon value obtained from another technique such as using a combustion analyzer or OES can be entered either manually or through software connection into the analytical software of the instrument. The latest software developments allow for the final XRF analytical result to be recalculated when the carbon value is obtained from the OES equipment in cases where this analysis is done after the XRF analysis.

## 5.6 Analysis of Ferroalloys

Ferroalloys are important materials in the specialty steel industry as their addition to molten steel in predetermined quantities produces steels with specific physical and chemical properties. Ferroalloys are analyzed to confirm compliance with their chemical specifications and allow precise additions in the ladle. In addition, this analysis can be used as a control of the supplied materials for invoicing purposes. Analyses of ferroalloys are therefore carried out at least once a week and on each new supply. However, in view of the ISO 9000 certifications of many suppliers, there is a trend to diminish the number of

**Table 13** Types of ferroalloys employed in the iron and steel industry

| | | | |
|---|---|---|---|
| Fe−B | Fe−P | Fe−Mn | Fe−Si−Mn |
| Fe−Cr | Fe−Nb | Fe−Mn−C | Fe−V |
| Fe−Cr−C | Fe−Ni | Fe−Mo | Fe−W |
| Fe−Cr−Si | Fe−Ti | Fe−Si | |

analyses carried out on ferroalloys and to rely on the analysis certificates submitted by the suppliers.

There are a large variety of ferroalloys (Table 13) and their preparation for XRF analysis will vary depending on the hardness of the material and the demands in terms of analytical precision and accuracy.

### 5.6.1 Sample Preparation

Preparation of ferroalloys for analysis is not a simple task. Three main procedures can be employed.

*5.6.1.1 Remelting with Pure Iron*　　This method allows a metal button to be obtained by remelting the ferroalloy mixed with pure iron chips in a high-frequency furnace. Casting is done through centrifugation of the melted metal. Crucibles of 20 mL are made of refractory material and molds of copper–beryllium are often used. The most important parameters to be controlled are the dilution ratio and the melting and casting times and temperatures. The best results are obtained with dilution ratios of sample to pure iron varying from 3 : 5 to 3 : 17 for the most difficult ones. Melting temperatures are chosen between 1300 and 1900 °C with melting times of about 2 min. The disks obtained look like thick coins and are polished with abrasive paper in the same way as steel samples.

Using the remelting method, the grade element concentration of all the ferroalloys can be determined with tolerances of ±0.2 and ±0.4% ($2\sigma$) and the relative standard deviation (RSD) values for the minor elements are below 5%.[23]

*5.6.1.2 Pressed Pellets*　　Ferroalloys are usually extremely hard and difficult to crush or mill, but this method is rapid and inexpensive. The grinding time and grain size (40–70 µm) must be strictly reproduced for the best results. Various binders are used, e.g. 10% methylcellulose, before pressing at 20–40 tons.

RSDs of 0.1–0.15% around the calibration curve can be achieved for the major elements, and between 3 and 5% for minor elements.

As the specimen preparation is the same for all ferroalloys a single analytical program can be built incorporating all of them (Table 14). This is a very useful starting point before refining the program into specific

**Table 14** Concentration ranges for a calibration for ferroalloys using pressed powders

| Element | Range (%) |
|---|---|
| Nb | 43–68 |
| Si | 0.01–91 |
| P (high) | 0.2–26 |
| P (low) | 0.01–0.3 |
| Ti | 0.5–37 |
| Mn | 0.1–90 |
| Cr | 53–74 |
| V | 0.1–81 |
| Mo | 59–76 |
| Al | 0.6–7.2 |

calibration curves for each type of ferroalloy in the quest for the best results.

The use of specialized synthetic multilayer crystals and the enhanced sensitivity of modern WDXRF spectrometers allows much improved precisions and LODs to be achieved for elements, which used to be impossible in the past. An element such as boron can now be determined in ferroboron prepared as pressed powder with good precision (Table 15).[24]

*5.6.1.3 Fusion Beads*　　In order to fuse ferroalloys with a flux and cast the resultant melt into a mold, the ferroalloy must first be converted into an oxide. Oxidation of ferroalloys by simple heating is possible but the reaction is exothermic and if done directly in a platinum–gold crucible considerable damage to the crucible takes

