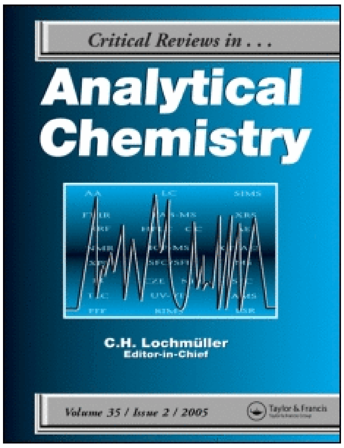

Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

X-Ray Fluorescence Analysis of Materials in the Iron and Steel Industry

Alexander P. Nikolsky; Jan K. Hurwitz

To cite this Article Nikolsky, Alexander P. and Hurwitz, Jan K.(1982) 'X-Ray Fluorescence Analysis of Materials in the Iron and Steel Industry', Critical Reviews in Analytical Chemistry, 13: 4, 373 — 417

To link to this Article: DOI: 10.1080/10408348208542755

URL: http://dx.doi.org/10.1080/10408348208542755

X-RAY FLUORESCENCE ANALYSIS OF MATERIALS IN THE IRON AND STEEL INDUSTRY

Author: **Alexander P. Nikolsky**
X-Ray Analysis Laboratory
All-Union Research Institute for
Iron and Steel Automation
Moscow, U.S.S.R.

Referee: Jan K. Hurwitz
United States Steel Corporation
Monroeville, Pennsylvania

TABLE OF CONTENTS

I. INTRODUCTION

A. Concept and Scope

This paper reviews the current state-of-the-art in the X-ray fluorescence analysis of various materials in the iron and steel industry.

The ferrous materials included in the scope of the present review are pig and cast iron, steels, iron- and nickel-base alloys, iron ores, sintering mixture, sinter, blast furnace slag, steelmaking slags, ferroalloys, steel sheets, refractories, and ferrites. Only the problems of macroscopic analysis are considered, including a few special cases in which instruments like microprobes, microanalyzers, diffractometers, etc. were used.

An attempt is made to highlight as many aspects of the topic as seemed pertinent to the author. These include some method fundamentals essential to its effective application in ferrous metallurgy, instruments of all types used in ferrous metallurgy, sampling and sample preparation, conversion of the analytical signal to element concentration, calibration and referencing, utilization of the method and instrumentation in various branches of ferrous metallurgy, especially in process control, development of the metallurgical and analytical control processes on the basis of the results of the X-ray analysis, forms of organization of X-ray analyses, and certain economic aspects. The features peculiar to the iron and steel industry are outlined, and the chief analytical problems as well as the test material characteristics are described in brief.

The following mainline trends in the former and current development of the X-ray fluorescence analysis method and apparatus are followed in this review:

1. Increasing the analytical signal level and the signal/noise ratio, particularly in light element determinations
2. Cutting the analysis time, mainly by accelerating sample preparation
3. Computerizing the X-ray analysis process, especially as regards measurement data processing and conversion of intensity measurements to element concentrations

4. Replacement of isolated X-ray instruments by automated analytical systems which are either based on X-ray instruments alone or combine different analyzers, the X-ray ones inclusive
5. Interfacing the X-ray analyzers and analytical systems with Automatic Control Systems

Extensive usage of the X-ray fluorescence method in the analysis of ferrous materials started nearly 25 years ago but only in the last decade has it advanced most markedly. This review, therefore, covers the achievements of this time span and a few earlier publications important for the concept of this paper referred to, also.

B. Historical Background

The advent of the X-ray spectrometry in the iron and steel industry dates back to about 25 years ago.[1-4] The modernization of the steelmaking process which resulted in a shorter production cycle stipulated reduction of the analysis time. Wet chemical procedures did not meet the challenge, with the constantly increasing amounts of analytical work to be done due to a steady rise in steel production. These circumstances called for a fast development of rapid physical analytical methods, among which the X-ray fluorescence techniques have acquired a very distinct position.

The X-ray analysis methods have been pushed to considerable advancement during the last three decades. Only in the period between 1959 to 1965 about 20 X-ray spectrometers have been put to use in the steel industry of Great Britain.[2] Its Japanese counterpart uses nearly 100 X-ray spectrometers by now.[1] About the same number of X-ray spectrometers are now used in the ferrous metallurgy in the U.S.S.R. and other developed countries. Up to 70% of the total amount of the analytical work utilize the following two physical concepts: optical and X-ray fluorescence spectroscopy,[5] with about 25% performed by the X-ray method alone.[6] The scope of application of the latter method has been steadily expanding over the period in question and its further progress is being planned for the forthcoming years.[7]

C. Characteristics of the X-ray Fluorescence Method

The X-ray fluorescence method in its macroscopic version, which is most commonly used for analytical purposes in the iron and steel industry, gives a composition averaged over a surface area of a specimen 2 to 5 cm^2 in size. In most applications it is a comparative method. It is based upon the functional relationship existing between the characteristic radiation (fluorescence) intensity I_x (the analytical signal) and the number of atoms emitting this radiation (element concentration C_x). Reference standards are necessary to find this relationship (i.e., perform the calibration process). The calibration results may be fixed in the form of a graph or equation, or the like. The common practice is to integrate the analytical signal (the number of counts) over a certain period of time (counting time) which normally ranges from 10 to 100 sec.

X-ray fluorescence is a secondary radiation emitted by an atom on removal of one of its electrons from some internal atomic shell causing its return to a less excited state. The salient characteristics of the X-ray fluorescence method are given in Table 1. Figure 1 shows the sequence of operations necessary to perform the analysis by X-ray spectrometry.

The method yields the elemental composition of the analytes, i.e., it gives a total amount of element producing the analytical signal. The X-ray method in its usual version makes no difference between analytical signals obtained from, suppose, Fe^{2+} and Fe^{3+}, or from Fe^{3+} in Fe_2O_3 and Fe^{3+} in Fe_3O_4, etc. It should be noted, however, that the

Table 1
X-RAY FLUORESCENCE METHOD CHARACTERISTICS

Item	Characteristic
Analytical signal	Intensity of characteristic radiation I_x, counts per sec; number of counts integrated over a time interval — N_x
Analytical curve shape $I_x = f(C_x)$	Linear or admits of linear approximation
Range of detectable chemical elements, Z_x	Generally, all elements having $Z_x > 2$; most favorable range $Z_x > 11$
Range of detectable concentrations, C_x	Generally, $C_x = 0.0001$—100%, most favorable range $C_x = 0.1$—100%
Sample state or form	May be in various forms: solid, powder, liquid, slurry, etc.
Approximately thickness of the sample layer giving the bulk contribution to analytical signal (90% or more)	0.001 cm
Requirements to analyte samples	No cracks, porosity, occlusions, etc., in the analytical signal producing layer; heat and electric conductivity (in some cases)
Change in the sample status due to analytical process	None or insignificant; method is nondestructive
Interelement (matrix) effect	Yes, but not as strong as in the optical emission method
Availability of standards	Practically essential
Analytical signal level (integrated) required for quantitative analysis	10^5—10^6

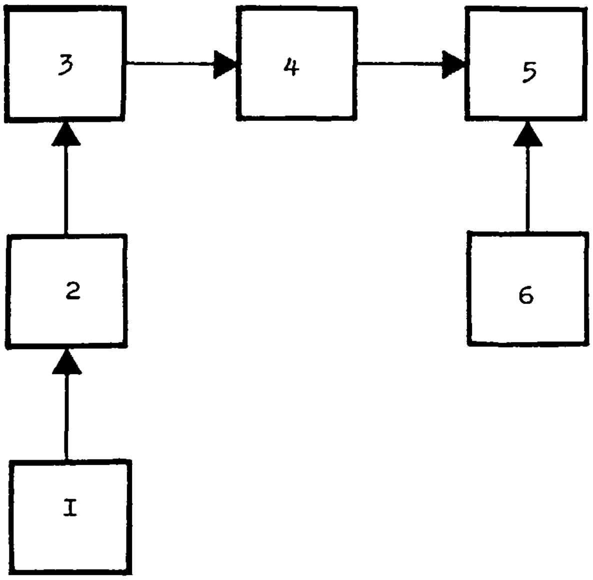

FIGURE 1. The operations constituting the X-ray analysis procedure. (1) Sampling; (2) sample preparation; (3) excitation of the characteristic X-ray spectra; (4) analytical signal separation and measurement; (5) analytical signal conversion to concentration; (6) calibration.

analytical signal may, if necessary, be separated from groups of atoms having different valent or ligand states.

Another feature of interpreting X-ray analysis results concerns oxide materials such as ore, sinter, slag, etc., in which cases concentrations of oxides rather than single elements are required, and they may be calculated occasionally through the stoichiometric relationships.

The analytical signal in X-ray analysis may be affected in some ways, each causing an error in the final analytical results:

1. By the chemical bond (the chemical or mineralogical effect)
2. By the grain size distribution in powder specimens, such as ore, sinter, slags (grain size effect), or surface layer status in case of metals, such as pig iron, steel, alloys (surface status effect)
3. By the matrix composition (matrix effect)
4. By the analytical spectrometer instability (apparatus effect)
5. By the analysis procedure (procedure effect)

The chemical bond effect is due to the changes of atomic level energies in function of the type of chemical bond. The result is the shifting of the characteristic X-ray spectra (chemical shift). This may increase the analysis error because of the displaced position of the spectral bands. On the other hand, the chemical bond effect may be used for analytical purposes, for example, for the determination of individual FeO and Fe_2O_3 concentrations.[8] Generally, the effect of chemical bond is not much of an obstacle to X-ray analysis of ferrous materials and can be eliminated by dissolving the samples.[9]

The grain size (or surface status) effect may be quite palpable. It will be discussed in detail in the sample preparation section of this article.

Matrix effect is brought about by two major reasons: (1) superposition of spectral lines and (2) selective absorption by matrix and additional excitation of X-ray fluorescence by the matrix radiation. Matrix effect may influence the analytical signal to a great extent. This effect may be eliminated or alleviated by applying a correction to the measured intensities based either on theoretical considerations or the regression approach. The correction methods are discussed in Section IV of the review.

Another way to alleviate the matrix effect is by adding to the sample some element having a high mass absorption coefficient which will prevail over the relatively small differences in mass absorption coefficients of the sample ingredients. This method is applicable to both powder and liquid samples. Dilution of samples with a flux for fusion or dissolution work to the same effect.

The features of analytical procedure, such as the calibration techniques, quality of standards, etc., also influence the analytical signal.

The influence of the X-ray apparatus instability on the analytical signal is quite obvious and can be decreased either by improving the spectrometer stability or by using some instability compensating devices (comparation channel).

The chemical bond, grain size (surface status), and matrix effects altogether affect the X-ray measured intensities distorting them by a methodical error (S_m). Instrumental instability distorts the measured intensities by an instrumental error (S_i).

One of the features specific to X-ray fluorescence analysis is the so-called statistical error (S_s) arising from the intrinsic random nature of X-rays. Statistical error may be reduced by increasing the number of integrated counts which can be done either by increasing the analytical signal level or by extending the counting time. The second way is often undesirable since it leads to prolonged analyses.

Table 2
COMPOSITIONS OF FERROUS MATERIALS

Chemical element (1)	Concentrations in mass percentage Raw materials (ore, sintering mixture, sinter) (2)	Iron (3)	Steels, alloys (4)	Ferro-alloys (5)	Slags (6)	Refractory materials, flux, etc. (7)
5 B			0.001—2			
6 C		2.5—4.5	0.01—1.5	0.1—8.0		
7 N			0.002—0.5			
9 F					0.01—4.0	
12 Mg	0.05—3		To 0.01		1—15	0.05—20
13 Al	0.2—3		0.05—7	0.03—8	0.2—20	0.1—33
14 Si	0.05—20	0.5—4.5	0.003—18	0.1—95	1—40	0.3—90
15 P	0.02—3	0.02—1.4	0.003—0.06	0.02—17	0.01—10	0.003—0.0
16 S	0.04—3	0.01—0.08	0.004—0.04	0.002—0.2	0.2—3	0.01—0.03
20 Ca	1—10		To 0.05	0.05—30	10—35	0.5—50
22 Ti	0.03—0.6	0.04	0.05—3.5	0.1—30	0.3—2	0.003—1.5
23 V	0.2	0.07	0.05—15	0.1—40	0.1	0.1—45
24 Cr		0.07—3.5	0.01—35	0.5—70	2	
25 Mn	0.5—60	0.5—4	0.02—15	0.1—90	0.1—10	0.01—1
26 Fe	30—75		To 100	10—55	0.5—1	0.04—1.2
FeO	25.0				0.5—30	0.03
Fe_2O_3						0.5—22
27 Co			0.5—35			
28 Ni			0.1—80	0.3—50		
29 Cu		0.22	0.01—6	0.1—4		
30 Zn			0.0001—0.01			
33 As	0.07—0.13		0.002—1.0	0.08		
34 Se			0.1—1.0			
(52 Te)						
40 Zr			0.1—1.0			
(72 Hf)						
41 Nb			0.1—4			
(73 Ta)						
42 Mo			0.03—30	0.1—55		
48 Cd			0.0001—0.01			
50 Sn			0.0001—0.01	0.25		
51 Sb			0.0001—0.01	0.1		
57 La (all lanthanides)			0.01—0.5			
74 W			0.1—30	To 80		
75 Re			0.1—1.2			
82 Pb			0.0001—0.01	0.05		
83 Bi			0.0001—0.01			

D. Analytical Problems in Ferrous Metallurgy

1. Materials Analyzed and Elements Determined

Generally, about 40 chemical elements currently have to be determined in the iron and steel industry: 5B, 6C, 7N, 8O, 9F, 11Na, 12Mg, 13Al, 14Si, 15P, 16S, 19K, 20Ca, 22Ti, 23V, 24Cr, 25Mn, 26Fe, 27Co, 28Ni, 29Cu, 30Zn, 33As, 34Se, 40Zr, 41Nb, 42Mo, 48Cd, 50Sn, 51Sb, 57La, 58Ce, 73Ta, 74W, 75Re, 82Pb, 83Bi. Compositions of metallurgical materials containing these elements are presented in Table 2. The elements indicated in brackets by the side of Se, Zr, and Nb are the latters' satellite elements.

Considering Tables 1 and 2 together, it is possible to outline roughly the most

Table 3
SOME FERROUS MATERIAL CHARACTERISTICS ESSENTIAL FOR THE X-RAY ANALYSIS

Item	Characteristic
Atomic numbers of analyzable elements, Z_x	$Z_x = 5—83$
Range of concentrations, C_x	$C_x = 0.01—100\%$ (sometimes $C_x < 0.01\%$
Valent state of the element being determined	Generally unimportant, but sometimes matters (in oxides such as FeO, Fe_2O_3; MnO, Mn_2O_3, MnO_2)
Interelement effects	Ca-Ti, Ti-Va, Ti-Cr, V-Mn, V-Cr, Cr-Mn, Cr-Fe, Mn-Fe, Mn-Co, Fe-Co, Fe-Ni
Effective atomic number of matrix, Z_e	$Z_e \approx 26$ for pig iron, steel and alloys; $Z_e < 26$ for oxide materials (ore, sinter, slags, lime, etc.); $Z_e \lesseqgtr 26$ for ferroalloys
Sample form	Solid metal (iron, steel, alloys), porous metal (ferroalloys), powder, slurry, lumps (oxide materials)
Heat and electric conductivity	Good in metals and ferroalloys; poor in oxide materials

favorable applications of the X-ray method to assaying the materials of ferrous metallurgy which include all the above elements except B, C, N, O, F, Na, Zn, Se, Cd, Sb, Re, Pb, and Bi.

It should be clear that these limitations are not absolute and that the boundaries may expand in both directions. For example, in 13 steel companies of Japan, united by a special subcommittee,[1] only 22 chemical elements starting from aluminum upwards are considered measurable by the X-ray fluorescence method, with no visible reasons for leaving the element magnesium out of the list. On the other hand, in the materials of the basic oxygen process (Republic Steel Corporation, Warren, Ohio), 23 elements including fluorine are analyzed in a routine way by the X-ray method.[10]

Table 3 lists some summarized characteristics of metallurgical materials.

2. *Measurement Accuracy Requirements*

The accuracy and precision categories assumed in this article are those prescribed in the "Guide for Use of Terms in Reporting Data in Analytical Chemistry" (Analytical Chemistry, 51, 173, 1979).

The requirements to analysis accuracy and reproducibility in ferrous metallurgy may lie within broad ranges of values depending on multiple factors, including the type of material, the type of element to be determined and its concentration range, the specific facilities, and process parameters. A few examples which, however, cover the entire range of the reproducibility requirements with eventual deviations are given in Table 4. The small values of relative standard deviation (r.s.d.) in Table 4 belong to high values of elemental concentrations and high r.s.d. values relate to smaller concentrations. Accuracy requirements run through similar values.[10]

From consideration of the data in Table 4 it follows that the least admissible value of r.s.d. is about 0.003. This value may be taken as the starting point for formulating precision requirements to X-ray instruments and analytical techniques.

3. *Analytical Tasks, Classified*

The miscellaneous analytical tasks in the iron and steel industry that can be handled by the X-ray fluorescence techniques can be put into five major groups:[11]

1. Certification analysis (This group includes analyses of metal sampled after the blast furnace tapping or a steelmaking process is over. This includes also analyses of previously certified raw materials if there are doubts about their real composition.)

