

# Determination of Minor Constituents in Low-Alloy Steels by X-Ray Spectroscopy

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The analysis of low-alloy steel by X-ray spectroscopy has been investigated for the determination of minor constituents. In this study, detection limits and interferences were examined for the following 20 elements: Ag, As, Co, Cr, Cu, Ge, Mn, Mo, Nb, Ni, Pb, S, Se, Si, Sn, Ta, Ti, V, W, and Zr. For most of the elements, the detection limit is below 0.01 percent which is sufficient for control analyses. Interferences or interelement effects in low-alloy steel were found not to be serious, but may be encountered; for example, zirconium interferes with the determination of molybdenum. The application of the National Bureau of Standards standard samples to these determinations is discussed.

## 1. Introduction

A recent development in the field of spectrometric analysis is the application of the X-ray spectrum for making rapid and accurate determinations, particularly of major constituents in complex alloys such as those used in jet aircraft and rockets. The general techniques and applications of X-ray spectrometric analyses have been described in the literature [1, 2].<sup>1</sup> Although X-ray spectroscopy has been used for trace analyses, most of the reported work has been with solution or powder samples [3, 4]. Application of the X-ray method for determining a wide range of minor and trace constituents in steels by means of direct excitation of the metal has not been reported in the literature. The purposes of this investigation were twofold: First, to examine the sensitivity of detection and possible interferences in the determination of 20 elements in iron and steel; and second, to observe the applicability of NBS standard samples of low-alloy steels for calibration in this system.

## 2. Principles and Equipment

The analytical technique for X-ray emission analysis involves irradiating a sample by an X-ray beam of high energy, producing secondary X-rays having wavelengths characteristic of the elements in the sample. The radiation is dispersed according to wavelength by a suitable crystal and the X-ray intensity measured at selected wavelengths. Standard samples are used to relate this intensity to the concentration.

The instruments generally available are designated as flat- or curved-crystal spectrometers depending on the type of analyzing crystal employed. In flat-crystal spectrometers, collimators with parallel flat plates provide optimum intensity and resolution; in the curved crystal or focusing type, slits are used.

In both types, the crystals are positioned according to Bragg's Law to obtain the wavelength of interest. Different crystals and radiation detectors with optimum characteristics may be used depending on the wavelength desired. Since the soft (longer wavelength) X-ray radiation of elements of low atomic number is easily absorbed by air, helium or hydrogen is substituted for air for the determination of elements below atomic number 22; recently vacuum spectrometers have been developed for the same purpose.

The detectors in common use include Geiger, proportional, and scintillation counters. Signal pulses from a detector may be counted by means of a scaler circuit, or the charge developed by the detector may be stored in a capacitor. An analytical curve can be established by relating the number of counts per unit time, or the integrated charge over a fixed time period, to the concentration.

A commercial multichannel X-ray unit of the curved crystal type served for this investigation. Incorporated in this unit is a series of crystal spectrometers, each with a detector and capacitor circuit. During the period of exposure of the sample, the intensities at each of 11 selected X-ray wavelengths can be integrated simultaneously. Instead of using the conventional millivolt chart recorder, a readout system especially designed for our laboratory is employed. In this arrangement, a digital voltmeter provides a measurement proportional to the voltage developed on each capacitor during exposure, and displays these numbers visually. At the same time, results can be typed and punched on tape by an electric typewriter. A four-digit number is obtained for each element by means of a sequential readout, and a feature of this equipment is that the response may be adjusted to be linearly related to concentration for most determinations.