**Table 15** Typical repeatability for boron analysis in ferroboron with WDXRF (conditions: AX20 crystal, 30 kV, 100 mA, 10-s counting time per run; instrument, ARL 9400 sequential spectrometer). (Reproduced by permission of ARL/Applied Research Laboratories SA.)

| Run no. | Boron (%) |
|---|---|
| 1 | 19.34 |
| 2 | 19.38 |
| 3 | 19.34 |
| 4 | 19.36 |
| 5 | 19.31 |
| 6 | 19.39 |
| 7 | 19.43 |
| 8 | 19.41 |
| 9 | 19.38 |
| 10 | 19.46 |
| 11 | 19.34 |
| Average | 19.38 |
| SD | 0.04 |

place. Various methods have been proposed[5,23,25–27] using muffle furnace or fusion machines. In some cases $Sr(NO_3)_2$ is used as oxidant, in others $NaNO_3$ with fluxes made of a mixture of $Li_2B_4O_7$ and $Na_2CO_3$. A recipe for Fe−Mo preparation proposes a flux made of $CaCO_3$, $NaCO_3$ and $Na_2B_4O_7$, while a mixture of only $CaCO_3$ and $Na_2B_4O_7$ is used for Fe−V and Fe−Ti. Dilution can be as high as a 1 : 35 sample to flux ratio, thus diminishing the matrix effects but also the intensities obtained on the XRF instrument, which can lead to difficulties with trace elements.

A successful method[28] protects the platinum crucible during oxidation of the ferroalloys by melting a known mass of lithium tetraborate ($Li_2B_4O_7$) and coating the walls of the crucible by rotating it during cooling. The oxidation is completed by chemical reaction with lithium carbonate ($Li_2CO_3$) and finally the oxidized ferroalloy is dissolved in $Li_2B_4O_7$ flux.

Using an appropriate fusion method, major elements present deviations around the calibration curve of about ±0.1% while RSDs for minor elements are better than 3%.[23]

Dissolution in acids followed by drying and then fusion of the residue with suitable fluxes into a glass disk has been used with success for main-element determinations on a limited number of ferroalloys. However, this procedure has the disadvantage of being time-consuming and labor intensive.[29]

## 5.7 Miscellaneous Analyses

### 5.7.1 Surface Analysis

For surface analysis of steel sheets,[30] specimens 50 mm in diameter are punched out of the metal sheet. They are analyzed directly for determination of the levels of nonmetallic elements present on the surface, such as $K^+$, $Na^+$, $Ca^{2+}$, P, S, Si and $Cl^-$. These can reveal or explain production anomalies or breakdowns. Stains and product appearance also depend on these surface elements. With constant and fast monitoring, remedial action can be taken in good time. Such determinations can be systematic in some cases.

Total surface iron is determined on the metal after pickling, rolling, annealing or degreasing. The specimen is taken by application of an adhesive tape to the sheet. The tape is removed from the sheet and adhered to a cellulose membrane. Adherent iron is measured on the membrane. These tests are performed occasionally in case of problems.

### 5.7.2 Coating Analysis

Deposition (hot-dipped or electrogalvanic) of different elements on steel sheet has become a common practice
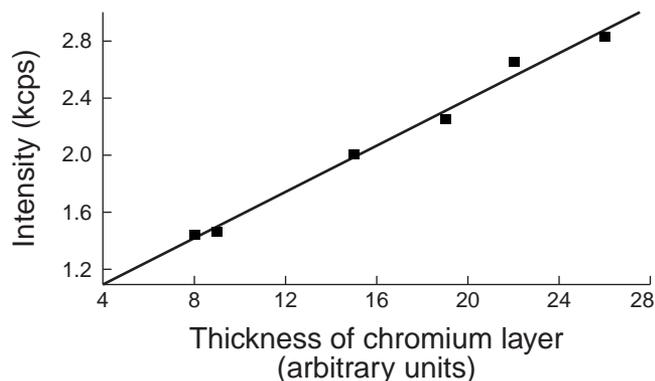
**Figure 6** XRF regression curve for chromium layer thickness on a series of steel samples. (Reproduced by permission of ARL/Applied Research Laboratories SA.)