Table 4
PRECISION REQUIREMENTS OF IRON AND STEEL INDUSTRY TO ANALYSIS RESULTS

Kind of material	Element to be determined	Concentration in mass percentage	Precision requirements	
			Standard deviation (%)	**Relative standard deviation**
Iron ore	13 Al	0.5—1.5	0.10	0.07—0.20
	26 Fe	40—65	0.20	0.003—0.005
Blast furnace slag	13 Al	3—6	0.15	0.025—0.05
	26 Fe	0.5—1	0.05	0.05—0.10
Pig iron	14 Si	0.6—4.0	0.03—0.1	0.025—0.05
	25 Mn	0.5—1.8	0.03—0.06	0.03—0.06
Ferroalloys (FeSi)	14 Si	15—80	0.3—0.5	0.006—0.02
	15 P	0.02—0.1	0.004—0.008	0.08—0.20
	16 S	0.002—0.1	0.002	0.20—1.0
Steel, alloys	6 C	0.01—4.0	0.003—0.06	0.0150—0.03
	50 Sn	0.001—0.01	0.0002—0.0005	0.05—0.20
	74 W	0.1—20	0.02—0.3	0.015—0.20

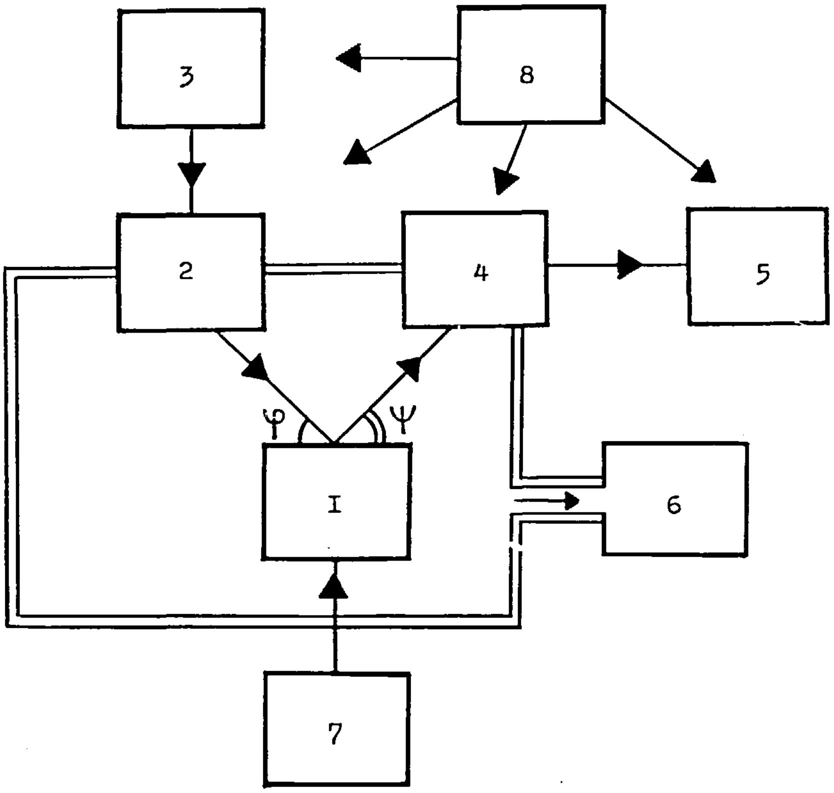

FIGURE 2. Functional block diagram of a typical X-ray spectrometric system. (1) Sample; (2) characteristic X-ray spectrum excitation source; (3) power supply; (4) signal separation and measurement unit (the spectrometric channel); (5) data output (plotter, printer, tape, display, etc.); (6) vacuum system; (7) sample monitoring assembly (rotating means, air-lock means for sample changing, cooling means, and current measuring instrument); (8) signal stabilizing device. φ is exciting radiation incidence angle, ψ is radiation take-off angle.

2. Analysis of metal and slag during steelmaking process and teeming operation (This kind of analysis is purported to control the steelmaking process, to monitor ladle additions, etc.)
3. Analysis of moving ore processing materials (ore, sintering mixture, sinter) with the aim of controlling ore processing
4. Analysis of finished products (ingots) if there are mistakes in its labeling, in store conditions,etc.
5. Determination of steel sheet coating thickness and chemical composition with a purpose to control the coating process

The certification analysis is performed periodically without any rigid requirements to its duration. It can be repeated if necessary. The composition of the analyte is approximately known prior to analysis. Ranges of component concentrations in samples are pretty narrow; for example, the concentration of chromium in alloy steel of grade X13 (Soviet nomenclature) is within the gap from 12 to 14%.

The second and the third analysis groups have to be completed within a definite time interval depending on the plant and process parameters, etc. Normally this time interval lies inside the range from 5 to 10 min.[12] In the basic oxygen process, the sampling-to-results time is under 3 min.[10] Such analysis cannot be repeated in a routine manner as it would delay the process. Ranges of component concentrations in samples are wide and uncertain.

The specificities of the fourth group consist in impossibility of sampling and in necessity to perform the analysis "on the spot". It means that the material analyzed is not taken to the spectrometer but the spectrometer has to be brought to the material analyzed.

Analyses of the last group also have to be done "on the spot". The analyzed material is most commonly moving steel sheet or strip.

II. INSTRUMENTATION

A. Introduction

Figure 2 shows the functional block-diagram of a modern X-ray spectrometric system composed of typical units.

The sample 1 is irradiated at an incidence angle φ by particles having a kinetic energy E_0, which is higher than the excitation potential of the element to be determined. The exciting particles (primary radiation) are emitted by a source 2 with a power supply unit 3. The radiation of the sample at a take-off angle ψ is received by a signal separation and measurement unit (spectrometric channel) 4 in which the radiation from the element to be determined is separated from the polychromatic radiation of the whole sample and measured. The measured data are in some conventional manner converted into element concentration and displayed by a data output unit 5 in a desired form. Analyses have more often than not to be conducted *in vacuo* for two reasons:

1. Vacuum environment of sample minimizes absorption of soft X-rays in light element determinations. A gas pressure of 10^{-2} torr is quite enough to minimize the absorption and single-stage pumping can provide that. Sometimes, where a further reduction of X-ray absorption is required (as in analyses of moving materials), helium-filled path technique is used instead of evacuation.[13,14]
2. A vacuum of 10^{-4} to 10^{-5} torr may be necessary for running such an excitation source as electron gun. Two-stage pumping has to be applied to such cases. To

enable sample replacement without violation of the vacuum in the whole system, a vacuum lock has to be provided. The vacuum lock, sample rotating means, and some other sample handling mechanisms constitute the sample handling system 7. The last unit of a typical X-ray spectrometer to be mentioned is a signal stabilizing unit 8 which ensures the admissible instrumental error level.

The maximum distinctions that differ the available commericial X-ray spectrometers consist in the different operating principles of the units 2 and 4 as well as in the techniques used to study a broad range of wavelengths.

The X-ray spectra may be excited by: X-ray photons, electrons, positive ions (protons, for instance), and gamma-radiation from radioisotopes. The electron-excited characteristic spectra are called primary spectra; the X-ray photon-excited characteristic spectra are called secondary spectra. Primary spectra are more intensive than secondary ones, especially in case of light elements, but the instruments working with the primary spectra are more complex.

Analytical signal separation from the background noise is based on two major effects: X-ray diffraction (wavelength dispersion) and the functional relation between photon energy and the pulse height furnished by the X-ray detector (energy dispersion). A detailed comparison of the two methods would take us far afield, and it has already been done by R. Jenkins.[15] In short, we may note that the wavelength dispersion is intrinsically capable of solving more complicated analytical problems than the latter one. However, the energy dispersive instruments are easier and cheaper.

One of the following two methods can be used in a spectrometric analysis of multicomponent samples: (1) determining the elements one by one (sequential or scanning method) or (2) determining all elements simultaneously (simultaneous or multichannel method).

Apparently, the second type requires much less time than the first. On the other hand, the first type is more versatile and thus more handy in research programs.

All these instrument varieties are widely used in the iron and steel industry.

B. Improvement of Excitation Conditions to Step up Analytical Signal Level

The analytical potential of the X-ray fluorescence method depends largely on the excitation mode.

One of the limitations of the X-ray fluorescence method that has long been stimulating the development of adequate apparatus consists in the relatively low signal from elements with Z_x below 20. This limitation drastically deteriorates the sensitivity C_{min} of detection of elements with Z_x below 20, which has been experienced in analyses of ferrous materials and reported.[4,5,16-19]

The physical cause responsible for this limitation is the rapid drop of fluorescence yield of elements with $Z_x < 20$, about proportionally to Z_x^4. The limitation is even graver when the characteristic spectrum is excited by radiation from a sealed X-ray tube, since the softer part of the exciting radiation which most effectively excites the lighter elements is substantially absorbed by the berillium window of the tube. The residual portion of the primary spectrum that participates in excitation of light elements is about the same for all light elements.[20] This effect is illustrated in Figure 3. The characteristic radiation from an element I of a wavelength λ_{i1}, corresponding to the i-shell ionization energy, is excited by the primary radiation portion ranging from λ_o to λ_{i1}. This portion will change as the wavelength λ_{i1} shifts in the range from λ_o to λ_1, but will remain constant after the wavelength λ_{i1} has exceeded λ_1. This will correspond to elements 2 and 3.

The fact that the exciting radiation remains constant as Z_x varies in a certain range leads, in case of materials having to be analyzed in the ferrous metallurgy, to the

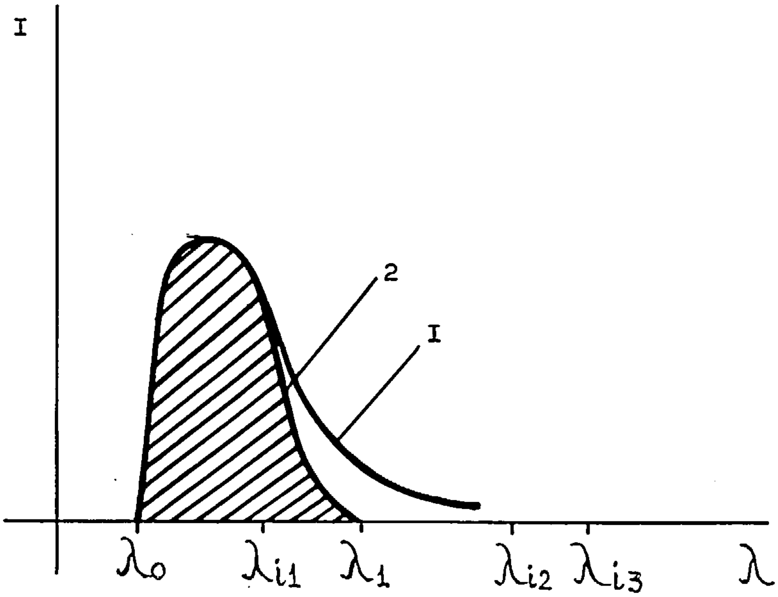

FIGURE 3. Intensity of continuum radiation emitted by an X-ray tube as function of wavelength. (1) Intensity at anode of the X-ray tube; (2) intensity modified by beryllium window absorption. λ_{i1}, λ_{i2}, λ_{i3} are wavelengths corresponding to the ionization energies of elements 1, 2, 3.

following relationship between the characteristic radiation intensity and the atomic number of the element in question:[20]

$$I_{2K} = C_2 Z_x^{12} \qquad (1)$$

where C_2 is a factor; I_{2K} is intensity of secondary K-spectrum of elements with $Z_x < 22$ dissolved in small amounts (roughly less than 1% by mass) in ferrous materials ($Z_e \approx 26$).

Equation 1 was obtained for a 0.5-mm thick window. For smaller thicknesses the power 12 should be decreased perhaps, but the general tendency would remain.

The following expression was derived for the intensities I_{1K} of the primary K-spectra from the same elements:[20]

$$I_{1K} = C_1 Z_x^{3.5} \qquad (2)$$

In deriving Equation 2 it was assumed that the electron beam energy E_o is equal to a value corresponding to the maximum of the primary characteristic spectrum. This E_o value may be found from:

$$(E_o)_{max} = \left[\frac{3 \times 10^5 \sin \psi}{\mu_m (\lambda_{Ki}) \sin \varphi}\right]^{2/3} \text{keV} \qquad (3)$$

where $\mu_m (\lambda_{Ki})$ is coefficient of mass absorption of radiation with wavelength λ_{Ki}[20].

It is worthwhile to note that if the secondary radiation is excited by a photon beam with $E_o = E_q$, where E_q is excitation potential for q-series, the following relationship will hold:[20]

Table 5
COMPARATIVE CHARACTERISTICS OF PRIMARY AND SECONDARY X-RAY SPECTRA

	Characteristics	
Item	**Primary spectrum**	**Secondary spectrum**
Excitation source	Electron gun	X-ray tube
Normal operating conditions	10 kV, 1 mA	50 kV, 50 mA
Power consumption	0.01 kW	2.5 kW
Required vacuum	0.5×10^{-4} torr	10^{-2} torr[a]
Preferred ranges of atomic numbers in ferrous materials	$Z_x < 26$	$Z_x > 20$
Special requirements to sample	Heat and electric conductivity	Not required
Excitation source lifetime (average)	300 hr (cathode has to be replaced after this time)	2500 hr (loss of emission, the whole tube has to be replaced)
Nature of background	Continuum radiation	Backscattered primary radiation

[a] If a windowless X-ray tube is used the vacuum conditions should be the same as in case of primary X-ray spectrum.

$$I_{2K} > I_{1K} \tag{4}$$

(per one exciting particle).

There are two ways available to overcome the limitation due to the filtration effect represented by Equation 1: (1) minimizing the beryllium window thickness and (2) replacing a sealed X-ray tube by another, more efficient excitation device.

Both ways have been developing successively over the time span under consideration. Initially (in mid 60s), it was the second way that was being developed more intensively and was regarded by some researchers as the most promising means of reducing the detectivity threshold in ferrous metallurgy analyses.[21] This viewpoint was later confirmed by analytical practices using electron beam excitation techniques.[8,14,18,22-25] Though presently the attitude to electron beam excitation is rather different from what it was 10 years back, this way of raising the analytical signal level is still valid. In a recently published work,[14] ferronickel was analyzed partly with electron beam excitation (elements Si, P, S) and partly with X-ray excitation (elements Cr, Co, Ni, Cu).[14]

Reducing the X-ray tube window thickness to 0.1 or even less may be an effective means of raising the analytical signal level, and the modern secondary type X-ray spectrometers well meet the requirements of the iron and steel industry, including the detection of light elements up to 9F.[10,26] Further thinning of the beryllium window is limited by the corresponding reduction of its mechanical strength and tightness, for it has generally to work under rather severe temperature conditions and under a pressure of 1 atm.

The number of papers devoted to the primary and secondary analysis methods as used in ferrous metallurgy scale approximately as 1:5, respectively. Researchers' attention is still focused on the excitation sources.[27] To conclude this section of the review, we refer the reader to Table 5 comparing the characteristics of the primary and secondary excitation modes. In view of the current world-wide energy crisis, line 3 of this table might be of special interest.

Apart from sealed X-ray tubes and electron guns, the following excitation sources have been tested in ferrous metallurgy:

1. Proton and helium ion beams[25,28]

2. A windowless X-ray tube generating X-rays together with anode-rediffused electrons[18,27]

The merits of proton excitation are well-known; owing to their large mass — protons, alpha-particles, and the like — they induce a weak bremsstrahlung radiation, since the latter's intensity is inversely proportional to the exciting particle mass. This allows the detection sensitivity for steels to be reduced by a factor of two or three compared to electron excitation.[25] Sensitivity may be improved in this manner both in wavelength and energy dispersive systems. Nevertheless, though really attractive, the practical use of proton excitation on the industrial scale is still rather doubtful because the apparatus needed to implement it is too complex.

X-ray and electron beams emitted by windlowless X-ray tube may be used for excitation either simultaneously or separately, in turns. This may provide additional analytical possibilities.

The intensity of the K α-line of aluminum generated in refractory steel on excitation by a windowless X-ray tube may be expected to be 50 to 100 times as high as that excited by a sealed X-ray tube with a 0.3-mm thick beryllium window.[20]

Windowless X-ray tube emitting only X-radiation and having a target operated at a high positive potential relative to earth has proved a good means of detecting fluorine in slags. A tube operating at 16 kV and 200 mA ensures a counting rate of 500 counts per second per 1% of fluorine in slag which is four to five times more than a conventional X-ray tube run at 50 kV, 50 mA.[29]

Apart from new excitation sources, methodological developments still bear a potential for improving the analytical signal level. One direction of such development consists in raising the X-ray tube potential. For example, voltages between 80 and 90 kV were successively used to determine elements Zr, Nb, and Hf in steels with concentrations in the ppm range. In case of electron excitation, a maximum signal level (but not necessarily the signal/noise ratio) may be obtained by adjusting the electron gun potential to a value given by Equation 3. Analytical signal level may also benefit from a proper choice of the X-ray anode material. Analytical experience in the iron and steel industry supplies plenty examples to this effect: P and S determinations by means of an X-ray tube with a rhodium anode[31] and palladium anode.[32] A palladium anode tube has been very effectively used for determining Si and Ca.[33]

C. Wavelength Dispersive Spectrometers

Commercial simultaneous X-ray spectrometers are the apparatus most commonly used in routine macroscopic analyses. Where necessary, this apparatus may be operated 24 hr a day, continuously for a fortnight or longer.[10,34] Normally, the instrument time of analysis is within 20 to 40 sec.[10,22] At the dawn of the X-ray fluorescence, the spectrometers used mostly were of the sequential type, and they are still in use, of course. However, the advantages in speed offered by simultaneous spectrometers have made them more attractive to the user. It is sometimes necessary to determine up to 17 chemical elements in one sample (low-alloy steel).[10]

The room in which an X-ray spectrometer is installed must, as a rule, be air-conditioned, for without it ambient temperature changes may affect the spectrometer characteristics resulting in increased instrumental error.[35-37] There will be practically no temperature-caused drift of spectrometer characteristics if ambient temperature variations are not allowed to exceed ±2 or ±3° C.[36]

Some analytical work was done with special type instruments (e.g., for "on-stream" oxide material analysis,[38-41,218] for continuous analysis of molten metal in an electron beam furnace[42-46]; attempts are made to run the X-ray analysis with apparatus not intended for macroscopic analysis, e.g., electron beam microanalyzers,[24,25,47-49] X-ray beam microanalyzer,[50] and X-ray diffractometer (the detection sensitivity of iron in sinter, blast furnace dust and iron scale attainable by this method is within about 0.1% by mass).[51]

D. Energy Dispersive Spectrometers

Amount of analytical work carried out with the aid of energy dispersive spectrometers has been steadily growing in the last decade and the number of papers published so far reporting such work comes to as much as 30% of the total.

Energy dispersive instrumentation has been developed along two mainlines: (1) use of *differential filters and (2) use of semiconductor detectors.*

Operation of the first type is based upon selective absorption characteristics of substances. An appropriate combination of filter materials mounted along the X-ray fluorescence path will separate the radiation of interest. For each element there should be a pair of filters, for example for Ti — Sc and Ti, for V — Sc and Ti, for Cr — Ti and V, etc.[52]

Operation of the second type instruments relies upon the high resolution of semiconductor detectors, lithium-doped silicon detectors Si(Li), and lithium-doped germanium detectors Ge(Li).

As regards to applications to ferrous materials, the second brand of energy dispersive analyzers has been developing more rapidly than the first in the last decade. Detailed description of the analytical potential afforded by spectrometers of the second type and of their applications in industrial control, including ferrous industry, has been published.[53,54]

X-ray tubes and radioisotopes are most often used for excitation of X-ray spectra in the energy dispersive apparatus.

Comparison of the two types of excitation sources employing proportional and Si(Li) detectors used for multielement analysis of carbon and low-alloy steels has shown that the use of the X-ray tube system as excitation source assures a much higher accuracy, possibly a whole order of magnitude better, than the isotope source (30 mCi^{238}, Pu).[55] A low power air-cooled X-ray tube has been tested (8 kV, 64×10^{-6} A).[56]

Energy dispersive spectrometers have been widely used in portable modifications.[57,58] Such spectrometers are not intended for precision measurements, some of them pursue determination of only one particular element, e.g., molybdenum in steel, and are equipped with pointer indicators from which concentrations can be read directly.[59] However, by using a special background subtraction technique it is possible to solve more difficult problems, e.g., determination of Cr, Fe, and Ni in stainless steel.[60]

E. Computerization of X-ray Spectrometry

Use of computers in the X-ray fluorescence analysis of ferrous materials has been one of the main concerns of X-ray instrument designers in recent years. The major functions a computer coupled to an X-ray spectrometer has to perform are the following: (1) concentration computations from measured spectral line intensities; (2) matrix corrections; (3) choice of an adequate equation for composition calculations and computation of coefficients; (4) statistical data processing; (5) spectrometer calibration and monitoring; (6) calculation of optimum alloying additions and process control; and (7) combining different analytical instruments, such as X-ray spectrometer, optical spectrometer, carbon analyzer, etc., into an integral analytical system.

Computers are sometimes charged with many extra functions, though not as important as above.[61]

Advantages provided by computerization of the X-ray analytical process are quite evident. Automatic matrix correction considerably improves the analysis accuracy, sometimes by a factor of 3 or more.[10,26,62] A computer can easily apply corrections to a large number of elements (20[61], 24[64]). Computerization solves the alloying optimization problem in the steelmaking process, giving a marked reduction in metal cost.[64]

Computerization of X-ray fluorescence systems has followed two main trends: (1) use of large multipurpose computers[32,65-69]and (2) use of special-purpose or small-capacity multipurpose computers with reduced computer memory requirements, interfaced with the spectrometer.[13,59,63,70-77]

There is an opinion that to ensure proper reliability a bigger computer should be used apart from the small one coupled to the spectrometer.[78] A similar two-computer concept has also been suggested in another paper.[79]

F. Analytical Systems and Complexes

One of the main features of the current state of analytical control in the iron and steel industry is the integration of individual analytical instruments into analytical systems and complexes. In such systems all the component instruments and devices are interrelated and function as a single integrated analytical complex. The characteristics of the individual units of such complexes may be correlated. A computer having inputs for one or more analytical tools and outputs for dispatching information is an essential component of such a complex.

A typical analytical system comprising an X-ray spectrometer as a basic tool is shown in Figure 4. A sample of metal or slag is taken out of the furnace and conveyed by means of pneumatic or vacuum transport to the analytical laboratory where it is prepared for analysis in some proper way. The sample is then fed into an X-ray spectrometer which measures the spectral line intensities. The measured intensities are converted into concentrations by a computer which also applies the necessary corrections and dispatches the results to all required addresses. Computer automatically controls the spectrometer operation. A second computer may be there to do some work which cannot be performed by the small computer coupled to the spectrometer. The total sampling-to-results time may be as little as 10 min or less in which the individual operations have the following share:

1. Sampling — 10 to 20 sec
2. Conveying the sample to a distance of up to 500 m — 40 to 50 sec
3. Sample preparation — 100 to 120 sec
4. Instrument time — 30 to 60 sec
5. Intensity-to-concentration conversion and print-out of the results — 20 sec
6. Additional operations (sample feeding, spectrometer adjustment, calibration, etc.) — 100 to 200 sec
7. Total — 300 to 470 sec

X-ray spectrometers are quite often used as part of more complex analytical systems and complexes, along with other analytical tools such as optical emission spectrometers, carbon and sulfur analyzers, neutron activators, etc.[12,26,70,71,79-89] Such complexes may comprise up to 15 different analyzers.[59] In an automated laboratory system FLANC-1, all analytical tools including chemical analyzers and optical and X-ray spectrometers, numbering 11 in total, are connected to an IBM®-1800 computer.[86]

A system like this can serve the analytical purposes for a group of shops of a steel plant[71,87] or even a group of plants.[70] An analytical complex consisting of 4 optical emission spectrometers and two X-ray spectrometers supplemented with a computer, can handle analytical work for two steel-making shops, four sintering machines, four blast

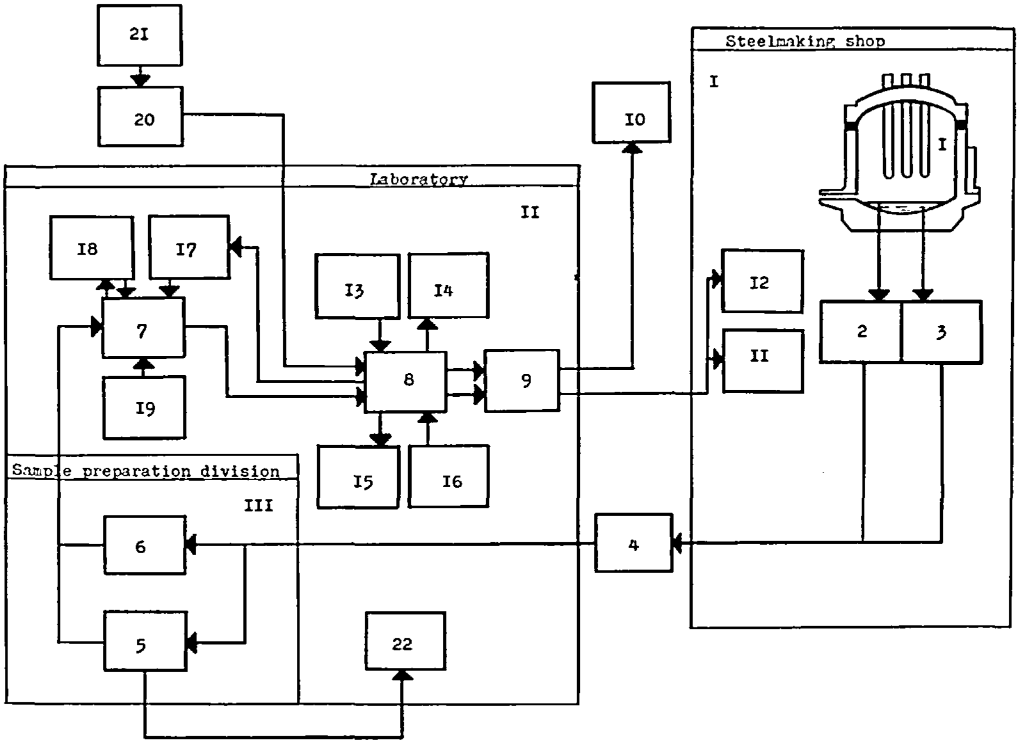

FIGURE 4. A typical analytical system based upon an X-ray spectrometer. (1) Steelmaking furnace; (2) slag sampling; (3) molten metal sampling; (4) sample transportation; (5) metal sample preparation; (6) slag sample preparation; (7) X-ray spectrometer; (8) computer interfaced with the spectrometer; (9) data transmission line; (10) a higher stage computer; (11) display terminal; (12) furnace teletype; (13) type in; (14) type out; (15) teletype; (16) data recorder (plotter, printer, etc.); (17) automatic spectrometer control system; (18) spectrometer fault detection device; (19) calibration standards; (20) computer for calculation of the analytical equation coefficients; (21) software; (22) other analizers (optical emission analyzer, carbon analyzer, etc.); (I) steelmaking workshop; (II) analytical laboratory; (III) sample preparation division.

furnaces, and a continuous casting machine. The complex can meet the analytical requirements of a steel plant producing 12 million tons per year. The complex has been in operation since 1971.[71] A similar system, but including one optical emission spectrometer and one X-ray spectrometer, handles the analytical work of a 1.6 million tons-per-annum steelmaking plant.[82] An analytical set at Sidmar consisting of two optical emission spectrometers, a simultaneous X-ray spectrometer, a neutron activation instrument, an X-ray diffractometer, a computer, and display terminals handles analyses of a whole plant.[84] An analytical set at Fagersta (Sweden) including two X-ray spectrometers (PW 1212 and PW 1600), an optical spectrometer ARL 31000, LECO-analyzers for carbon and sulfur, and two computers (P 100 and P 855) perform daily analyses of 150 samples of ore, sinter, slags, and steel scrap.[12]

The analytical work is allocated between the analyzers of an analytical set.[71,80,81,84,85] This is usually done with an aim of obtaining some analytical result, e.g., to assure an error which is below a certain predetermined value in analyses of various steel grades.[81] In another example, slags, sinter, ore processing materials, and alloy steel are being analyzed by the X-ray spectrometer, while cast iron, pig iron, and steels are analyzed by an optical emission spectrometer.[71] Further examples include assaying metallic samples by an optical spectrometer, oxides by an X-ray spectrometer, oxygen by the neutron activation method,[84] etc.

A sophisticated data processing system used at Westfalenhüttewerke (Hoesch AG) facilities has been described.[85]

III. SAMPLING AND SAMPLE PREPARATION

A. Introduction

This stage of the analytical process is very important, as it essentially affects the analysis duration and accuracy. As seen from Table 1, Parameter 6, only a very thin surface layer provides information about the composition of the sample bulk. This layer must therefore be sufficiently representative of the bulk of sample, and should thus be prepared in a manner to warrant such representativeness.

The development of the sample preparation procedure for X-ray analysis has come up as a result of two major conflicting trends: (1) improving thoroughness of sample preparation, since this is liable to reduce the methodological share in the total analytical error, and (2) cutting the sampling and sample preparation time, since this is the most time consuming stage of the analytical process.

Sample preparation is subject to the following further requirements: low cost; and preventing sample contamination in preparation.

The amount of work involved in sample preparation for X-ray analysis may be estimated from the following examples: sinter samples are taken every half hour;[58] in a blast furnace process, 30 slag samples, 5 sinter samples, 5 liquid fuel samples, and 30 samples of the charge have to be taken daily;[82] refractories are sampled 80 to 120 times daily.[37]

The importance of sample preparation may be additionally emphasized by reference to the fact that, when used in conjunction with certain special techniques (chemical treatment of samples and the like), it may serve to increase the analytical signal level.[90,91]

Sample preparation procedures are different for different materials.

B. Sampling and Preparation of Iron, Steel, and Alloy Samples

There is a broad variety of devices for taking molten metal samples from furnace baths. Figure 5 shows steel and alloy samples used in the electrometallurgy of U.S.S.R.[34] The conically- or pyramidally-shaped samples have approximate dimensions of 25 × 50 × 60 mm, and those of the third type shown size as 30 × 50 × 10 mm in their flat part and 40 × 10 mm in their cylindrical part. Samples used in other countries have about the same shapes and sizes.[92-94]

The time required for taking a sample with an immersion type device depends on the molten steel temperature: at 1500° C it is 8 sec and at 1640° C it is 3 sec.[92] All research in the field of sampling aims at simplifying the sampling procedure per se, curtailing its cost and duration, and improving reliability. As the sample is cooled in the mold it may undergo various processes as, for example, component segregation, diffusion, etc., which may affect the representative quality of the sample. To avoid this, special molds have been designed.[95]

To effect a continuous compositional control of a molten and/or solid metal, a new series of sampling methods, which are still in the development stage, appear to be promising.[96,97] One of these contemplates continuous ejection of molten metal through a special port in the furnace wall by an ejection device.[96] The ejection device immersed in molten metal takes up liquid metal, turns it to dust, and transports the dust by means of an inert carrier gas to the analyzer. An article in which this method was first suggested was published back in 1970, but, as far as we know, it has not yet been developed any further.

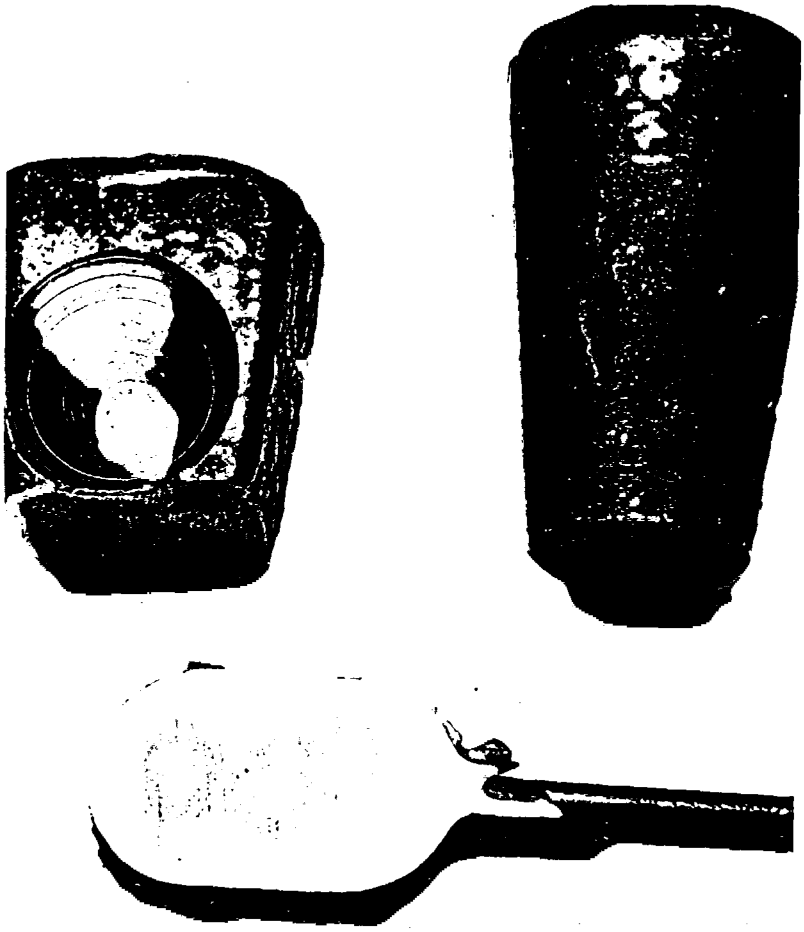

FIGURE 5. Examples of steel and alloy samples. The samples in the top portion of the photograph are picked up with a spoon; those in the bottom portion are taken by means of an immersion type sampling device.

The other method seeks to take a solid metal sample by atomizing it with a d.c. arc;[97] the dust is then also transported by an inert carrier gas.

The preparation of conical, cylindrical, or pyramidal samples most often includes the following steps, whatever the excitation method used (after the sample has been taken from the furnace and conveyed to the laboratory):[22,34,82,94,98-101] (1) cutting; (2) coarse finishing of the working surfaces; (3) finer finishing with another grinding medium; and (4) washing and drying (or wiping). Steps 2 and 3 may be combined.

Sometimes, to ensure homogeneity of the sample it is additionally annealed (at 1200°C) and then hardened.[24]

The sample is cut into several pieces. One of these goes to chemical analysis, another to the optical emission analysis, and still another to the X-ray fluorescence analysis. Cutting is done at a high tool speed so that a high temperature is developed at contact, resulting in formation of an oxide film on the working surface whose composition becomes different from that of the bulk. The difference was measured in 13% Cr steel to be 0.2% of chromium.[34]

Table 6
INTENSITY OF X-RAY CHARACTERISTIC LINE AlK_{α} EXCITED IN A REFRACTORY STEEL SAMPLE BY ELECTRON BEAM AS FUNCTION OF SAMPLE SURFACE FINISH[a]

	Sample finishing process		
Parameter	Wheel with 25—50 grain	Emery paper with 2—10 grain	Polishing with wet grit belt
Intensity	100	103	120
$S_{r.\Omega}$[b]	0.028	0.006	0.002

[a] $C_{Al} = 6.14\%$, $E_o = 9.3$ keV, $i = 0.365$ mA, ADP, $\Delta t = 30$ sec

[b] $S_{r.\Omega}$ is relative standard deviation of $AlK\alpha$-line intensity measured for eight different scratch orientations relative to the take-off direction, $\psi = 30°$.

From Nikolsky, A. P., Korolev, E. F., Zubkov, S. N., and Uzikhin, V. V., *Appar Metody Rentgenovskogo Anal.,* 15, 141 (1974). With permission.

Surfacing the sample with a grinding wheel or belt will remove the oxide layer. Another purpose of surfacing is to flatten the radiating ("working") face of the sample. The layer that can be removed by surfacing process may be 2 mm or more thick.[100] According to author's own experience, this figure looks unduly high. Suitable surfacing tools include an abrasive wheel,[22,34] dry No. 80 grit belt,[10] and wet No. 220 grit belt.[94]

The abrasive composition used for the sample surfacing operation is important. Most frequently, the abrasive for surfacing steel samples is either alumina or silicon carbide which contaminate the sample with aluminum or silicon, respectively.[10,98] Silicon carbide may be used as the abrasive, unless silicon was one of the elements to be determined in the analysis. If both aluminum and silicon are among the elements to be determined, the sample must be treated in two stages by different abrasives. First the sample is treated with alumina as abrasive and analyzed for silicon, then it is resurfaced with a silicon carbide abrasive and analyzed for aluminum. The reference samples and standards are machined with a diamond grinding wheel to avoid contamination. The use of a diamond grinding wheel for machining routine sample is too costly, though polishing with 1-mcm diamond paste is sometimes practiced.[25]

Another way of avoiding sample contamination is to use a cutting tool. A special milling system has been designed to machine up to 300 samples per set of inserts at a comparatively low cost, with good surface flatness and no loss in analytical accuracy with tool wear.[102] Surface machining takes a little over 10 sec.[94]

Quality of the surface finish may affect analytical results in a twofold manner:

1. Surface quality may affect the position and shape of the analytical curve, since the X-ray fluorescence and scattered radiation intensities depend on the sample surface status.[32,34,99]
2. The scratches left after machining may cause the shadow effect which depends on the fluorescence take-off angle ψ and on its direction with respect to the direction of scratches.

In the case of stainless steels, the intensity of secondary spectra increases by about 2.5 to 4.5% when the depth of residual scratches is reduced from 8.8 to 0.32 mcm.[99] Similar primary X-ray spectra data are given in Table 6.[22] The $S_{r,n}$ values for secondary X-ray spectra are about four to eight times smaller than those listed in Table 6 for the primary spectra. To eliminate the error generated by the shadow effect the sample should be rotated during the analysis.[101]

As a general observation drawn by the author from his own experience, it may be concluded that the contribution of the sample preparation procedure to the total analysis error is the greater when the smaller element concentration is to be determined. Here are a few figures to illustrate this tendency: $S_r = 0.002$ to 0.005 for $C_x = 10\%$; $S_r \approx 0.01$ for $C_x \approx 1\%$; $S_r \approx 0.05$ for $C_x \approx 0.3\%$. The above values of S_r were obtained on steel samples surfaced with a No. 2 to 10 wheel. The samples were installed in the spectrometer in an arbitrary manner to preclude any coordination between the direction of machining scratches and take-off direction, and the secondary spectra were analyzed for the presence of Ti, V, Cr, Mn, Fe, Co, Ni, Mo, and W.

A further group of sample preparation methods uses dissolution of metal samples and/or other wet chemical procedures (preconcentration, vaporization, ion exchange, etc.).[90,91,103-110,220] The solvent is usually a mixture of acids HCl and HNO_3.[107,110] Then, prior to analysis, the solution may be poured into a liquid sample holder or used to impregnate some porous material. The step of dissolution and related operations can last as long as 10 min or more. Usage of wet chemical techniques often results in a material reduction in the light element detection sensitivity. Combination of chemical separation of sulfur as $BaSO_4$ by the conventional gravimetric technique with X-ray fluorescence analysis of the residue can give very accurate results of sulfur content in basic process iron, carbon steel, or stainless steel down to a level of 0.001%.[109]

Dissolution of metal samples offers, generally, the following advantages: (1) sample homogeneity; (2) simple preparation of standard and blank (for background measurements) samples; (3) straightforward auxiliary operations, e.g., separation, concentration, etc.; and (4) diminished matrix effects.

However, the chief disadvantages inherent in methods involving dissolution (time and labor consuming) do not permit to list them among the routine techniques of rapid X-ray analysis in the iron and steel industry.