**Table 16** XRF calibration results for chromium thickness on steel plates. (Reproduced by permission of ARL/Applied Research Laboratories SA.)

| Sample no. | Intensity (kcps) | Chromium thickness (arbitrary units) | |
|---|---|---|---|
| | | Nominal | Calculated |
| 01 | 2.250 | 19 | 18.30 |
| 02 | 2.001 | 15 | 15.22 |
| 03 | 2.649 | 22 | 23.15 |
| 07 | 2.827 | 26 | 25.32 |
| 08 | 1.439 | 8 | 8.36 |
| 09 | 1.461 | 9 | 8.64 |
| SEE | | | 0.8 |

in order to achieve various properties, e.g. anticorrosion. The layers vary between, among others, Zn, Zn−Al, Zn−Ni, Zn−Fe, Sn, Cr and plastic, depending on the desired property.

XRF can be used to quantify the thickness or surface density of the layer deposited subject to certain conditions. As an example, Figure 6 shows the calibration curve obtained for a chromium layer deposited on a steel plate. Table 16 gives the corresponding numerical results. Other elements in the layer have also been measured. Surface densities down to $20 \, mg \, m^{-2}$ can be measured.[31]

Examples of analysis of other types of coating are shown in Table 17, where the determination of thickness and composition is reported; the term ''Given'' indicates the result obtained by gravimetric analysis (mass thickness) or by atomic absorption (concentration) and ''Found'' indicates the XRF result.[32]

Plastic coatings of different colors are used on steel sheets. Their thickness ranges between 25 and 200 µm and they contain inorganic elements that vary depending on the coating manufacturer and the date of delivery. Analysis by WDXRF provides evidence on claims about poor quality such as color changes or adhesion problems due to insufficient stabilizer or other necessary additives.[33]

### 5.7.3 Other Analyses

Systematic analyses per incoming batch of materials and weekly analysis are carried out for other types of materials which are used in the iron and steel industry, e.g. bauxite, olivine, dolomite, limestone, calcium hydroxide, casting fluxes and mold powder. Specimens are prepared either as pressed powder or fused beads depending on the plant.

Coal ash and coke ash are analyzed for the determination of elements and oxides such as $SiO_2$, $Al_2O_3$, CaO, MgO, Fe, S and P.

Determination of the presence of toxic heavy metals is required in the dust from electro-filters.

## 6 CHOICE OF SPECTROMETER

Various types of WDXRF spectrometer are employed in the analysis of samples from the iron and steel industry. The correct type of instrument depends very much on the analytical requirements of the individual application, e.g. speed of analysis, number of elements and throughput required. It is worth reviewing the capabilities of these instrument types as they each have specific applications.

**Table 17** Analysis results for Sn and Zn coatings on steel plates by XRF.[32] (Reproduced by permission of Koninklijke Philips Electronics NV.)

| Sample/side | Given ($g \, m^{-2}$) | Found ($g \, m^{-2}$) | Sample/side | Given | Found |
|---|---|---|---|---|---|
| 1B/top | 2.0 | 1.7 | A6/top ($g \, m^{-2}$) | 46 | 45.7 |
| 1B/bottom | 2.0 | 1.7 | Fe (%) | 13.1 | 14.4 |
| Sn25/top | 11.2 | 10.6 | Al (%) | 0.23 | 0.96 |
| Sn25/bottom | 2.8 | 3.2 | A9/bottom ($g \, m^{-2}$) | 59.0 | 56.2 |
| Sn60/top | 5.6 | 5.2 | Fe (%) | 11.1 | 11.4 |
| Sn60/bottom | 5.6 | 5.4 | Al (%) | 0.17 | 0.8 |

## 6.1 Sequential X-ray Fluorescence Spectrometer

Modern sequential XRF spectrometers, with improved tube to sample coupling, high-power generator (up to 4.2 kW) and X-ray tube fitted with a thin beryllium window (down to 50 μm), are capable of producing very high count rates from solid samples. Faster electronics allow linearity of counting on detectors up to $2 \times 10^6$ counts per second, making it possible to exploit the better sensitivity of these instruments.

This high sensitivity permits the use of short counting times. In some instances the required precision can be reached with counting times as short as 2 s. Hence it is possible for sequential spectrometers to be used in the determination of up to 12 elements in metal samples, slags or sinters in less than 2 min. The limitation of the sequential spectrometer appears as soon as the number of elements requiring determination increases. Typically low-alloy steels require up to 22 elements, for which complete analysis can only be achieved in about 5 min (see Table 20). This is inadequate when the ladle holding time is 3 min.

LODs close to 1 ppm in a 100-s counting time can be reached for many of the important elements. As can be seen in Table 18, the limits of detection for a 4-s counting time are five times higher, but for many of the elements are still acceptable for the requirements of the iron and steel industry. Evidently the counting time can be selected depending on the element and the performance required.

**Table 18** Typical LODs ($3\sigma$) for a sequential XRF spectrometer for iron base with different counting times (3-kW X-ray tube excitation). (Reproduced by permission of ARL/Applied Research Laboratories SA.)

| Element | LOD (ppm) | |
|---|---|---|
| | In 100 s | In 4 s |
| Aluminum | 2.7 | 13.5 |
| Carbon | 60 | 300 |
| Chromium | 2.1 | 10.5 |
| Copper | 2.2 | 11 |
| Manganese | 2.3 | 11.5 |
| Molybdenum | 1.2 | 6 |
| Niobium | 1.4 | 7 |
| Nickel | 1.8 | 7.5 |
| Phosphorus | 1.1 | 5.5 |
| Lead | 5.4 | 22 |
| Sulfur | 1.0 | 5 |
| Silicon | 3.6 | 18 |
| Tantalum | 7.0 | 35 |
| Titanium | 1.4 | 7 |
| Vanadium | 1.0 | 5 |
| Tungsten | 5.0 | 25 |
| Zinc | 2.2 | 11 |

In the manufacture of specialty steels, the group of elements requiring determination can change as the demand for the product changes. Thanks to its universal goniometer, the sequential XRF spectrometer is capable of determining up to 84 elements of the periodic table (beryllium to uranium) provided that the appropriate crystals and collimators are fitted. This versatility makes it an ideal choice when the number of elements amounts to about a dozen. In addition, large-capacity sample changers can be fitted. Batches of up to 170 samples can then be analyzed automatically. Mixtures of pressed powder briquettes and glass fusion beads are possible with these large-capacity changers.

### 6.1.1 Standardless Analysis

Although X-ray instruments in the iron and steel industry are predominantly used for routine analysis of process control samples, there is often a need for flexibility to handle nonroutine samples submitted to the laboratory. For example, new sources of raw materials, coal, fluxes or environmental dust and specialty products may need to be characterized. Difficulties arise when these nonroutine samples do not fit into any of the calibrated programs. The development of the so-called "standardless" or semiquantitative analysis packages has met this requirement. Two types of semiquantitative programs have been developed. One employs a global scanning procedure followed by spectral processing while the other measures individual peaks and backgrounds at predetermined spectral positions followed by intensity processing. These packages require a universal goniometer, as fitted in a sequential instrument, and the necessary crystals, collimators and detectors to cover the elements of the periodic table from fluorine to uranium. They are generally calibrated at the XRF manufacturer's plant using standards made as much as possible of a pure element or oxide and sophisticated spectral and matrix corrections.

With such a standardless analysis package, the spectrometer is ready for analysis of a wide range of material types and matrices upon delivery to site. Analysis of unknown samples can commence immediately. Loading of the prepared sample into the XRF spectrometer followed by activation of the program yields a comprehensive determination of all major, minor and trace elements present. Even shift operators with no XRF knowledge can obtain an analysis in 10–15 min. Although the accuracy and precision achieved with these programs are not as good as those obtained with quantitative programs calibrated with matching standards on limited ranges, their capabilities are improving as more efficient matrix correction algorithms, spectral line overlap and background correction models are developed.

## 6.2 Simultaneous X-ray Fluorescence Spectrometer

In a stainless-steel plant, the turnaround time is critical and analyses for up to 28 elements or more may be required. A high-power XRF spectrometer (up to 4 kW) fitted with fixed-element monochromators will do the job as the elements are measured simultaneously. Each monochromator is generally based on a curved crystal geometry where the XRF from one given element of the specimen is focused into the detector slit. The detector will be selected from a flow-proportional counter (FPC) for the lighter elements to a sealed detector with appropriate gas filling for the light and medium elements. A scintillation counter will be used for the analysis of the shorter wavelengths typical of the K$\alpha$ or K$\beta$ lines of heavier elements. For light elements, either a curved or a flat crystal geometry can be chosen. Typical counting times for elements in stainless steels are 30–40 s (Table 19), with loading and unloading of the sample taking 20 s, hence a turnaround time of 1 min is easily achievable for metal samples.