C. Preparation of Samples of Oxides (Ore, Sinter, Slag, etc.)

Powder sample preparation comprises the following steps: (1) grinding; (2) pressing; and (3) fusion (glass bead techniques). In some special-purpose applications steps 2 and 3 may be repeated several times over. Optional steps further include: drying, sifting, and mixing with an appropriate flux or binder. Slag samples have to go through magnetic metal separation;[111] blast furnace slag pellets are slightly surfaced;[73] briquettes are varnish-coated.[112]

1. Grinding

Particle size tangibly affects the analytical signal.[13,33,76,113-117] The characteristic X-radiation intensity depends on the ratio between particle size and radiation layer depth and on the analyte concentration. The general rule is that the smaller the particles the higher the analytical signal level, all other conditions the same. From the curve in the reference material,[13] it may be deduced that the analytical signal level becomes constant when the particle size (d) is less than about 0.1 or less than the sample layer thickness (Δ), giving the major contribution to the analytical signal. This relationship between d and Δ was obtained at $\varphi = 60°$ and $\psi = 30°$. Under different conditions, the relationship between d and Δ below which the particle size may be neglected may be other than above. Since it is not always possible to know the value of Δ for the specific conditions in question, the recommended practice is to use a certain $d_{max} < 0.1$ mm,[118] $d_{max} = 0.044$ mm,[119] etc.

The extent to which particle size may affect signal level may be great. Line Fe K β_1 intensity is increased by about a factor of 2 if ore particle size is reduced from 200 mesh to 0.002 mm.[113] Grinding powder to a particle size below 200 mesh is the commonly recognized way of overcoming the grain size effect.[9,76,113] The grain size effect is particularly disturbing at high analyte concentrations.[33]

Depending on the type of grinding device the operation may last from 1 to 5 min.

2. *Pressing*

This operation immediately follows the grinding step. Powder premixed with a binder is pressed into pellets. Suitable binders include the following materials: boric acid,[10,66,120-122] graphite,[123,124] sugar powder,[125] wax, cellulose (individually or in mixture),[126] starch,[127] Somar-Mix,[128] certain kinds of gum,[39] polyvinyl alcohol,[119] polystyrene,[113] and polystyrene mixed with maleic acid.[129]

Powders are sometimes pressed into pellets in cups made of boric acid;[33] sometimes they are just placed inside special sample holders.[130] Pressing may be affected at different pressure settings: 0.4 t/cm^2,[125] 1 t/cm^2,[37] 1.35 t/cm^2,[119] 1.6 t/cm^2,[126] 2 t/cm^2,[121] 3 t/cm^2,[9] 4 t/cm^2,[127,131] 10 t/cm^2,[66] and 20 t/cm^2.[128] A good reproducibility of the pellet shape is obtained by using a special press die.[132] In the case of F_2O_3 and SiO_2 it can assure $S_r = 0.004$ and $S_r = 0.0035$, respectively.

3. *Fusion of Powder Samples (Glass Bead Technique)*

This operation has a great and still increasing importance. Fusion is one of the most effective ways of obviating most of the difficulties encountered in X-ray analysis of powder materials. Fusion presents the following advantages:

1. Eliminates grain size and chemical bond effects
2. Diminishes matrix effect due to dissolution of sample with flux
3. Homogenizes samples
4. Improves sample surface conditions
5. Provides opportunity for introducing into the sample an internal standard or a heavy absorber element
6. Allows to use synthetic calibration standards which can be prepared in the best way to fit the task in hand

Fusion may reduce the analytical error but not always to a great extent. It has been found, for instance, that $S_r = 0.0023$ for pressed samples and $S_r = 0.0021$ for fused samples.[133]

Fusion technique is now being extensively used worldwide;[1,2,9,10,29,73,82,84,124,131,133-145] to effect fusion, samples are mixed with a flux with a view to reduce the fusion temperature. The glassy mass is poured onto a plate and cooled. The resultant glass bead may then be surfaced and analyzed[140,143] or it can first be ground to 200 mesh, pressed, and then analyzed.[9]

The sample material/flux ratio may vary within from 1:1 to 1:25. More flux in the composition reduces the fusion temperature but also decreases the fluorescence intensity from an element due to its dilution.

Proper choice of flux is very important. The following materials may be used: sodium hexametaphosphate and lanthanum oxide;[9] $Li_2B_4O_7$ or $Na_2B_4O_7$[10,29,84,137,143-146] ($Li_2B_4O_7$ being used more often as it ensures a higher characteristic radiation intensity[144]); graphite;[124] $Na_2B_4O_7 \cdot 10H_2O$;[1,82,114,133-136] and $K_2S_2O_7 \cdot SiO_2$.[140]

Experiments with different fluxes have shown that the best results are obtained when $Li_2B_4O_7$ or $Na_2B_4O_7 \cdot 10H_2O$ are used. The fusion temperature in this case is 1000°C

Table 7
EXAMPLES OF FUSION TEMPERATURE AND DURATION IN GLASS-BEAD TECHNIQUE

Sample	Flux	Duration of fusion (min)	Temperature of fusion (°C)	Ref.
Sinter (0.5 g)	$Li_2B_4O_7 \cdot 5H_2O$ (3g) + Li_2CO_3(0.5g) + $NaNO_3$(0.25g)	3—5	1250	137
Refractory Materials	$Na_2B_4O_7 \cdot 10H_2O$ (1:10)	4	1100—1400	134
Sinter and blast furnace slag	Graphite	3	1150	124
Refractory materials, slags, fluxes	$Na_2B_4O_7 \cdot 10H_2O$ or $Li_2B_4O_7$ (1:10)	10	1000	145
Slag	$Li_2B_4O_7$ + KBr (1:10:0.1)	8	900—1100	29
Iron ore	$Na_2B_4O_7$ + $NaNO_3$	6—8	1180	146

and process time is 10 min or slightly more. The best sample material/flux ratio has been found to be 1:10.[145]

Various additives may be incorporated in the flux to improve the bead quality or to modify the fusion process itself: Li_2CO_3 and $NaNO_3$ are added to $Li_2B_4O_7 \cdot 5H_2O$ to cut the fusion time (to 3 to 5 min),[137] and Li_2CO_3 and La_2O_3 are added to $Li_2B_4O_7$;[143] addition of some La_2O_3 improves the bead surface quality.[143] The ore/flux/La_2O_3 proportions are 1:8:0.5;[9] lanthanum oxide may be present in an amount up to 10% based on flux.[143]

Larger amounts of KBr or NaBr are added to $Li_2B_4O_7$ in order to improve the homogeneity of the beads, and Co_2O_3 may be added to serve as the internal standard.[144] Minor amounts of KBr are added to prevent foaming. The slag/flux/KBr proportions are then 1:10:0.1.[29]

Fusion process time is in the range from 3 to 10 min; fusion temperature is in the range from 1000 to 1400° C. Some exemplary times and temperatures are indicated in Table 7.

The glass bead technique may be used for metal samples as well, provided that the sample preparation includes dissolution and it is the dry residue which is to be analyzed.[109]

To reduce the oxide sample preparation time to a point where its output rate would be adequate to the X-ray analysis stage per se, a novel automatic fusion apparatus has been designed.[147] The apparatus uses gas-compressed air burners and ensures an average fusion time of 12 min. Fusion time may be optimally coordinated with other conditions.

The powder sample preparation process, including the steps of grinding, pressing, and fusion, is liable to change the original sample composition because it is diluted with the flux, moisture is evaporated in drying, etc. It has been found that the ore weight substantially decreases in grinding due to evaporation of the crystallization water.[148] Where the sample preparation is a routine procedure, these variations may be known and compensated for. However, the situation is different when moving materials are to be analyzed, i.e., when it is impossible to prepare samples in a routine manner. The analysis results in this case are affected by the conditions under which the analyzed material had been stored, especially the ambient humidity.

The effect of humidity may be accounted for by the following correction:[149]

$$I_H = I_D\left(1 + \frac{k\,C_H}{1 - C_H}\right)^{-1} \tag{5}$$

where C_H is moisture concentration in sample, I_H is characteristic radiation intensity from wet material, I_D is characteristic radiation intensity from dry material, k is a factor. For iron ore Equation 5 yields satisfactory results in the C_H range of from 0 to 8% by mass.

D. Ferroalloy Sample Preparation

Ferroalloy samples are more often than not prepared in the same manner as oxide samples.[129,136,150-152] The glass bead technique and addition of $Li_2B_4O_7$ and V_2O_5 as flux were used for Fe-Nb, Fe-W, Fe-Ti, Fe-V, Fe-Mo, and MoO_3. For Fe-V it is $NaNO_3$ or KNO_3 which is added instead of V_2O_5. Fusion time is 20 min, temperature 1200° C.[150] Similar procedures are used for ferroalloys Fe-Mn, Fe-Si-Mn, Fe-Si, and Fe-Cr.[151] Preparation of ferro-silicon samples consisting of grinding and pressing can also give good results in analyses of large silicon concentrations (70 to 80%).[129]

An alternative way of preparing ferroalloy samples is to dissolve them in a mixture of acids.[107,136] Ferroalloys Fe-W, Fe-Nb-Ta, and Mo-W are dissolved in a mixture of HF and HNO_3; Fe-Mo is dissolved in a mixture of HF, HNO_3, and H_3PO_4;[107] Fe-Mn is dissolved in mixed HNO_3, H_2SO_4, and HF.[156] Dissolution is also applied to ferrites.[153]

E. Automated Sample Preparation

Automation of powder sample preparation is of special importance because it is the most time and labor consuming operation of the entire analytical process. There have been efforts to create automatic sample preparation systems.[134,154,155]

Figure 6 is a schematic view of an automatic apparatus for preparing iron ore samples.[155] This system gives samples for X-ray fluorescence analysis[40] which determines the calcium oxide concentrations and provides the grain size of $\leqslant 5$ mm. Time of sample preparation for periodic analysis is about 3 min, volume of a sample is about 20,000 cm^3

IV. CONCENTRATION CALCULATIONS FROM MEASURED INTENSITIES

A. Equations

Calculation of concentrations from measured intensities is based on mathematical relationships between the characteristic radiation intensity I_x of an element Z_x and its concentration C_x:

$$C_x = f(I_x) \tag{6}$$

In reality, however, the measured intensity $\tilde{I}_x$ may differ from its "true" value I_x, since it is affected by the matrix elements Z_i with concentrations C_i, so that

$$C_x = f(\hat{I}_x, C_1, C_2, C_3, \ldots, C_i, \ldots, C_n) \tag{7}$$

Instead of C_i their respective I_i are usually known. For this reason the above equation contains measured values of $\tilde{I}_x$, $\tilde{I}_i$, and the coefficients of influence of Z_i on I_x, i.e., A_{xi}, B_{xi}, D_{xi}, etc.

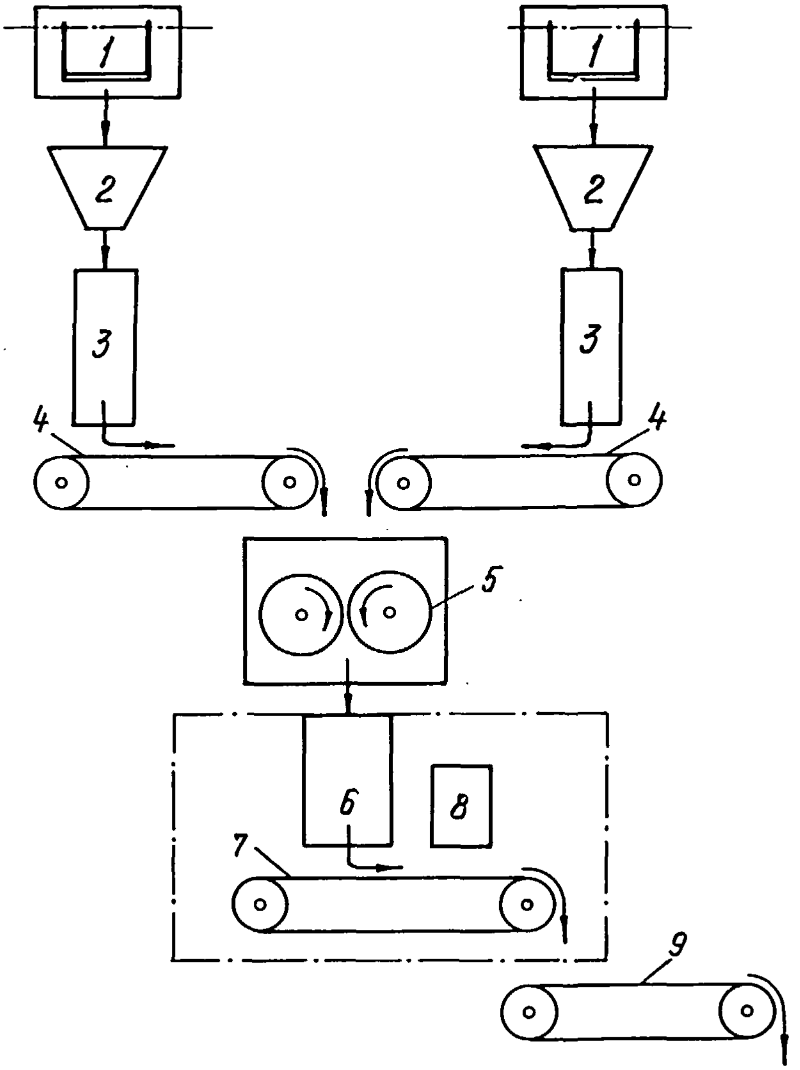

FIGURE 6. Schematic view of an automatic sample preparation arrangement for samples of moving materials in ore processing. (1) Sampling arrangement; (2) charge hopper; (3) leak pipe; (4) feeding belt conveyor; (5) roll crusher; (6) bin (7) belt conveyor; (8) X-ray analyzer; (9) belt conveyor for carrying the material being analyzed to the charge hopper. (From Kochmola, N. M. and Nikolsky, A. P., *Zavodskaya Lab.*, 44, 163 (1978). With permission.)

Finding a proper form of Equation 7 and its coefficients is one of the major problems in today's X-ray analysis. There are two basic approaches to the problem: (1) regression approach and (2) fundamental parameters approach.

The first approach makes use of experimental coefficients obtained by measuring the intensities I_x, I_i on a large number of samples of known composition. The equation of this approach has the form:

$$C_x = A_x + \sum B_{xi} I_i + I_x \sum D_{xi} I_i + \ldots \quad (8)$$

The coefficient B_{xi} accounts for the overlapping of the spectral lines of the sample elements; D_{xi} accounts for the inter-element interactions. For practical ends, the following simplified form of Equation 8 may be useful:

$$C_x = A_x + B_{xx} I_x \qquad (9)$$

For the X-ray analysis of iron ores, Equation 9 was inferred from 127 samples selected from routine samples over a lapse of 1 month. The resultant equation assured a high analysis accuracy in calcium oxide determination in concentrations of from 1.5 to 5.5% by mass.[155]

The chief advantage of the regression approach is its versatility, since it is essentially the same for any materials, any elements, and any concentrations. Its drawback is that it requires a large number of standards. When it is necessary to account for the interelement interactions between a large number of elements, say, 10 or 15, the number of standards required rises to 50 which becomes impractical. This approach is also impractical and insufficiently flexible in cases where element concentrations may vary in broad limits.

The second (fundamental parameters) approach relies upon a theoretical treatment of the effect coefficients, which means using a number of physical characteristics for each element, such as absorption coefficients, fluorescence yields, spectral distribution of exciting radiation, etc. The key advantage of this approach resides in relaxed requirements to the reference samples. One reference sample per one element is enough for a sample of unknown composition. In an analysis of multicomponent materials the number of reference samples may be even less than the number of components. A fundamental parameters method needing neither standards nor pure elements has been developed for application to energy dispersive analysis of alloys containing elements with atomic numbers above 20.[156]

The chief drawback of the fundamental parameters approach resides in the uncertain parameter values, especially of the absorption coefficients.

There are many simplified or combined varieties of the two mainline approaches mentioned above, each of which is conventionally referred to by its author's name and is used in the X-ray analysis of metallurgical materials: Lucas Tooth, Beatty-Brissey,[125] Lachance-Traill,[157] Shiraiva-Fujino,[50] Rasberry-Heinrich,[158] Criss-Birks,[159] and others.[10] A detailed description of all these modifications would be beyond the scope of this review; moreover, it has been published.[160] The analytical potentials afforded by the two mainline approaches in the iron and steel industry have been compared by some authors.[88,161]

Quite a lot of mathematical programs have been elaborated for a broad variety of analytes and elements to be determined. First, a large computer is used to calculate the coefficients of the above equations either from the fundamental parameters or from experimental results. Time of these preliminary calculations is not limited and may last up to an hour. Then these coefficients are substituted into the concentration algorithm in a small on-line computer. The time of this final calculation is part of the total analysis duration and should therefore be limited to within a few seconds, which, however, is not hard to achieve in practice. Various languages — ALGOL, FORTRAN, and machine codes — have been used to write the programs.

Application of either pure mainline (regression and fundamental parameters) approaches or their blends or modifications to the concentration calculations in both wavelength and energy dispersive analyses has now become very sophisticated and has been adapted to cover a very broad variety of ferrous materials, particularly low and high alloy steels and ores.[10,50,63,67,69,72,84,85,89,146,156,159,162-170,172,176]

Matrix corrections performed by means of computers reduce the analytical error by a factor of about 5.[10,50,69]

B. Reference Techniques

External and internal reference techniques have become a common feature of the X-ray analysis of ferrous materials. Some analyses are, however, performed with the use of background references.

The external reference technique uses a special reference sample whose analytical signal is measured either concurrently or alternately with that from the analyzed sample. In the internal reference technique the reference sample is introduced into the unknown sample; in the background reference method, the background intensity is used for reference.

The external reference method is the major one in analyses of metal samples,[1,22,34,35,72,73,100,173] ore, and sinter.[33,39,113]

The external reference may be installed in the spectrometer and analyzed concurrently with the unknown sample if there are provisions for this in the spectrometer design. If there are not, the reference sample is inserted periodically, once per a series of unknown samples.[22,34] The radiating surface of reference samples has to be periodically refreshed, which is particularly important in case of electron beam excitation.[22]

The internal reference technique is most often used in analysis of powder samples, for in this case it is easy to introduce the internal reference into the sample. Examples are reported in ore,[123,133,135,148,174-176,180] iron scale,[147] and slags.[112,175,178,179]

The internal reference technique may be used in application to metal samples, too, provided the latter are first dissolved or melted.[46] As a reference, use can be made of one element of the analysis sample whose concentration is known.[181] CoO_3 is most often used as a reference for iron ores.