The disadvantage of the simultaneous system lies in its inflexibility: no element other than those chosen as monochromators at the time of purchase of the equipment are possible and no backup exists in case of failure of a monochromator.

**Table 19** Typical LODs (3$\sigma$) obtained on a modern simultaneous WDXRF instrument in a 30-s counting time on the monochromators (3.6 kW)

| Element | Line | Crystal | Detector | LOD (ppm) |
|---|---|---|---|---|
| C | K$\alpha$ | ML[a] | FPC | 170 |
| Si | K$\alpha$ | PET[b] | Sealed | 7.5 |
| Mn | K$\alpha$ | LiF200 | Sealed | 5.9 |
| P | K$\alpha$ | Ge111 | Sealed | 2.8 |
| S | K$\alpha$ | Ge111 | Sealed | 1.5 |
| Cr | K$\alpha$ | LiF200 | Sealed | 3.1 |
| Mo | K$\alpha$ | LiF200 | Scintillation | 1.9 |
| Ni | K$\alpha$ | LiF200 | Scintillation | 6.1 |
| Al | K$\alpha$ | PET | Sealed | 4.9 |
| As | K$\beta$ | LiF200 | Scintillation | 15.0 |
| Ca | K$\alpha$ | LiF200 | Sealed | 5.0 |
| Co | K$\alpha$ | LiF200 | Sealed | 10.3 |
| Cu | K$\alpha$ | LiF200 | Scintillation | 5.0 |
| Nb | K$\alpha$ | LiF200 | Scintillation | 1.4 |
| Pb | L$\beta$ | LiF200 | Scintillation | 7.1 |
| Sb | K$\alpha$ | LiF200 | Scintillation | 9.9 |
| Sn | K$\alpha$ | LiF200 | Scintillation | 9.5 |
| Ti | K$\alpha$ | LiF200 | Sealed | 5.6 |
| V | K$\alpha$ | LiF200 | Sealed | 4.6 |
| W | K$\alpha$ | LiF200 | Scintillation | 11.9 |
| Zn | K$\alpha$ | LiF200 | Scintillation | 5.0 |
| Zr | K$\alpha$ | LiF200 | Scintillation | 1.9 |

[a] ML, multi-layered synthetic microstructure pseudo-crystal.
[b] PET, pentaerythritol.

Sometimes low-power (200 W) simultaneous instruments are used exclusively for specific control of the oxides, e.g. iron ores, sinters and slags, when the response time is not critical. The disadvantage of these low-power systems is their inability to serve as backup of the OES equipment for the metals analysis.

## 6.3 Simultaneous/Sequential X-ray Fluorescence Spectrometer

The option to have fixed-element monochromators, which perform an analysis in parallel to a sequential device, is often of considerable benefit in the iron and steel industry. In general, these instruments have a high capacity of fixed channels, e.g. 28 or more, and are fitted with sequential devices, which can be scanners or goniometers. Scanners are limited in angular range and are fitted with only one or two crystals and a single detector. More than one scanner is always necessary to handle all the elements of the periodic table covered by the XRF technique and generally the elements below aluminum ($Z = 13$) are not included. In contrast, a true goniometer as used in sequential XRF instruments is universal. It can be fitted with several crystals and collimators and a minimum of two detectors in order to determine the elements of the periodic table from beryllium to uranium (with some restrictions for the ultralight elements). There are many advantages of having a simultaneous/sequential instrument fitted with a universal goniometer:

- the goniometer can be employed for the quantitative analysis of any elements that are not fitted as fixed monochromators;
- it can back up any of the fixed channels if needed;
- the goniometer can be employed for qualitative determination of any element through wavelength scanning;
- it can be used for "standardless analysis" of nonroutine samples (see section 6.1.1).

Table 20 presents the measurement time necessary to achieve the precision values listed in Table 12. Various configurations of instrument are considered:

- simultaneous, fitted only with fixed channels, a counting time of 40 s is used for all channels, fast instrument but without flexibility for any additional element;
- pure sequential, fitted with one universal goniometer, counting time is chosen depending on the element, flexible but slow;
- simultaneous/sequential system with one goniometer and 14 fixed channels, almost as fast as a simultaneous spectrometer and has the flexibility of adding extra elements whenever required.

**Table 20** Measurement times (s) required to obtain the precision levels ($2\sigma$) generally needed in the iron and steel industry with various configurations of instruments

| Element | Instrument type | | |
|---|---|---|---|
| | Simultaneous: 22 fixed channels | Simultaneous/ sequential: 14 fixed channels + goniometer | Sequential: 1 goniometer |
| Si | 40 | Fixed | 8 |
| Mn | 40 | 5 | 3 |
| P | 40 | Fixed | 14 |
| S | 40 | 3 | 2 |
| Cr | 40 | Fixed | 12 |
| Mo | 40 | Fixed | 8 |
| Ni | 40 | Fixed | 16 |
| Al | 40 | Fixed | 14 |
| As K$\beta$ | 40 | Fixed | 48 |
| Ca | 40 | 6 | 4 |
| Co | 40 | Fixed | 12 |
| Cu | 40 | 6 | 4 |
| Fe | 40 | 2 | 2 |
| Nb | 40 | 7 | 6 |
| Pb L$\beta$ | 40 | Fixed | 20 |
| Sb | 40 | Fixed | 30 |
| Sn | 40 | Fixed | 34 |
| Ti | 40 | Fixed | 10 |
| V | 40 | 7 | 6 |
| W L$\alpha$ | 40 | Fixed | 18 |
| Zn | 40 | Fixed | 18 |
| Zr | 40 | 8 | 6 |
| Total time | 40 | 44 | 295 |

The complementarity between fixed monochromators and a universal goniometer in a simultaneous/sequential instrument is demonstrated: fixed channels are chosen for the elements requiring long counting times while the goniometer is used for the easier elements.

## 6.4 Simultaneous/Sequential X-ray Fluorescence Spectrometer with X-ray Diffraction Capability

Given the increasing demand for process integration and total characterization of materials, a wavelength-dispersive spectrometer has been developed which effectively combines WDXRF and XRD within the same instrument. Employing the same pressed powder briquette as prepared for XRF analysis, the integrated XRD system is capable of the quantitative analysis of specific phases or minerals present in the sample. The performance of the XRF monochromators and goniometers being in no way degraded by the addition of the XRD capability, such an instrument can bring some advantages for process control in the iron and steel industry, notably for the determination of iron phases in iron ores and of FeO in sinters and monitoring of the reduction in the DRI process.

### 6.4.1 The X-ray Fluorescence/X-ray Diffraction System for Direct Reduced Iron Production

New and improved processes for the conversion of iron ore to metallic iron involve direct reduction where iron ore is reduced to iron without going through the pig iron stage. The iron oxide can be in the form of ore, concentrate or pellet and the reduction process uses either gas or coal as the reducing agent. The advantages of this process are low levels of impurities and chemical and physical consistency.[31]

Close monitoring of the progress in the reduction of $Fe_2O_3$ (hematite) to Fe is important. The determination of the metallic component in the reduced material is possible by wet chemical procedures, but is time-consuming, needing at least 30 min for the analysis of one phase, and therefore cannot be classified as a process control analysis. Because hematite has a distinctive XRD peak, it is possible to monitor the progress of this conversion by observing the decrease in the iron oxide (hematite) concentration in the material. Therefore, the quantitative determination of the hematite content of the ore passing through the system can be achieved using the integrated XRF/XRD instrument.[34]

## 7 CONCLUSION

As we enter the 21st century, there are various trends in the iron and steel industry as concerns the XRF technique:

- Routine analyses are increasingly carried out by nonexperts. In addition, scientists wish to focus on the details of the chemistry rather than on the particularity of the measurement technique. Therefore, instruments must become more and more autonomous and include the required analytical expertise.

- The WDXRF technique is being used for more varied applications, which call for innovative methods and standardless analysis programs.

- There is a need for more complete information about the sample, e.g. elemental and phase information, which will promote instruments combining different analytical techniques.

- There is a trend to decentralize the measurements and to bring the analytical equipment closer to the process. This means very often that the instruments

are to be fully automated with connection to automatic sample preparation and located in protected cabins.