The background reference technique has been applied to iron ore.[133,182] The reference in this case was the inelastic scattered radiation in the RhKα line from an X-ray tube with an anode made of rhodium.[133]

C. Calibration Samples

As already noted in Section I.C., analytical curve has to be plotted prior to the analysis proper for the reason that the X-ray method is a relative method. This stage of the analytical process is salient for it largely determines the total analytical error. In Japan, calibration and related aspects of the X-ray analysis form a special program of work of the Fluorescent X-ray Analysis Subcommittee.[1]

To carry out calibration, i.e., to find the relationship between the characteristic radiation intensity and elemental concentration, samples of appropriate composition are needed as calibration standards. Sample standardization is usually performed through chemical analysis. The type, structure, shape, and sometimes properties of standards (e.g., electric conductivity, when the excitation is done by charged particles) must be the same or at least close to those of unknown samples to be analyzed. The required number of standards is determined by the equation used for concentration calculations, and the manner of usage of the standards is determined by the adopted reference technique.

The most authoritative standards are those certified by a special federal body, such as National Bureau of Standards, U.S.A., or Institute of Standard Samples, U.S.S.R. Standards prepared and certified by these bodies, as well as British Standard Samples, B.C.S.,[9] and the like, are those most extensively used in the iron and steel industry. Commercial standards are not, however, always ready at hand for any current problem. This circumstance stipulates development of other ways of preparing standards or reference samples.

The fundamental parameters method may use pure elements as standards; pure elements may be used as standards in other cases as well.[24] In the regression method the process samples analyzed in a routine way may be used sometimes, although the metrological quality provided by such calibration technique cannot, of course, be high.[30,34]

When the suitable commercial reference samples are not available the usual practice is to prepare synthetic standards.[157,183,184] Below there are examples of the preparation of standards for X-ray analysis of metals, powders, and for surface analysis.

A simple laboratory method for the preparation of a set of metal standards has been developed and reported.[157] The method is a variant of the standard additions method: one standard is prepared having a typical composition; other samples are prepared by adding to the typical composition one or more elements to be analyzed.

A fast procedure for preparing synthetic standards having a broad range of compositions has been worked out for application to analysis of the oxide materials of ferrous metallurgy (iron and manganese ores, refractories, sinter, etc.).[183] Six standard mixtures comprised of 18 elements form the basis of the synthetic standard system. They are used in conjunction with appropriate prefused oxides as matrix additions and with a prefused trace element mixture. Calibration standards are then routinely prepared by taking fixed amounts of each of these components. The mixtures are then fused together to produce beads. The beads are then milled and the powders pressed.

For preparing standard samples for surface analysis a certain quantity of the standard solution of the element to be determined is placed on a cold-rolled steel sheet inside the area irradiated by X-rays and the dried. The standard solutions for the purpose are prepared in advance.[184]

D. Combination of Ferrous Materials into Groups

The types, grades, and varieties of ferrous materials are many. The number of steel and alloy grades alone is perhaps on the order of 2000. It is natural, therefore, to attempt to combine ferrous materials into groups such that the analytical procedure, the standards and concentration calculation programs inclusive, were common for all the materials within one group. In works published to date the size and composition of the groups have been widely different: some iron ore types;[166] all iron ore types;[135] ore and sinter;[146] ores of various metals, iron ore, and ore processing materials inclusive;[185] carbon and chromium-containing steels;[185] ironmaking and steelmaking slags;[142] and all varieties of ferrous materials (grouped on the fundamental parameters method basis).[145]

In one reference source,[1] all ferrous materials are grouped as follows: (1) stainless steels; (2) cast and pig iron, carbon, and low-alloy steels; and (3) heat-resisting superalloys.

A unified procedure has been developed for determination of sulfur in various ores, including iron ore, in a broad range of concentrations (1 to 60%); this procedure is too lengthy, however, taking as much as 75 to 80 min per sample.[185]

V. APPLICATIONS

A. General

The ferrous materials analyzable by the X-ray techniques are listed, together with the corresponding references, in Table 8. Figure 7 graphically illustrates the proportions of papers devoted to each of the listed varieties of ferrous materials out of all considered in the present review.

Table 9 lists the elements detectable by X-ray analysis in ferrous materials and the pertinent references. Figure 8 is a graphical illustration of the relative number of works reporting on determination of a particular element. Iron is the element most often analyzed in ferrous materials, which is quite natural indeed. Other frequent analytes include aluminum, phosphorus, sulfur, calcium, the 3d-elements, niobium, and tungsten.

Table 8
FERROUS MATERIALS ANALYZED BY THE X-RAY METHOD

Material	Ref.
Ore processing materials (ore, sinter, sinter feed charge, blast furnace burden, etc.)	10, 13, 33, 37, 39, 40, 51, 56, 58, 71, 80, 82, 113, 121, 123, 125, 128, 133, 135, 140, 144, 146, 148, 149, 154, 155, 170, 174, 175, 176, 180, 182, 185, 187, 188, 189, 190, 191, 192, 193, 195, 221, 222
Iron	10, 33, 54, 62, 71, 86, 90, 93, 95, 109, 128, 196, 197
Steels and alloys based on iron and nickel (including pipes, sheet, ingot)	1, 10, 12, 22, 24, 30, 32, 34, 35, 36, 42, 43, 44, 45, 46, 47, 48, 49, 50, 52, 54, 55, 57, 59, 60, 61, 63, 64, 67, 69, 71, 73, 74, 76, 77, 81, 86, 88, 90, 91, 94, 100, 101, 103, 105, 107, 109, 110, 156, 158, 159, 162, 163 164, 165, 166, 167, 168, 181, 186, 195, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 210, 211, 212, 214
Slags of all kinds, including iron scale and pipe rolling slag	10, 12, 26, 29, 51, 57, 66, 71, 73, 80, 82, 84, 111, 112, 121, 126, 127, 128, 131, 133, 138, 139, 175, 178, 179, 195, 215
Ferroalloys	2, 14, 97, 107, 116, 117, 129, 136, 150, 151, 152, 169, 172, 186, 209
Coating on steel sheet, surface sticking materials	55, 171, 184, 195, 223
Refractory materials, lime clinker, cement	9, 10, 37, 68, 82, 219
Ferrits	68, 114, 119, 125, 153, 177

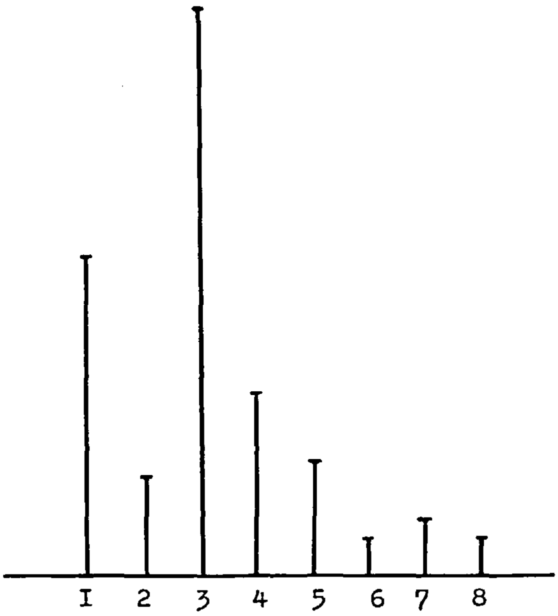

FIGURE 7. Distribution of published papers between different ferrous materials analyzed by the X-ray method. (1) Ore processing materials (iron ore, sinter, sinter charge, blast furnace burden, etc.); (2) iron; (3) iron- and nickel-base steels and alloys (in the form of pipes, sheets, ingots); (4) slags of all kinds, including iron scale and pipe rolling slag; (5) ferroalloys; (6) steel sheet coatings, surface contaminants; (7) refractories, lime, clinker, cement; (8) ferrites.

Table 9

ELEMENTS, DETERMINED IN FERROUS MATERIALS BY THE X-RAY METHOD

No.	Z_x and element	Ref.
1	5 B	209, 210
2	6 C	49, 199
3	9 F	10, 29
4	11 Na	10, 184
5	12 Mg	9, 10, 80, 128, 146, 184, 209
6	13 Al	9, 10, 22, 25, 28, 39, 46, 71, 80, 101, 121, 122, 128, 146, 159, 195, 199, 202, 204, 215
7	14 Si	9, 10, 14, 33, 39, 46, 76, 80, 93, 95, 101, 112, 121, 122, 126, 128, 129, 146, 159, 162, 165, 166, 184, 195, 199, 202, 204, 209, 215
8	15 P	10, 14, 18, 25, 31, 32, 76, 80, 93, 95, 112, 126, 128, 146, 166, 184, 199
9	16 S	10, 14, 18, 31, 32, 76, 90, 93, 95, 109, 128, 166, 184, 185, 215
10	19 K	10, 128
11	20 Ca	9, 10, 33, 38, 40, 41, 80, 111, 112, 121, 122, 126, 128, 146, 149, 155, 184, 189, 191, 195, 215
12	22 Ti	10, 25, 28, 34, 35, 36, 46, 63, 72, 76, 77, 80, 100, 101, 122, 128, 150, 159, 199, 202, 205, 211
13	23 V	10, 25, 34, 36, 46, 55, 63, 72, 150, 199, 205, 209, 211, 214
14	24 Cr	1, 9, 10, 14, 24, 25, 28, 34, 55, 36, 50, 55, 60, 63, 72, 76, 77, 100, 101, 122, 156, 158, 159, 162, 166, 184, 195, 199, 205, 209, 211
15	25 Mn	10, 24, 25, 28, 33, 50, 55, 76, 77, 80, 93, 95, 100, 101, 112, 119, 128, 146, 156, 158, 159, 162, 166, 199, 205, 207, 209, 211, 214, 215
16	26 Fe	1, 8, 9, 10, 24, 25, 28, 33, 50, 51, 57, 60, 80, 101, 112, 113, 119, 121, 122, 126, 128, 133, 144, 146, 148, 153, 156, 158, 159, 162, 174, 176, 180, 182, 187, 188, 194, 195, 199, 215, 221, 222
17	27 Co	10, 14, 25, 34, 35, 36, 153, 159, 199, 202, 208, 214
18	28 Ni	1, 10, 14, 25, 28, 34, 35, 36, 50, 60, 76, 77, 100, 101, 153, 156, 158, 159, 162, 165, 166, 199, 202, 205, 207, 209, 211
19	29 Cu	10, 14, 25, 34, 36, 50, 76, 80, 101, 156, 159, 166, 174, 199, 202, 211
20	30 Zn	10, 119, 153, 195, 219
21	33 As	10, 91, 96, 97, 119, 200
22	34 Se	10
23	40 Zr	10, 30, 46, 91, 103, 199
24	41 Nb	1, 10, 30, 34, 36, 50, 91, 103, 107, 150, 159, 199, 205, 209
25	42 Mo	1, 10, 34, 35, 36, 46, 50, 55, 59, 63, 72, 76, 77, 100, 101, 107, 150, 156, 159, 162, 165, 166, 174, 195, 199, 205, 207, 209, 211, 214
26	47 Ag	200
27	50 Sn	10, 195, 199, 200, 223
28	51 Sb	10, 199, 200
29	57 La	10, 103, 105, 107, 110 (All lanthanides and rare earths included)
30	72 Hf	30, 91
31	73 Ta	91, 103, 107, 199
32	74 W	34, 35, 36, 63, 72, 76, 91, 101, 107, 150, 174, 199, 205, 214
33	82 Pb	10, 54, 195, 199, 200

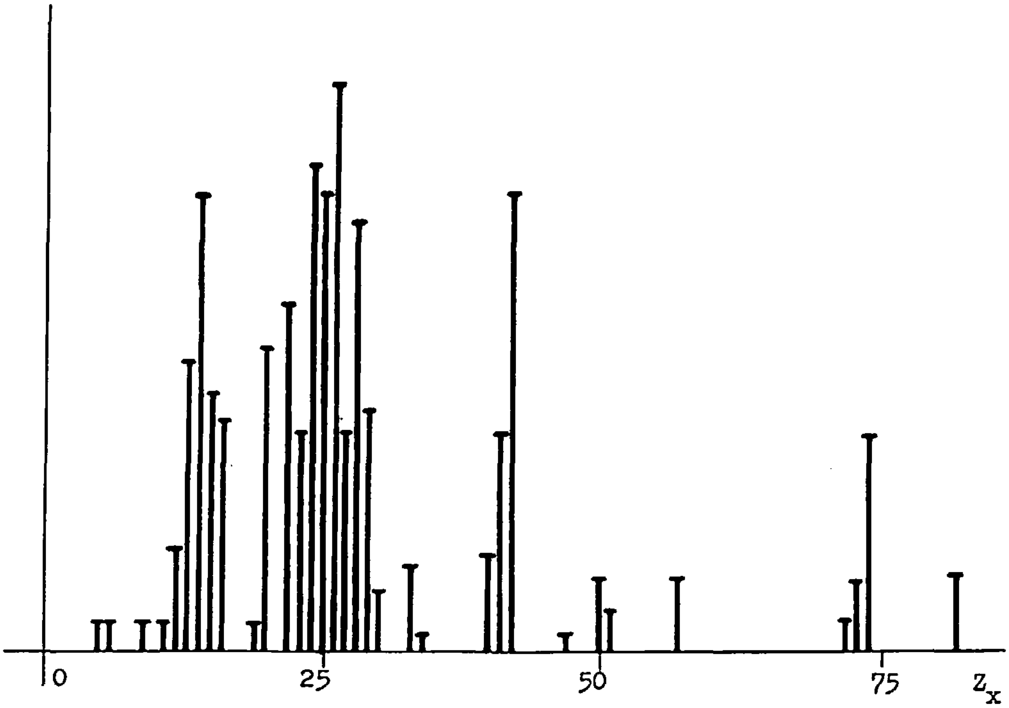

FIGURE 8. Distribution of published papers between different elements Z_x analyzed by X-ray fluorescence method in ferrous materials, Z_x = 57 covers all lanthanides and rare earths.

Table 10 presents selected data to illustrate the progress achieved so far in raising the sensitivity of X-ray fluorescence analysis of ferrous materials. As a rule, the detection sensitivities in metals (iron, steels, alloys) is two to ten times better than in other materials, such as iron ore, sinter, slags, etc.[10]

Many authors observe that the X-ray method ensures very high metrological parameters, especially in analysis of steels.[10,22,34,35,67,100,101] A few illustrative examples are given in Table 11.

The shortest time achieved so far in analysis of powder samples seems to be cited in one reference,[82] where it was about 3 min (steelmaking slag) and was comprised of 20 sec for sample transportation, 100 sec for sample preparation, and 60 sec for analysis and data output (a wavelength dispersive spectrometer was used). Analysis of metal samples takes about the same or even less time.

B. Iron Ore Processing

Iron ore has been analyzed by X-ray techniques in many instances:[37,39,40,52,113,121,133,146,170,174-176,180,187-191,194,221,222] iron concentrate,[33,195] magnetite,[114] iron ore tailing,[182] iron ore sinter feed, sinter,[10,13,33,39,56,80,82,155,175,191-193,195] pellets,[175] and flotation pulp.[188]

Low enough concentrations of light elements have been determined in iron ore: MgO — 0.09%, Al_2O_3 — 0.4%, P — 0.02%, etc.[80]

If analysis is made periodically, sampling is done from portions of the material being analyzed; weight of each portion may amount to thousands of tonnes, e.g., 2000 t.[82]

In analyses of ore processing materials it is very convenient to use radioisotopic excitation of the X-ray spectra, since radioisotopic sources are extremely stable and need no power supply or maintenance; they may be easily placed for on-line control. Radioisotopic excitation sources have been widely practiced in the X-ray fluorescence analysis of iron ore processing materials.[174,180,182,187-189,195,221,222]

Table 10
SENSITIVITIES OF ROUTINE X-RAY ANALYSIS IN THE IRON AND STEEL INDUSTRY (LOWER LIMIT OF DETECTION LLD, 2σ)

Element Z_x	Matrix	Excitation	C_{min} (%)	Ref.
6 C	Carbon steel	e	0.022	49
9 F	Blast furnace slag	X	0.20	10
11 Na[a]	Blast furnace slag	X	0.027	10
15 P	Cast iron	X	0.00044	10
24 Cr	Cast iron, low alloy steel	X	0.0007	10
33 As	Iron, steel, alloys	X	0.003[b]	96
42 Mo	Cast iron, low alloy steel	X	0.0007	10
82 Pb	Low alloy steel	X	0.008	10

Note: e = Electron beam excitation; X = X-ray excitation.

[a] Oxide is determined.
[b] No exact definition of term "sensitivity" is given.

Table 11
PRECISION AND ACCURACY OF THE X-RAY ANALYSIS IN THE IRON AND STEEL INDUSTRY

Element Z_x	Concentration (%)	Matrix	Excitation	S_1	S_2	Ref.
6 C	1.0	Steel	e	—	0.0535	49
9 F	1.05	Slag	X[a]	0.08	0.03	29
11 Na	0—0.5	Slag	X	—	0.04	10
13 Al	3.9	Steel	e	—	0.016	22
15 P	0—0.1	Steel	X	—	0.002	10, 32
22 Ti	1.5—1.9	Steel	X	0.001	—	34
26 Fe	65—75[b]	Ferrite	X	0.047	—	119
42 Mo	3.0	Steel	X	0.0032	—	82
74 W	0.005	Steel	X	0.000025[c]	—	91
82 Pb	0.05	Steel	X	0.0015	—	200

Note: S_1 = Standard deviation of reproducibility; S_2 = Standard deviation between X-ray concentration values and standard specified values.

[a] A windowless X-ray tube; only X-radiation is used.
[b] The concentration range for oxide Fe_2O_3.
[c] The X-ray method was combined with chemical technique.

The ever growing need for automation in iron ore processing requires continuous measurement of material compositions, and much has already been done in that direction. An important dilemma facing an X-ray researcher is to choose between the wavelength and energy dispersive method for application to continuous X-ray analysis of ore processing materials.[194] A special study of the topic has shown that in the X-ray analysis of iron ore mixtures having a grain size of up to 2.5 mm, the energy dispersive

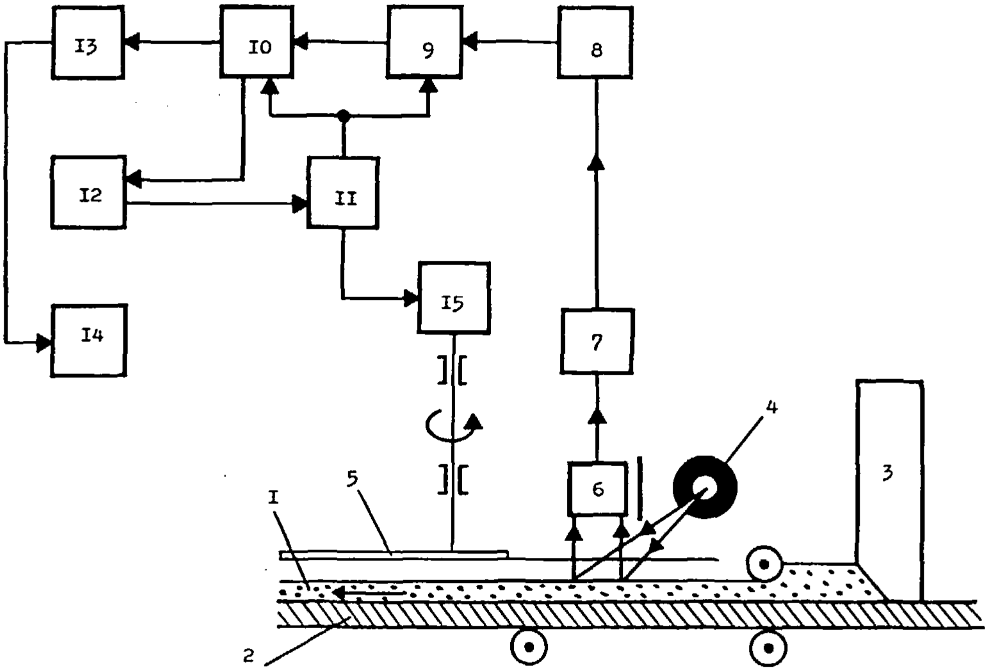

FIGURE 9. X-ray analyzer for continuous determination of calcium oxide in an iron ore stream. (1) Iron ore; (2) conveyor belt; (3) hopper; (4) radioisotope source; (5) rotatable plate with reference sample; (6) X-ray detector; (7) preamplifier; (8) amplifier; (9) pulse height analyzer tuned in to the characteristic radiation of calcium; (10) analytical signal selector; (11) control unit; (12) ratemeter for the reference sample; (13) ratemeter for the analyte; (14) data output; (15) reference sample rotating mechanism.

method can provide precision no worse, and perhaps even better, than the wavelength dispersive method. The reason for this is that the averaging in the energy dispersive analysis involves larger sample surface areas than in the other method.

A block diagram of a continuous X-ray analyzer for measuring calcium concentrations in iron ore is shown in Figure 9.[40] The characteristic radiation excited in ore is registered by an X-ray detector 6 and the electric pulses furnished by the detecter are, after amplification by amplifiers 7 and 8, fed to a pulse height analyzer 9 which separates the pulses generated by calcium from the background. An analytical signal selector 10 sends pulses either to a counter 12 or to a counter 13, depending on the position of the rotatable plate 5. When the plate with reference sample is in the position where it is irradiated by a source 4, the pulses are sent to the counter 12; when on the other hand the plate is out of the irradiated locus, the pulses are sent to counter 13 and then printed out or displayed in the form of a curve in unit 14. For synchronization, selector 10 is coupled, via a control unit 11, to a device 15 for rotating the reference sample plate.

Continuous on-line analysis systems of similar design have been developed and put into operation at other ore processing plants.[13,41,56,195]

C. Blast Furnace Process

In the blast furnace process the X-ray method is used to analyze blast furnace burden,[128,154] iron,[10,33,54,62,128,196,197] and slag.[33,73,121,127,128,195]

The daily analytical routine on a 5000-t blast furnace includes 21 iron ore analyses, 24 sinter analyses, 12 slag analyses, 6 coke analyses, 12 cast iron analyses, and lime analyses on demand. The compounds and elements analyzed include MgO, Al_2O_3, SiO_2, P, S, K, CaO, TiO_2, Mn, and Fe.[128] X-ray fluorescence analysis is viewed as the basic method of assaying both pig and cast iron. It is used to determine rather low concentrations of Si (0.3%), P (0.01%), S (0.01%), and Ce (0.01%.)[196,197]

D. Steelmaking Process

Steelmaking processes, especially electric furnace process, present the widest field of application of the X-ray analysis in the iron and steel industry. Various steel and alloy grades have been analyzed,[12,22,24,30,32,34,35,42-45,47-49,55,67,74,91,96,100,101,156,158,195,198-208] as well as slags.[10,57,66,82,111,112,126,131,139,195]

Metal is analyzed both after tapping and in the melting process. The kinds of materials analyzed, elements determined, metrological parameters, and sensitivities achieved are presented in Tables 8, 9, 10, and 11.

Typically, the analysis time is about 10 min, which includes 2 to 5 min for molten metal sample cooling, 1 min for transportation, 0.5 min for preparation.[205]

Some of the relevant publications deal with a rather special application of the X-ray method to boron determinations in steel,[209,210] the detection sensitivity for boron there being evaluated to be in the p.p.m. level;[210] to determination of carbon in martensitic steel,[198] in carbon steel;[49] to determination of rare earth traces (0.0001 to 0.0025%) in steel with a high accuracy (S_r = 0.0036 to 0.0018);[105] determination of lanthanide traces (~0.002%) in steel;[103] determination of trace elements (0.01 to 0.00001%) in steel using a microanalyzer;[47] to analysis of grain surface composition in stainless and refractory steels;[181] to analysis of nonmetallic occlusions in magnetic alloys.[202]

It has been found that steel structure influences the results of X-ray analysis. The analysis results obtained for ferritic and austenitic steels were found to be somewhat different.[82] The slopes of analytical curves for high-speed steel, annealed and tempered, were 5 to 10% different.[201] In a special study it was found that the X-ray analysis results were the same for ingot and forged steel.[101] Theoretical investigation of the structure effects has led to some formulas for its evaluation.[206] According to some observations, there is no microstructure effect in refractory and stainless steels.[211] When carbon in steel is determined, a specific difficulty arises due to sample surface contamination by the oil vapor combustion products under the action of the electron beam. Special intricate techniques have been resorted to overcome the difficulty.[49]

The possibility of using a Si(Li) energy dispersive spectrometer to steel grades NBS 845 to 850, 1161 to 1168 has been investigated. It was found that determination of Nb and Mo concentrations at 0.01% level with an error of about 10% relativity required 10 min.[1] A method of interpreting the energy dispersive spectra of iron-base alloys has been suggested.[212]

Aimed excitation has been used in not very complex energy dispersive analytical work. For example, chromium, manganese, nickel, and molybdenum have been determined in stainless steels by this method.[207]

Attempts have been made to effect continuous monitoring of molten metal which may prove an important step toward automation of the steelmaking process.[42-46,213] Most of these have been related with electron-beam remelting, in which part of the electron beam energy is converted to the characteristic X-ray radiation of the molten metal, thus eliminating the need for a special excitation source.[42-46] Other attempts in this direction involved insertion into the furnace of an X-ray tube as spectrum excitation source and a water-cooled spectrometric system. The gap between the X-ray tube and molten metal surface was about 65 mm.[213]

Figure 10 shows schematically an experimental setup for continuous X-ray fluorescence analysis of molten metal in the bath of an industrial electron-beam furnace without an extra excitation source,[44,45] which appears to us to be a more elaborated trend

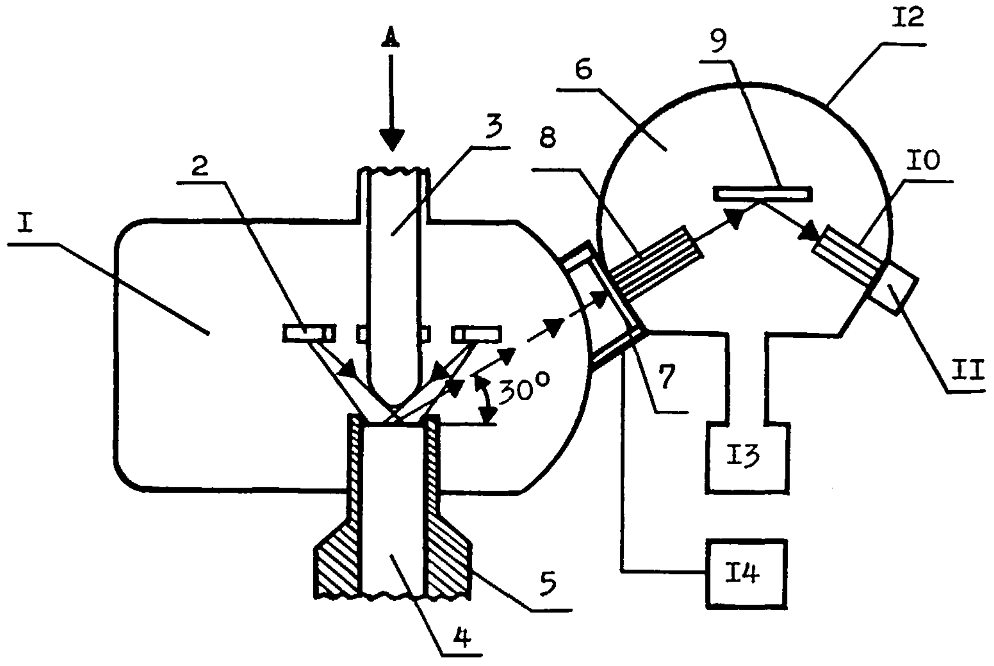

FIGURE 10. Schematic view of an experimental arrangement for continuous analysis of molten metal in an industrial electric beam furnace bath (domestic, type U-254). (1) Furnace body; (2) electron guns (a total of ten guns are equally spaced along circumference); (3) metal ingot prior to melting; (4) molten metal; (5) mold; (6) means for adjusting the spectrometer on the radiating spot; (7) beryllium partition; (8) Soller primary collimator; (9) crystal-analyzer; (10) Soller secondary collimator; (11) X-ray detector; (12) spectrometer housing; (13) vacuum pump; (14) water cooling system. (From Nikolsky, A. P., Shilman, V. H., Topilin, V. V., Pokrovsky, A. A., Vershinin, A. S., and Duimakaev, S. I., *Appar. Metody Rentgenovskogo Anal.*, 15, 20 (1974). With permission.)

than X-ray tube. A 17.0 keV and 33.0 A electron beam emitted by electron guns 2 melts a metal rod 3 and simultaneously excites the X-radiation in molten metal 4 held in a 380-mm diameter mold 5. Part of this radiation passes through a beryllium partition 6, 0.1 to 0.2 mm thick, to reach an X-ray spectrometer of special design. Radiation path length is about 2 m. The spectrometer body is evacuated by means of a vacuum pump. The spectrometer can be focused on any radiating portion of the molten metal surface with the aid of a special water-cooled device. During the melting process, molten metal falls in drops into a water-cooled mold where it gradually solidifies. The metal is drawn from the mold either continuously or cyclically with the molten metal surface level either remaining constant throughout or cyclically changing within certain limits. The time history curve of the characteristic radiation intensity supplies important information about the metal composition along the ingot extracted from mold. This method, for example, has allowed to detect nickel content variations in the range of from 18.86 to 19.07% by mass over an ingot length of about 2.5 m.[44]

In another continuous analysis arrangement for analyzing molten metal in the bath of an electron beam furnace X-radiation enters the spectrometer via a 0.1-mm round hole. To protect the spectrometer components from deposition of molten metal vapors, a weak argon stream from spectrometer to furnace is induced.[42,43,46]

E. Production of Ferroalloys

X-ray fluorescence analysis has been used for analyzing all kinds of ferroalloys and for all of their main components (iron, silicon, tungsten, etc.).[2,107,116,117,136,151,152,169,172,186] The peculiarity of ferroalloy analysis resides, in particular, in the sample preparation procedure which has been discussed in detail in Section III.D. of this review.

F. Manufacture of Finished Ferrous Metal Products

The importance of the X-ray method in the analytical control in this branch of ferrous metallurgy has been steadily growing over the past decade, although the nature of its utilization in this branch is somewhat different from that in the other branches of the industry.

Many kinds of finished products are analyzed or measured: pipe rolling slag,[112] scale,[138] pipes and sheets,[52,54,57] coat thickness,[55,171,195,223] surface quality,[184] and ingot identification.[214]

While the X-ray analysis of pipe rolling slag, scale, pipes, and sheets is carried out in the same manner as of powder and metal samples, surface analysis and coating thickness measurements are performed somewhat differently.

Most common metals used for coating steel sheets are zinc and tin. Their high cost makes coating thickness control essential. The third very common coating metal is aluminum.

Coating thickness is monitored by measuring the characteristic X-radiation intensity either of the coating proper or of the substrate. In the former case the following equation is used:

$$I = I_\infty [1 - \exp(-\mu l)] \qquad (10)$$

where l is coating thickness, I is measured intensity, I_∞ is characteristic radiation intensity from the coating material under assumption of an infinitely thick coating ($l \rightarrow \infty$).

In the second case the equation is

$$I = I_0 \exp(-\mu l) \qquad (11)$$

where I_0 is the characteristic radiation intensity of the substrate (usually iron) when there is no coating.

The X-ray analysis is particularly useful and accurate where the atomic numbers of the coating and substrate metals are not greatly different (chromium, nickel on iron, and the like).

In the branch of application of X-ray analysis in question it is the energy dispersive technique which is most important, more important in fact than in any other field of ferrous metallurgy. All work in this branch has used the energy dispersive method. The reason lies in the advantages of the energy dispersive apparatus discussed in Section V.B which renders this kind of apparatus especially suited for solving such problems as, for example, analysis of the interior sides of walls of long (to 2.5 m) and small diameter (about 6.35 cm) pipes.[54]

Another group of problems for which the advantages of the energy dispersive systems seem to be most essential is ingot identification in storage, where portable X-ray apparatus is perhaps the only possible way of doing it.[54,214]

The purpose of surface analysis is to determine the amount of contaminants on the steel sheet surface, or of chemicals left on the surface after chemical treatment, or still of any materials that may have stuck to the surface. The ultimate goal of such measurements is the determination of the corrosion resistant properties of the material or monitoring the cold-rolled sheet chemical treatment process.[184]

For surface analysis there are such well-known and commendable methods as Auger electron spectroscopy and X-ray photoelectron spectroscopy. But to effect these methods a very high vacuum (about 10^{-7} torr or higher) is required, which hampers their use in routine analysis programs. The X-ray fluorescence method is quite suitable for surface analysis purposes, for it is capable of providing information about the chemical composition of a layer only a few dozen of microns in thickness. The LLD of Na, Mg, Cl, and Ca was found to lie within the range of 0.04 to 0.17 g/cm^2.[184]

G. Miscellaneous Uses

The X-ray method is used to determine elements Mg, Al, Si, Ca, Ti, Fe,[37,122] and Zn[219] in such materials as lime, clinker, cement, refractories, etc. Also, ferrite systems and films have been analyzed[68,114,119,125,153] with a conclusion that the X-ray fluorescence method yields exclusively accurate results in this case.[119] The method has allowed to establish that the compositions of the ferrite film and the ferrite from which is had been made were different.[68]

Application of X-ray analysis to research of the crystal structures of ferrous materials and the valent states of their components has proved useful. Concentrations of FeO and Fe_2O_3 could be determined separately.[8] X-ray method has allowed to obtain important information concerning the chemical bonds of elements Al, Si, S, Mn, and Fe in blast furnace and steelmaking slags, their valent states, coordination numbers, complexing reactions, etc.[215]

VI. X-RAY ANALYSIS IN PROCESS CONTROL

Availability of valid elemental analysis is vitally important for controlling many ferrous metallurgy processes. The use of X-ray instruments and analytical systems in process control has progressed markedly in the past decade. Owing to its nondestructive and noncontacting character, the X-ray method is very well suited for use in automatic control systems. Practically, the X-ray method has been employed in automatic control systems in all of the most important technological processes of the iron and steel industry.

By now a considerable number of automatic control systems have been put into operation all over the world, in which the X-ray analysis data make up an important part of the overall data traffic.[56,70,73,78,82,139,173,216] An automatic control system of a pelletizing plant incorporating an X-ray multichannel spectrometer allowed to stabilize the SiO_2 concentration within $S = 0.2\%$ and the CaO/SiO_2 ratio within $S = 0.05\%$. Control of the sintering process with the aid of an X-ray energy dispersive apparatus also allowed to improve the compositional stability of sintering mix and yielded some new data concerning the correlation between sinter mix/sinter compositions.[193]

In the basic oxygen process the results of the X-ray analysis of metal and slag are used to control the oxygen lance position, calculate the required amounts of alloying additions,[78,205] adjust the basicity of slag and raw materials, select ladle additions,[10] control the blow conditions, and calculate the amounts of additions.[173] The results of the X-ray analysis of the sinter feed contained in charge hoppers have been used for controlling the sinter feed rate to maintain the scheduled sinter composition.[38] Thickness measurements by X-ray apparatus have been used to control the coating process.[171,213]

VII. ORGANIZATION OF X-RAY ANALYSIS

Two forms of X-ray analytical control organization prevail in the iron and steel industry: (1) centralized X-ray analytical control and (2) local X-ray analytical control.

In the organizational form of the first type, the X-ray apparatus, either alone or in conjunction with other analytical instruments, are set up in a central laboratory and used to serve the needs of a group of workshops, a whole plant, or even a group of plants.[7,22,34,35,71,84-86,101]

Samples taken from a furnace, a sintering machine, etc. are transported via pneumatic or vacuum transportation systems to the central laboratory. Apart from the minicomputers built into most of the analytical instruments, the central laboratory is usually equipped with one or more large computers to process the data furnished by the analytical instruments and dispatch the control signals to the pertinent addresses.

In the organizational form of the second type the X-ray spectrometers belong to one furnace, machine, or process: blast furnace,[217] electron beam furnace,[46] sintering machine,[40,41] steelmaking converter,[10,173] and coating process.[171]

In all these cases the X-ray apparatus are interfaced to a relatively small computer, the further information processing being done, where necessary, at another place.

VIII. ECONOMICS

The advent of the X-ray fluorescence analysis into ferrous metallurgy processes has in many respects had a great impact on the analytical control as well as on metallurgical technology per se.[6,10,21,34,71,112,171,187,195]

Figure 11 illustrates the development of the analytical control in iron and steel industry over the last decade.[6] Beginning from 1969 onwards the share of X-ray techniques in the overall analytical work has been steadily growing and by now is about 15% of the total. Mean analysis time per one element has been reduced 15 times.[34] This has allowed to shorten the steelmaking process by several minutes as well as to improve conformity of the finished product to specification, which in both cases meant improved economics.

According to the averaged data in the nonferrous metallurgy of the German Democratic Republic, the cost and duration of X-ray analysis per one element is about 4.5 and 5.5 times smaller than the respective figures attainable by the chemical methods.[21] In ferrous metallurgy the indices, we expect, are of the same order.

The use of X-ray fluorescence analysis of slag at steelmaking and pipe rolling mills of Great Britain has allowed to reduce the number of staff engaged in the analytical work by about 25%.[112] The use of X-ray spectrometers in the on-line coating thickness measurements saves tin and zinc on the order of several percent based on the total consumption.[195] Tin economy may be as high as 5% which means an extra $30,000 saved monthly in a country like Austria.[171]

IX. CONCLUSIONS

- The importance of the X-ray fluorescence method in the analytical control of ferrous metallurgy processes has been steadily growing during the past decade and by now accounts for nearly 15% of the total amount of analytical work. Approximately 35 elements are being determined by this technique, of which Mg, Al, Si, P, S, Ca, Ti, V, Cr, Fe, Co, Ni, Cu, As, Zr, Nb, Mo, and W are determined most often. Elements B, C, F, Na, K, Zn, Se, Ag, Sn, Sb, La, Hf, Ta, and Pb are also determined, though not as often.

Although in the overwhelming majority of cases the metrological parameters afforded by the X-ray technique are meeting the requirements of the iron and steel industry, it should be noted that the overall analytical error is contributed to most by improper sample preparation. This component of the total error may be by about a factor of 5 greater than any other one component.