## ACKNOWLEDGMENTS

## ABBREVIATIONS AND ACRONYMS

| | |
|---|---|
| BOF | Basic Oxygen Furnace |
| BOS | Basic Oxygen Steelmaking |
| CRM | Certified Reference Material |
| DRI | Direct Reduced Iron |
| EDXRF | Energy-dispersive X-ray Fluorescence |
| FPC | Flow-proportional Counter |
| ISO | International Standardization Organization |
| LOD | Limit of Detection |
| LOI | Loss on Ignition |
| ML | Multi-layered Synthetic Microstructure |
| OES | Optical Emission Spectrometry |
| PET | Pentaerythritol |
| RSD | Relative Standard Deviation |
| SD | Standard Deviation |
| SEE | Standard Error of Estimate |
| SPC | Statistical Process Control |
| SRM | Secondary Reference Material |
| WDXRF | Wavelength-dispersive X-ray Fluorescence |
| XRD | X-ray Diffraction |
| XRF | X-ray Fluorescence |

## RELATED ARTICLES

*Steel and Related Materials* **(Volume 10)**
Steel and Related Materials: Introduction • Automation of Analytical Control in the Steel and Metals Industry • Iron Ore, Sample Preparation and Analysis of • Metal Analysis, Sampling and Sample Preparation in

*X-ray Spectrometry* **(Volume 15)**
X-ray Techniques: Overview • Sample Preparation for X-ray Fluorescence Analysis • Wavelength-dispersive X-ray Fluorescence Analysis

## REFERENCES

1. U.E. Senff, 'X-ray Fluorescence Spectrometry in the Iron and Steel Industry', presented at the Australian X-ray Analytical Association Conference, 1993.
2. F. Claisse, 'Accurate X-ray Fluorescence Analysis Without Internal Standards', *Norelco Rep.*, **4**, 3–7 (1957).
3. A. Kohler, P. Laederach, K. Juchli, D. Bonvin, R. Yellepeddi, 'Total Oxide X-ray Analyzer', *Int. Ceram.*, **1**, 84–88 (1999).
4. K. Norrish, J. Hutton, 'X-ray Spectrographic Method for the Analysis of a Wide Range of Geological Samples', *Ecochim. Cosmochim. Acta*, **33**, 431–453 (1969).
5. M. Davidts, 'Les Flux du Futur', Proceedings of the Rayons X et Matière Conference, Université de Strasbourg, Strasbourg, C4-683 to C4-691, 1996.
6. *XRF Calibration Specifications*, ARL, Ecublens, Switzerland, 1999
7. ISO 9516, 'Iron Ores – Determination of Silicon, Calcium, Manganese, Aluminum, Titanium, Magnesium, Phosphorus, Sulfur and Potassium – WDXRF Spectrometric Method', ISO, Geneva, 1996.
8. M. Veloso de Castilho, 'Development of a System for the Quality Assurance of Ore Shipments Based on Mapping the Chemical Composition of the Ore in the Mining Area', Proceedings of the CETAS Conference on *Progress of Analytical Chemistry in the Iron and Steel Industry*, Luxembourg, 408–416, 1992.
9. R.S. Yellepeddi, 'Ironmaking Using an XRF/XRD Spectrometer', *Adv. Steel*, July, 39–43 (1997).
10. J. Barralis, G. Maeder, *Précis Métallurgie: Elaboration, Structures–Propriétés, Normalisation*, Nathan, Paris, 1–7, 1997.
11. J. Martin, 'Suggested Method for X-ray Emission Spectrometric Analysis of Sinters', Method E-1 SM 10-39, ASTM, Philadelphia, PA, 1992.
12. J.C. Hoet, 'Sinter Plant Autocontrol by Using Low Power X-ray Spectrometer', presented at the 1998 CETAS Conference, Luxembourg.
13. T. Kitaide, T. Sugihara, 'Analysis of FeO in Sinters by Integrated X-ray Spectrometer Combining the Virtues of XRF and XRD', presented at the 1998 CETAS Conference, Luxembourg.
14. E. Uitbeijerse, 'Slag Formation and Analysis by ED-XRF Spectroscopy', *Int. Lab. News*, **26**, 23–24 (1996).
15. N. Bannenberg, 'Requirements of the Production Engineer in View of Analytical Chemistry', presented at the 1998 CETAS Conference, Luxembourg.
16. D. Stefanescu, 'Classification of Ferrous Casting Alloys', in *Metals Handbook*, ASM, Materials Park, Ohio, Vol. 15, 627–629, 1988.
17. V. Buhrke, R. Jenkins, D. Smith, *A Practical Guide for the Preparation of Specimens for XRF and XRD Analysis*, Wiley-VCH, Weinheim, 93–96, 1998.