Total analytical process time is normally within 5 to 15 min per sample, sometimes less than 5 min. Despite all efforts to cut the sample preparation time, this stage of the analytical process, which includes the steps of sampling, sample transportation, and

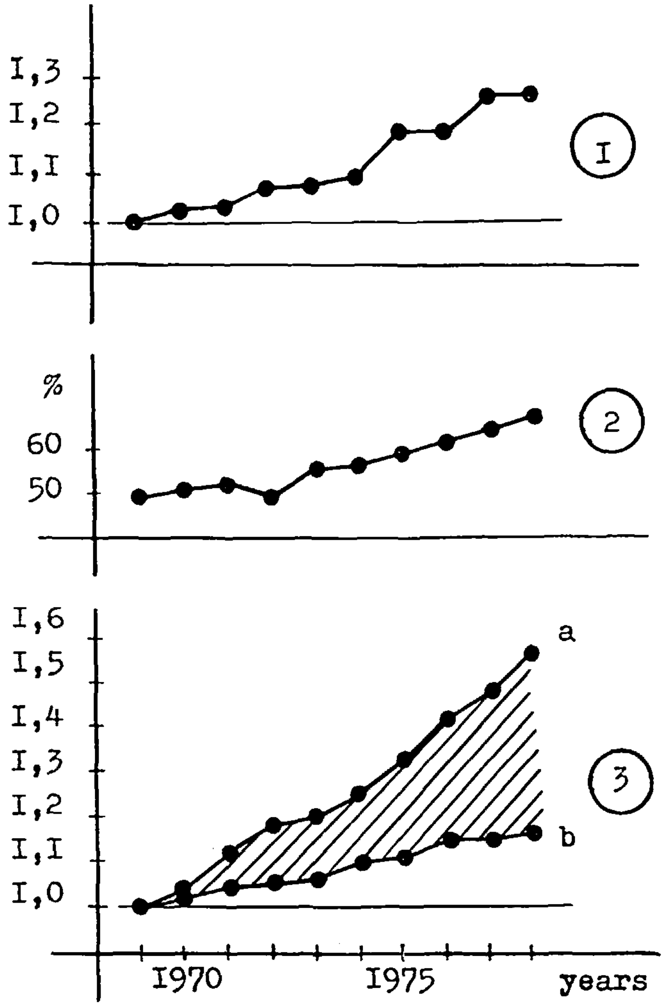

FIGURE 11. Development of analytical control of electric furnace steelmaking in the period between 1968 to 1978. (1) Number of analytical determinations per one staff member (in relative units); (2) portion of total analytical work done by spectrometric methods (in percents); (3) number of determinations carried out by the X-ray (a) and optical emission (b) methods (in relative units).

sample preparation per se, still remains the most time-consuming one, especially in case of powder samples (ore, sinter, slags, ferroalloys, refractories, etc.).

The significance of development of continuous sampling methods must be stressed in conclusion, especially as regards X-ray analysis of molten metal.

- Many commercial X-ray spectrometer models are used. An increase in the relative share of multichannel and energy dispersive apparatus, especially those with semiconductor detectors, has been notable.

A considerable amount of special-purpose instruments coupled with a particular furnace, machine, or process have been in use.

One of the strongest trends in the development of X-ray spectrometry in the iron and steel industry is, at present, the use of computers for data processing and process control purposes, which is inseparable from the tendency for a systems approach to analytical problems.

Although the characteristic X-ray intensities attainable now do not constitute the limiting factor either for analysis speed or metrological parameters, increasing the analytical signal level and the signal/noise ratio is a problem still as urgent as it was before. For this reason there has been a constant search for improved spectrum excitation conditions.

- X-ray spectrometry has been applied to all but few materials analyzable in ferrous metallurgy and to most of its processes: ore processing, blast furnace process, steelmaking processes, finished products, rolled products, auxiliary processes. The scope of materials analyzed covers ores, sinter, iron, steel, alloys, slags, pipes, sheets, ingots, lime, refractories, ferroalloys, ferrites, coatings, etc. These materials are analyzed for certification and marking purposes, as well as for controlling the process. The X-ray fluorescence method has been successfully used in continuous automatic analysis of ore processing materials, the molten metal in an electron beam furnace bath without any sampling, rolled products (steel strip coating thickness and composition). By employing X-ray analysis it is possible to obtain considerable time and money savings.
- As regards the future development of the X-ray fluorescence method in its applications in ferrous metallurgy, the reviewer has been able to discern the following trends that have outlined themselves by now:

1. Expansion of the range of analytical problems solved by the X-ray fluorescence method in general, in particular, the determination of the "3d" elements (Mn, Fe, etc.) present in various valent and/or ligand states, or continuous analysis of molten metal
2. Expansion of the range of analytical problems that can be tackled by the energy dispersive systems in particular, especially by those incorporating semiconductor detectors
3. Further elaboration of the sampling and sample preparation procedures with a view to cut the time consumed by these steps of the analytical process and thus perfect them to the level achieved presently in the other stages, as for example, in the spectral intensity measurements and data processing
4. Standardization of sample preparation with a view to reduce its contribution to the analytical error
5. Integration of the available X-ray instrumentation and analytical systems into close-loop automatic control systems

X. SYMBOLS AND ABBREVIATIONS

I — X-ray intensity, counts per second
C — Concentration, percent by weight
S — Standard deviation
S_r — Relative standard deviation (r.s.d.)
E_o — Energy of exciting particles, keV
λ — wavelength, Å
Z — Atomic number of element
φ — Incident beam angle
ψ — Take-off angle
N — Number of counts integrated over a lapse of time, counts
ω — Fluorescence yield
S_q — Absorption jump ratio for q-series
μ — Absorption coefficient
C_{min} — Detection sensitivity, % by weight or ppm
r.m.s. — Root mean square deviation

$\tilde{I}$ — Measured value of "true" intensity I
A_{xi}, B_{xi}, D_{xi} — Coefficients of element Z_i effect on the intensity I_x of an element Z_x
C_H — Moisture concentration in powder materials
l — Coating thickness
d — Particle size
Δ — The sample layer thickness giving the bulk contribution to analytical signal
LLD — Lower limit of detection

REFERENCES

1. **Sato, H.,** *Trans. Iron Steel Inst. Jpn.,* 17, 551 (1977).
2. **Shanagan, C. E. A.,** *Determination of Chemical Composition: Its Application to Process Control,* Iron and Steel Institute, London, 1971, 3.
3. **Lucas-Tooth, J.,** *Rev. Univers. Mines Metall. Mec.,* 17, 180 (1961).
4. **Kopineck, H. J.,** *Rev. Univers. Mines Metall. Mec.,* 17, 214 (1961).
5. **Bruch, J. and Wutshel, A.,** *Arch. Eisenhüttenwesen,* 41, 433 (1970).
6. **Nikolsky, A. P., Zabavnikov, V. A., Fedotkin, K. Y., Chekhov, B. T., and Korolev, E. F.,** *Zavodskaya Lab.,* 45, (1979).
7. **Folfasinski, M. and Feret, F.,** *Przeglad Nowosci Hutnictwe Zelaza,* 3, 98 (1975).
8. **Namdar-Irani, R.,** Essais d'identification des Oxydes de fer ay Moyen du Microanalyseur á Sonde Ionique, Rapport IRSID P305, Mai 1977, 1461.
9. **Banerjee, S. and Olsen, B. G.,** *Appl. Spectrosc.,* 32, 576 (1978).
10. **Sherker, T. O. and Rose, R. N.,** *Sci. Ind.,* 13, 32 (1979).
11. **Nikoslky, A. P.,** *Zavodskaya Lab.,* 43, 1206 (1977).
12. **Van der Berge, H.,** Iron Steel Int., 51, 249 (1978).
13. **Görtz, W.,** *Z. Erzbergbau Metall.,* 21, 160 (1968).
14. **Aleksandruk, T. D., Khlopina, T. N., and Shwartz, D. M.,** *Zavodskaya Lab.,* 44, 167 (1978).
15. **Jenkins, R.,** The Comparison of Wavelength Dispersive and Energy Dispersive X-ray Fluorescence Analysis, Proc. 20th Colloq. Spectrosc. Int. and 7th Int. Conf. At. Spectrosc., Praha, 1977, invited lecture, 1, 219.
16. **Höpfner, G.,** *Lab. — Prax.,* 17, 214 (1961).
17. **Höpfner, G.,** *Electr. Ausrüstung Ind. Elektron. Autom.,* 9, 20 (1968).
18. **Höller, P.,** *Determination of Chemical Composition: Its Application to Process Control,* Iron and Steel Institute, London, 1971, 52.
19. **Backerud, L.,** *X-ray Spectrom.,* 1, 3 (1972).
20. **Stadnikov, A. G. and Nikolsky, A. P.,** *Dokl. Akad. Nauk S.S.S.R.,* 191, 315 (1970).
21. **Ehrhardt, H. and Sanner, G.,** *Neue Hütte,* 15, 497 (1970).
22. **Nikolsky, A. P., Korolev, E. F., Zubkov, S. N., and Uzikhin, V. V.,** *Appar. Metody Rentgenovskogo Anal.,* 15, 141 (1974).
23. **Fox, J. C. M.,** *J. Inst. Met.,* 91, 239 (1962—1963).
24. **Kamenova, C., Nenchev, H., and Andreev, T.,** *Tekhn. Mysl.,* 14, 133 (1977).
25. **Renter, W. and Lurio, A.,** *Anal. Chem.,* 49, 1737 (1977).
26. **Shah, R.,** *Iron Age Metalworking Int.,* 14, 25 (1975).
27. **Johnson, D.,** *Iron Steel Int.,* August, 306 (1974).
28. **Deconninc, G. and Demortier, G.,** *Nuclear Techniques in the Basic Metal Industries,* Proc. Symp., Helsinki, July 31 to August 4, International Atomic Energy Agency, Vienna, 1973, 573.
29. **Sato, K., Tanaka, I., and Otsuki, T.,** *X-ray Spectrom.,* 8, 68 (1979).
30. **Reed, D. J.,** The Determination of Zirconium, Niobium and Hafnium in Low Alloy Steels by X-ray Spectrography, Mines Branch Res. Dept. R 174, Dept. Mines Tech., Survey, Ottawa, Canada.
31. **Bruch, J.,** *Determination of Chemical Composition: Its Application to Process Control,* Iron and Steel Institute, London, 1971, 77.
32. **Kailinin, B. D., Plotnikov, R. I., and Popov, N. V.,** *Appar. Metody Rentgenovskogo Anal.,* 14, 15 (1974).
33. **Fedorova, L. M. and Kalinin, B. D.,** X-ray analysis of ore processing materials, in Proc. Symp. X-ray Emission Methods Anal., Moscow, Znaniye, 1975, 15.
34. **Zabavnikov, V. A., Sakharnikov, P. A., Korolev, E. F., Blokhin, M. A., Duimakaev, S. I., Nikoslky, A. P., Evlanov, I. Y., and Belitsky, I. Z.,** *Appar. Metody Rentgenovskogo Anal.,* 10, 148 (1972).

35. **Nogteva, N. K., Ioffe, V. N., and Kadyshman, T. A.**, *Zavodskaya Lab.*, 42, 423 (1976).
36. **Nikolsky, A. P., Evlanov, I. Y., and Kondratova, L. A.**, *Byull. Inst. Chermetinformatsiya/Ferrous Metall. Inf. Bull.*, 23, 49 (1972).
37. **Hepp, H.**, *Z. Erzbergbau Metall.*, 21, 151 (1969).
38. **Kochmola, N. M., Yuksa, L. K., Tsvetkov, V. P., and Nikolsky, A. P.**, *Zavodskaya Lab.*, 45, 825 (1979).
39. **Gorokhov, K. I., Kalosha, V. K., Kochmola, N. M., and Yuksa, L. K.**, *Zavodskaya Lab.*, 38, 936 (1972).
40. **Kochmola, N. M. and Gorokhov, K. I.**, *Zavodskaya Lab.*, 41, 424 (1975).
41. **Yuksa, L. K., Tsvetkov, V. P., Kochmola, N. M., and Kalosha, V. K.**, *Zavodskaya Lab.*, 42, 1348 (1976).
42. **Daigne, B. and Girard, F.**, *Rev. Int. Hautes Temp. Refract.*, 5, 213 (1968).
43. **Daigne, B. and Girard, F.**, *Vide*, 26, 69 (1971).
44. **Nikolsky, A. P., Shilman, V. H., Topilin, V. V., Pokrovsky, A. A., Vershinin, A. S., and Duimakaev, S. I.**, *Appar. Metody Rentgenovskogo Anal.*, 15, 20 (1974).
45. **Nikolsky, A. P., Shilman, V. H., and Duimakaev, S. I.**, Study of X-Radiation from Molten Metal in an Electron Beam Furnace Bath, in Proc. Symp. X-ray Emission Methods Anal., Moscow, Znaniye, 1975, 70.
46. **Daigne, B. and Girard, F.**, *Rech. Aerosp.*, 4, 231 (1977).
47. **Smirnova, V. A. and Batyrev, V. A.**, *Zavodskaya Lab.*, 39, 699 (1973).
48. **Ivanov, A. N. and Pristavko, V. V.**, *Zavodskaya Lab.*, 36, 1072 (1970).
49. **Anma, M.**, *Shizuoka Kogyo Shikenjo Hokoku*, 21, 95 (1977).
50. **Shiraiva, T. and Fujino, N.**, *Adv. X-ray Anal.*, 11, 63 (1968).
51. **Novosel-Radovic, V. J.**, *Metalurgija*, 16, 23 (1977).
52. **Ambrose, A. D., Croall, G., Henrys, F., and McGavin, R. F.**, *Determination of Chemical Composition: Its Application to Process Control*, Iron and Steel Institute, London, 1971, 153.
53. **Langheinrich, A. P., Forster, J. W., and Linn, T. A.**, *Nuclear Techniques in the Basic Metal Industries*, Proc. Symp., Helsinki, July 31 to August 4, International Atomic Energy Agency, Vienna, 1973, 429.
54. **Woldseth, R.**, *X-ray Energy Spectrometry*, KEVEX, Burlingame, Calif.,
55. **Clayton, C. G., Packer, T. W., and Fisher, J. C.**, *Nuclear Techniques in the Basic Metal Industries*, Proc. Symp., Helsinki, July 31 to August 4, International Atomic Energy Agency, Vienna, 1973, 319.
56. **Grosstuck, P., Gumprich, M., Ihlefeldt, Y., Kopineck, H. J., and Tappe, W.**, *Stahl Eisen*, 97, 1106 (1977).
57. *Metallurgia*, 82, 163 (1970).
58. *Metallurgia*, 81, 162 (1970).
59. **Lunner, S. E.**, *Determination of Chemical Composition: Its Application to Process Control*, Iron and Steel Institute, London, 1971, 166.
60. **Comins, N. R. and Thirwall, J. T.**, *X-ray Spectrom.*, 7, 92 (1978).
61. **Stricker, F., Friedhoff, P., and Heinen, M.**, *Appl. Spectrosc.*, 28, 467 (1974).
62. **Willmer, T. K., Waffenschmidt, K. H., Lohr, W., and Zimmermann, K.**, *Tech. Mitt. Krupp Wersberichte*, 33, 79 (1975).
63. *S. Afr. Min. Eng. J.*, 24, 191 (1969).
64. **Wurth, G.**, *Stahl Eisen*, 95, 12 (1975).
65. **Bisch, H. and Harm, B.**, *Siemens Z.*, 45, 665 (1971).
66. **Balin, F.**, *Determination of Chemical Composition: Its Application to Process Control*, Iron and Steel Institute, London, 1971, 76.
67. **Gurvich, Y. M., Kalinin, B. D., Mezevich, A. N., Plotnikov, R. I., Rogachev, I. M., and Serbin, A. Y.**, *Appar. Metody Rentgenovskogo Anal.*, 13, 122 (1974).
68. **Bondarenko, G. V., Ivanova, L. B., and Sadilov, K. A.**, *Zavodskaya Lab.*, 39, 688 (1973).
69. **Velichko, Y. I., Kalinin, B. D., Pavlinsky, G. V., Plotnikov, R. I., Popov, N. V., and Revenko, A. G.**, *Zavodskaya Lab.*, 40, 668 (1974).
70. **Büchel, E., Habel, K., and Lemm, H.**, *Arch. Eisenhüttenwesen*, 48, 19 (1977).
71. **Endo, J., Saito, K., and Matsumura, J.**, *Kawasaki Seitetsu Giho, Kawasaki Steel Tech. Rep.*, 7, 70 (1975).
72. **Lafollie, H.**, *DEW Tech. Ber.*, 8, 128 (1968).
73. Dofasco's Research Center, *Can. Controls Instrum.*, 10, 29 (1971).
74. **Bartell, D. M., Wreeler, B. D., and Cooper, J. A.**, Computerized Energy Dispersive Spectrometers for Process Monitoring, Abstr. Pittsburgh Conf. Anal. Chem. Appl. Spectrosc., Cleveland, Ohio, Pittsburgh, Pa., 1977, 480.
75. **Vasilieva, V. G., Gorsky, Y. I., Mezevich, A. N., Plotnikov, R. I., and Tatkin, L. Z.**, *Appar. Metody Rentgenovskogo Anal.*, 16, 13 (1975).

76. **Plotnikov, R. I.,** X-ray Analysis Applications in Ferrous and Nonferrous Metallurgy, in Proc. Symp. X-ray Emission Methods Anal., Moscow, Znaniye, 1975, 15.
77. **Vakurova, V. A.,** *Zavodskaya Lab.*, 43, 1526 (1977).
78. **Scharf, G., Buhr, W., and Börnig, R.,** *Neue Hütte*, 6, 361 (1976).
79. *Elektrotech. Z.*, A100, 175 (1979).
80. **Hirayama, Y., Yamadzaki, M., Tanaka, E., Hayase, H., and Hirata, H.,** *Nissin Seiko Giho, Nissin Steel Tech. Rep.*, 35, 71 (1976).
81. **Koch, W. and Bosch, H.,** *Mikrochim. Acta*, 4, 593 (1971).
82. **Stetter, A., Dobner, W., Ohls, K., Jaensch, P., Staats, G., and De Lafollie, H.,** *Stahl Eisen*, 94, 744 (1974).
83. **Vorsalz, B.,** *Neue Hütte*, 23, 112 (1978).
84. **Flament, P., Soete, D. D., Smul, W. D., and Keymolen, J. V.,** Some Features of Analytical Control at Sidmar, Proc. 28th Chem. Conf., Scarborough, 1975, London, 1976, 55.
85. **Loose, W., Koch, K. H., and Auskel, H.,** *Arch. Eisenhüttenwesen*, 49, 341 (1978).
86. **Naoharu, Y.,** *Nippon Steel Tech. Rep. Overseas*, 9, 94 (1977).
87. **Jackson, P.,** *Steel Times*, 206, 860 (1978).
88. **Croke, J. F., Westberg, R. G., and Jenkins, R.,** Applications of the PW 1600 Automatic Simultaneous X-ray Spectrometer to Industrial Control, Abstr. Pittsburgh Conf. Anal. Chem. Appl. Spectrosc., Cleveland, Ohio, 1977, Pittsburgh, Pa., 1977, 85.
89. **Brauner, J., Stricker, F., Friedholf, P., and Heinen, M.,** *Arch. Eisenhüttenwesen*, 48, 25 (1977).
90. **Kato, K. and Tanaka, K.,** *Bunseki Kagaku Jpn. Anal.*, 27, 175 (1978).
91. **Endo, Y., Matsumura, Y., and Sugihara, T.,** *Tetsu Hagane J. Iron Steel Inst. Jpn.*, 65, 120 (1979).
92. **Moucha, V.,** *Hutnik (C.S.S.R.)*, 28, 296 (1978).
93. **Brhaček, L., Hohn, J., and Golonka, A.,** *Hutnik (C.S.S.R.)*, 28, 9394 (1978).
94. **McKaveney, J. R., Baldwin, H. E., and Vasselaros, G. L.,** *J. Met.*, 20, 54 (1968).
95. **Yegorov, N. D., Kostrov, V. A., Ivanov, E. A., Smolich, L. A., and Novikov, V. F.,** *Metallurgija (U.S.S.R.)*, 5, 13 (1975).
96. **Williams, R. V. and du Bois, E. A.,** *Determination of Chemical Composition: Its Application to Process Control*, Iron and Steel Institute, London, 1971, 86.
97. **Thoma, C. and Brost, U.,** *Stahl Eisen*, 21, 1027 (1976).
98. **Bruch, J.,** *Determination of Chemical Composition: Its Application to Process Control*, Iron and Steel Institute, London, 1971, 74.
99. **Eschalier, G.,** *Metaux Corros. Ind.*, 49, 424 (1974).
100. **Pulina, A. K. and Goreva, E. I.,** *Zavodskaya Lab.*, 42, 428 (1976).
101. **Kalinin, B. D., Plotnikov, R. I., Popov, H. V., and Fedorova, S. I.,** *Appar. Metody Rentgenovskogo Anal.*, 14, 7 (1974).
102. **Kerr, R. M.,** Sample Preparation for Steel Analysis, 29th Pittsburgh Conf. State Art Anal. Chem. Appl. Spectrosc., Cleveland, Ohio, 1978; Abstr., Monroeville, Pa., 249 A.
103. **Klima, Z. and Sholes, P. H.,** *Analyst*, 98, 351 (1973).
104. **Bertin, E. P.,** *Adv. X-ray Anal.*, 11, 1 (1968).
105. **Inokuma, Y. and Endo, C.,** *Tetsu Hagane J. Iron Steel Inst. Jpn.*, 61, 346 (1975).
106. **Goto, H. and Saito, A.,** *Sci. Rep. Res. Inst. Tohoku Univ.*, 20, 59 (1968).
107. **Schreider, H.,** *Z. Erzbergbau Metallhüttenwesen*, 22, 338 (1969).
108. **Kashuba, A. T. and Hines, C. R.,** *Anal. Chem.*, 43, 1758 (1971).
109. **Narita, K., Taniguchi, M., Ota, N., Kotani, N., and Goto, T.,** *Tetsu Hagane J. Iron Steel Inst. Jpn.*, 64, 631 (1978).
110. **Clift, B. and Bourke, T. M.,** *BHP Tech. Bull.*, 20, 34 (1976).
111. **Lach, T., Ostrowski, K., Rulikowska, E., and Wolny, J.,** *Hutnik (Poland)*, 35, 594 (1968).
112. **Reida, A. and Ronnie, E. K.,** *Steel Times*, 198, 344 (1970).
113. **Bezverkhnyaya, I. P., Adamova, E. A., and Chumak, A. D.,** *Appar. Metody Rentgenovskogo Anal.*, 16, 40 (1975).
114. **Pyatkov, A. G., Romanenko, I. M., Shushpanov, A. P., and Lukash, V. I.,** *Zavodskaya Lab.*, 41, 431 (1975).
115. **Klockenkämper, R.,** *Z. Anal. Chem.*, 285, 345 (1977).
116. **Ebel, H., Wagendristel, A., Maix, R., and Burger, R.,** *Arch. Eisenhüttenwesen*, 39, 755 (1968).
117. **Wagner, F.,** *Arch. Eisenhüttenwesen*, 39, 759 (1968).
118. **Novosel-Radovič, V., Sokolean, D., and Sever, S.,** *Metalurgija*, 14, 39 (1975).
119. **Murata, M.,** *X-ray Spectrom.*, 2, 111 (1973).
120. **Koch, K., Ohls, K., and Becker, G.,** *Arch. Eisenhüttenwesen*, 41, 25 (1970).
121. **Moučka, M.,** *Hutnicke Listy*, 24, 302 (1969).
122. **Moučka, M.,** *Hutnicke Listy*, 24, 594 (1969).

123. **Sato, K. and Uzuki, J.,** *Nihon Kinzoku Gakkai-Shi J. Jpn. Inst. Met.*, 36, 648 (1972).
124. **Wittmann, A. and Chmeleff, J.,** *Analysis*, 2, 271 (1972).
125. **Raevkaya, T. N., Korepanova, N. I., and Vasilenko, V. T.,** *Zavodskaya Lab.*, 35, 937 (1969).
126. **Andreini, G. P., Barsellini, C., and Fragala, M.,** *Bol. Tech. Finsider*, 370, 801 (1977).
127. **Hartl, M.,** *Hutnicke Listy*, 24, 301 (1969).
128. **Russ, J. C.,** *X-ray Spectrom.*, 6, 37 (1977).
129. **Tanaka, I., Otsuki, T., and Sato, K.,** *Nihon Kinzoku Gakkai-Shi J. Jpn. Inst. Met.*, 43, 304 (1979).
130. **Shiroky, V. K., Bochenin, V. I., and Yablonsky, E. D.,** *Zavodskaya Lab.*, 35, 937 (1969).
131. **Muir, S.,** *Determination of Chemical Composition: Its Application to Process Control*, Iron and Steel Institute, London, 1971, 161.
132. **Fabbi, B. P.,** *X-ray Spectrom.*, 1, 39 (1972).
133. **Arai, T.,** *Trans. Iron Steel Inst. Jpn.*, 17, 636 (1977).
134. **Ohls, K.,** *Z. Anal. Chem.*, 286, 36 (1977).
135. **Niimi, J., Inokuma, J., and Inone, K.,** *Sumitomo Met.*, 23, 539 (1971).
136. **Staats, G.,** *Z. Anal. Chem.*, 255, 22 (1971).
137. **Paris, V. and Marino, S.,** *Metall. Ital.*, 63, 248 (1971).
138. **Ambrose, A. D., Rutherford, R., and Muir, S.,** *Metallurgia*, 82, 119 (1970).
139. **Ohls, K.,** *Determination of Chemical Composition: Its Application to Process Control*, Iron and Steel Institute, London, 1971, 74.
140. **O'Neil, M. J. and Fitzsimons, F. J.,** *Trans. Inst. Min. Metall.*, 81, B210 (1972).
141. **Koch, K. H., Ohls, K., and Becker G.,** *Arch. Eisenhüttenwesen*, 41, 87 (1970).
142. **Hughes, H.,** *Determination of Chemical Composition: Its Application to Process Control*, Iron and Steel Institute, London, 1970.
143. **Novosel-Radovič, V. J., Šolič, M., Divjakinya, M., and Pavlovic, P.,** *Metallurgija*, 17, 35 (1978).
144. **Sato, H.,** *Trans. Iron Steel Inst. Jpn.*, 18, 721 (1978).
145. **Abe, T.,** *Nihon Kinzoki Gakkai Kaiho Bull. Jpn. Inst. Met.*, 13, 425 (1974).
146. **Giroud, J., Lampert, J. C., and Lallier, A.,** *Analyses*, 5, 385 (1977).
147. **Büchel, E., Lemm, H., Leiber, F., and Becker, W.,** *Arch. Eisenhüttenwesen*, 48, 391 (1977).
148. **Sato, K.,** *J. Jpn. Inst. Met. Nihon Kinzoku Gakkai-Shi*, 38, 736 (1974).
149. **Kochmola, N. M. and Nikolsky, A. P.,** *Zavodskaya Lab.*, 45, 709 (1979).
150. **Bianchi, G., Grimaldi, R., and Randi, G.,** *Metall. Ital.* 11, 435 (1977).
151. **Randi, G., Grimaldi, R., and Meucci, A.,** *Metall. Ital.*, 69, 110 (1977).
152. **Okuta, K.,** *Bunseki Kiki Anal. Instrum.*, 9, 719 (1971).
153. **Schrey, F. and Gallagher, P. K.,** *Am. Ceram. Soc. Bull.*, 56, 981 (1977).
154. **Suzuki, G., Higuchi, M., and Satomi, K.,** *Determination of Chemical Composition: Its Application to Process Control*, Iron and Steel Institute, London, 1971, 23.
155. **Kochmola, N. M. and Nikolsky, A. P.,** *Zavodskaya Lab.*, 44, 163 (1978).
156. **Kis-Varga, M.,** *X-ray Spectrom.*, 8, 73 (1979).
157. **Lister, D. B. and Kurtz, C.,** A Simple Analytical Method for Alloy Heat Analysis, Abstr. Pittsburgh Conf. Anal. Chem. Appl. Spectrosc., Cleveland, Ohio, 1977, Pittsburgh, Pa., 1977, 83.
158. **Foster, M. J. and Barbi, N. C.,** A Modified Rasberry-Heinrich Correction Technique for use with Quantitative Energy Dispersive X-ray Fluorescence Analysis, Abstr. Pittsburgh Conf. Anal. Chem. Appl. Spectrosc., Cleveland, Ohio, 1977, Pittsburgh, Pa., 1977, 82.
159. **Verbeke, P., Nullens, H., and Adams, F.,** *Anal. Chim. Acta*, 97, 283 (1978).
160. **Lavrentiev, Y. G. and Kuznetsova, A. P.,** *Zavodskaya Lab.*, 45, 315 (1979).
161. **Bartell, D. M., Gedicke, D. A., and Wheller, B. D.,** Fundamental Parameters Versus Regression Analysis Accuracy, 29th Pittsburgh Conf. State Art Anal. Chem. Appl. Spectrosc., Cleveland, Ohio, 1978; Abstr., Monroeville, Pa., 667.
162. **Shen, R. B. and Russ, J. C.,** *X-ray Spectrom.*, 6, 56 (1977).
163. **Kawamura, K.,** *Tetsu Hagane J. Iron Steel Inst. Jpn.*, 58, 1317 (1972).
164. **Kramer, J., Ebel, H., and Tschimarov, F.,** *X-ray Spectrom.*, 6, 30 (1977).
165. **Plesch, R.,** *Z. Anal. Chem.*, 282, 417 (1976).
166. **Niimi, J., Inokuma, Y., and Inoue, K.,** *Bunseki Kiki Anal. Instrum.*, 8, 457 (1970).
167. **Münchow, P.,** *Chem. Ztg. Chem. Appar.*, 92, 697 (1968).
168. **Hunt, C. R.,** *Metallurgia*, 77, 135 (1968).
169. **Tertian, R.,** *X-ray Spectrom.*, 3, 95 (1973).
170. **Hughes, H.,** *Analyst*, 97, 161 (1972).
171. **Donhoffer, D. K. and Beswick, C. K.,** *Nuclear Techniques in the Basic Metal Industries*, Proc. Symp., Helsinki, July 31 to August 4, International Atomic Energy Agency, Vienna, 1973, 299.
172. **Laguitton, D. and Momtler, M.,** *Adv. X-ray Anal.*, 20, 515 (1977).
173. **Koch, K. H.,** *Chem. Labor Betrieb*, 7, 167 (1975).
174. **Bochenin, V. D.,** *Zavodskaya Lab.*, 42, 433 (1976).

175. **Watanabe, T., Koguchi, H., and Shukuya, I.,** *Nippon Steel Tech. Rep. Overseas,* 9, 78 (1977).
176. **Kawamura, K., Watanabe, T., and Nasydzaka, K.,** *Bunseki Kiki Anal. Instrum.,* 7, 568 (1969).
177. **Amertrano, E. and Bernagozi, A.,** *Metall. Ital.,* 63, 525 (1971).
178. **Carlson, G.,** *X-ray Spectrom.,* 1, 155 (1972).
179. **Creton, F., Montanaro, E., and Scalise, M.,** *Metall. Ital.,* 64, 392 (1972).
180. **Kawamura, K., Watanabe, T., and Nasydzaka, T.,** *J. Jpn. Inst. Met. Nihon Kinzoku Gakkai-Shi,* 33, 679 (1969).
181. **Zherdev, A. M. and Yakhontov, A. G.,** *Appar. Metody Rentgenovskogo Anal.,* 5, 104 (1969).
182. **Bochenin, V. I.,** *Zavodskaya Lab.,* 37, 930 (1971).
183. **Knott, A. C., Mills, J. C., and Belcher, C. B.,** *Can. J. Spectrosc.,* 23, 105 (1978).
184. **Tzumura, K. and Oshiba, S.,** *Trans. Iron Steel Inst. Jpn.,* 19, 137 (1979).
185. **Savina, E. V., Semiletkina, E. G., and Kostin, V. G.,** X-ray Determination of Sulfur in Ores and Ore Processing Products, in Proc. Symp. Increase Efficiency Qual. Anal. Control, Znaniye, Moscow, 1978, 44.
186. **Adachi, T., Ito, M., and Marita, M.,** *Denki Seiko Electr. Furnace Steel,* 43, 179 (1972).
187. *Coal Gold Base Miner. S. Afr.,* 18, 7 (1970).
188. **Cesario, R. and Frazzoli, F. V.,** *Nuclear Techniques in the Basic Metal Industries,* Proc. Symp., Helsinki, July 31 to August 4, International Atomic Energy Agency, Vienna, 1973, 119.
189. **Nazarov, I. A., Semushev, M. I., and Pokhiluk, N. V.,** *Zavodskaya Lab.,* 42, 159 (1976).
190. *J. Iron Steel Inst. Jpn.,* 63, 1204 (1977).
191. **Kochmola, N. M., Kalosha, B. K., Yuksa, L. K., and Zheltukhin, Y. E.,** *Zavodskaya Lab.,* 40, 960 (1974).
192. **Brhaček, L. and Golonka, A.,** *Hutnik (C.S.S.R.),* 6, 262 (1978).
193. **White, G.,** *Determination of Chemical Composition: Its Application to Process Control,* Iron and Steel Institute, London, 1971, 40.
194. **Nikolsky, A. P., Kochmola, N. M., and Yuksa, L. K.,** *Zavodskaya Lab.,* 45, 1107 (1979).
195. **Papez, K. and Cameron, J. F.,** *Nuclear Techniques in the Basic Metal Industries,* Proc. Symp., Helsinki, July 31 to August 4, International Atomic Energy Agency, Vienna, 1973, 21.
196. **Cohen, S. and Bryan, F. R.,** *Appl. Spectrosc.,* 22, 342 (1968).
197. **Matsumura, T., Kotani, N., Goto, T., and Narita, K.,** *Tetsu Hagane J. Iron Steel Inst. Jpn.,* 58, 2049 (1972).
198. **Sasaki, M. and Susuki, K.,** *Trans. Iron Steel Inst. Jpn.,* 11, 282 (1971).
199. **Stricker, F., Friedholf, P., Heinen, M., and Brauner, J.,** *Appl. Spectrosc.,* 28, 467 (1974).
200. **Barbier, M. and Rondeau, J. M.,** *Chim. Anal.,* 53, 470 (1971).
201. **Buravliov, Y. M. and Titovets, A. V.,** On Influence of the Interelement Effects and Sample Structure on the X-ray Analysis of Iron-Base Alloys, in Proc. Symp. X-ray Emission Methods Anal., Moscow, Znaniye, 1975, 88.
202. **Ulianina, G. F., Bychev, V. M., and Morozov, V. V.,** Research of Microsegregation in Magnetic Alloy I-OHDK35T35 by the X-ray Method, in Proc. Symp. X-ray Emission Methods Anal., Znaniye, Moscow, 1975, 17.
203. **Nikolsky, A. P., Uzikhin, V. V., and Koroliev, E. F.,** Determination of Light Elements in Steel and Alloys by Means of Analysis on Primary X-ray Spectra, in Proc. Symp. X-ray Emission Methods Anal., Znaniye, Moscow, 1975, 59.
204. **Ito, R., Sato, A., and Narita, M.,** *Tetsu Hagane J. Iron Steel Inst. Jpn.,* 64, 363 (1978).
205. **Van den Berge, H.,** *Sci. Ind. (Neth.),* 13, 22 (1979).
206. **Batyrev, V. A. and Reznikova, N. Z.,** *Zavodskaya Lab.,* 40, 1468 (1974).
207. **Glinsky, E. E. and Verman, B. S.,** *Appar. Metody Rentgenovskogo Anal.,* 16, 183 (1975).
208. **Mannens, W. and Kinson, K.,** *Appl. Spectrosc.,* 32, 109 (1978).
209. **Takao, O. and Isami, I.,** *Tetsu Hagane J. Iron Steel Inst. Jpn.,* 64, 357 (1978).
210. **Brauner, J.,** *Arch. Eisenhüttenwesen,* 49, 183 (1978).
211. **Nikitina, O. I., Antipenko, L. L., and Ivanova, N. K.,** X-ray Analysis of Iron Alloys, in Proc. Symp. Increase Efficiency Control, Znaniye, Moscow, 1978, 44.
212. **Cooper, J. A.,** *Int. Lab.,* May-June, 51 (1977).
213. **Wenzel, W., Block, F.-R., and Splinter, P.,** *Forsc. Landes Nordhein-Westfalen,* 2531, 142S (1976).
214. **Rhodes, J. R. and Fuguta, T.,** *Adv. X-ray Anal.,* 11, 249 (1968).
215. **Sumita, S., Kikuchi, N., Maekawa, T., Shinmei, M., and Yokokawa, T.,** *Tetsu Hagane J. Iron Steel Inst. Jpn.,* 65, 107 (1979).
216. **Popa, A. and Farkas, L.,** *Metalurgia (Rumania),* 24, 321 (1972).
217. **Timoshenko, N. N.,** *Zavodskaya Lab.,* 41, 1158 (1975).
218. **Kochmola, N. M., Yuksa, K. L., Nikolsky, A. P., and Fomin, V. B.,** *Avtom. Metall. Proizvodstva (Annu. Iron Steel Minist. U.S.S.R.),* 7, 26 (1978).
219. **Dziunikowski, B. and Tetten, G. K.,** *J. Radioanal. Chem.,* 49, 79 (1979).

220. Trojan, W., Wutrowska, S., and Stankiewiecz, W., *Rudi Met.*,

221. Pshenichny, G. A. and Plotnikov, R. D., *Appar. Metody Rentgenovskogo Anal.*, 4, 145 (1969).

222. Pshenichny, G. A., Komissarzhevskaya, G. F., Orlov, V. N., Ochkur, A. P., Tomsky, I. V., Plotnikov, R. I., Zakasovsky, G. V., and Spiridonov, G. A., *Appar. Metody Rentgenovskogo Anal.*, 4, 153 (1969).

223. Salm, D., Wiltshire, N. D., and Kaan, D., *B.H.P. Tech. Bull.*, 21, 31 (1977).