18. ISO 14284, 'Steel and Iron – Sampling and Preparation of Samples for the Determination of Chemical Composition', ISO, Geneva, 1996.

19. ASTM Norm E322, ASTM, Philadelphia, PA, 1982.

20. P. Delaurie, D. Mutez, G. Butin, 'Automatic Analysis of Iron at Sollac Dunkerque Steelmaking Plant', Proceedings of the CETAS Conference on *Progress in Analytical Chemistry in the Iron and Steel Industry*, Luxembourg, 311–318, 1992.

21. D. Bonvin, B. Adamson, K. Juchli, 'The Use of X-ray Fluorescence Spectrometry as an Analytical Technique in the Iron and Steel Industry', Proceedings of the CETAS Conference on *Progress in Analytical Chemistry in the Iron and Steel Industry*, Luxembourg, 519–525, 1992.

22. W. Marschinke, H.-J. von Wachtendonk, 'The New Automated Laboratory at Thyssen Stahl, Ruhrort Works', Proceedings of the CETAS Conference on *Progress in Analytical Chemistry in the Iron and Steel Industry*, Luxembourg, 264–274, 1996.

23. A. Gomez Coedo, J. Jimenez Seco, E.M. Lopez Rodriguez, 'Development of Methodologies for Instrumental Analysis of Ferroalloys', Proceedings of the CETAS Conference on *Progress in Analytical Chemistry in the Iron and Steel Industry*, Luxembourg, 157–164, 1992.

24. D. Bonvin, K. Juchli, 'New Developments in XRF', presented at Anwendertreffen Röntgenfluoreszenz- und Funkenemissionsspektometrie Dortmund, 1999.

25. J. Pétin, A. Wagner, F. Bentz, 'Combination of Oxidation and Melt Treatment for Metal Sample Preparation for XRF Analysis', *Steel Res.*, **56**(4), 215–218 (1985).

26. H.L. Giles, G.M. Holmes, 'The X-ray Fluorescence Analysis of Ferroniobium by a Fusion Method', *X-ray Spectrom.*, **7**(1), 2–4 (1978).

27. G. Staats, 'Study of Ferroalloys with X-ray Fluorescence Analysis', *Arch. Eisenhüttenwes.*, **45**(10), 693–697.

28. R.T. Rutherford, 'Ferroalloy Analysis by X-ray Fluorescence Spectrometry', *X-ray Spectrom.*, **24**, (1993).

29. M.A. Guerrero, E. Andres, 'New Procedure of Preparation and Analysis of Ferroalloys with Additional Advantages Over Current Methods', Proceedings of the CETAS Conference on *Progress in Analytical Chemistry in the Iron and Steel Industry*, Luxemburg, 594–597, 1996.

30. C. Schwendimann, F. Hoffert, 'Rapid Analysis of the Surface of Coated and Uncoated Flat Products by GDS and XRF', Proceedings of the CETAS Conference on *Progress in Analytical Chemistry in the Iron and Steel Industry*, Luxembourg, 125–131, 1992.

31. R. Yellepeddi, A. Bapst, D. Bonvin, B.W. Adamson, 'Process and Quality Control in the Iron and Steel Industry Using the ARL Total Iron X-ray Analyzer', ARL Lecture Transcript LT/XRF/0395, 1995.

32. H. de Koning, 'Speed and Flexibility of XRFS in the Steel Industry', Presented at the Ustron Conference on Analytical Spectroscopy (PL), Ustron, 1998.

33. J. Viiret, I. Ala-Vainio, 'Identification of Plastic-coated Steel Sheet by X-ray Fluorescence Spectrometry', Proceedings of the CETAS Conference on *Progress in Analytical Chemistry in the Iron and Steel Industry*, Luxembourg, 210–215, 1996.

34. R. Yellepeddi, D. Bonvin, 'Process Integration of Modern X-ray Spectrometers: Future Perspectives in the Steel and Metal Industries', Proceedings of the CETAS Conference on *Progress in Analytical Chemistry in the Iron and Steel Industry*, Luxembourg, 700–707, 1999.