The wavelength settings and other details of the X-ray equipment are given in table 1. The array indicated is designed primarily for the analysis of high-temperature alloys, although other applications

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. Details of the X-ray equipment

Element	Wavelength	Crystal		Atmosphere	Detector	Slit	
		Radius	Material			Primary	Secondary
	<i>A</i>	<i>in.</i>				<i>in.</i>	<i>in.</i>
S.....	K <sub>α</sub> 5. 373	4	NaCl	He.....	Flow Geiger <sup>a</sup>	0. 040	0. 080
Mn.....	K <sub>α</sub> 2. 103	4	LiF	Air.....	Proportional <sup>b</sup>	. 010	. 005
Si.....	K <sub>α</sub> 7. 126	4	EDDT	He.....	Flow Geiger	. 040	. 020
Ni.....	K <sub>α</sub> 1. 659	11	LiF	Air.....	Proportional	. 015	. 030
Cr.....	K <sub>α</sub> 2. 292	11	LiF	do.....	do	. 010	. 050
V.....	K <sub>α</sub> 2. 505	4	LiF	do.....	do	. 020	. 010
Mo.....	K <sub>α</sub> 0. 711	11	LiF	do.....	do	. 030	. 015
Ti.....	K <sub>α</sub> 2. 750	4	LiF	do.....	do	. 040	. 020
Al.....	K <sub>α</sub> 8. 339	4	EDDT	He.....	Flow Geiger	. 040	. 020
Co.....	K <sub>α</sub> 1. 791	11	LiF	Air.....	Proportional	. 040	. 020
W.....	L <sub>α1</sub> 1. 476	11	LiF	do.....	do	. 010	. 020
Nb.....	K <sub>α</sub> 0. 749	11	LiF	do.....	do	. 030	. 015
Scanner.....		11	LiF	do.....	do	. 020	. 030

<sup>a</sup> Miniature tube with 2-cm window.

<sup>b</sup> Counter measures average current for integration.

such as to steel also were considered. All channels but one are fixed with respect to the individual wavelengths. The scanner, which may be set to measure any of the shorter wavelengths, provides additional flexibility for the determination of the elements of higher atomic numbers (atomic numbers 22 and above) not included in the fixed program.

As an external standard, a small copper sample is irradiated by the primary X-ray beam, and the undispersed secondary radiation measured by a Geiger detector operating in the proportional region. A preset value of integrated intensity for this channel terminates the exposure for all other channels.

Each spectrometer is set for the particular element by selecting the type of crystal and detector, choice of helium or air path, and settings of primary and secondary slit systems. These factors markedly influence the detectability, although other factors also are important such as the current and voltage of the X-ray tube, thickness and material of the tube window, path length, time of counting or integration, and the material irradiated.

The X-ray tube was supplied with an end window and a platinum target. Platinum was chosen since the determination of tungsten at low concentrations was required and this precluded the use of a tungsten target. Although studies were made to determine optimum power settings of the X-ray tube for the determination of some elements at low concentrations, it was found satisfactory to use one setting for all of the reported work—50 kv and 35 ma. Exposure times generally were either 1 min for the K series spectra of medium atomic number elements, or 4 min for the lighter elements and for the L series spectra of the heavier elements.

### 3. Standard and Reference Samples

The set of eight NBS Spectrometric Standard Samples of Ingot Iron and Low-Alloy Steel, NBS

Nos. 1161 through 1168,<sup>2</sup> served for most of this investigation. Table 2 shows the values of the recently revised Provisional Certificate of Analyses for the eight standards. Other samples used in this investigation include the following: (a) Eight proposed NBS white cast-iron standard samples, (b) several of the older NBS spectrographic low-alloy steel samples which were originally ½ in. in diameter but were upset forged to a size suitable for X-ray spectroscopy (NBS Nos. 805a, 810a, 820a, and 821), (c) two solid sections of the NBS chemical standard samples (NBS Nos. 130a and 159), (d) seven reference samples of stainless steel containing a graded series for selenium, and (e) one reference sample of steel for silicon. A surface grinder was used for preparing all samples for analysis.

## 4. Results

### 4.1 Analytical Curves for Elements Commonly Determined

The analytical curve for manganese in iron and steel is shown in figure 1.<sup>3</sup> Each plotted point on this and subsequent curves generally represents the average of four individual determinations. With linear coordinates the plotted points closely fit a straight line. Log-log coordinates can be used to spread the analytical scale at the low concentrations when this is desirable. Note that the digital voltmeter response reads directly in terms of concentration; one digit response is equal to 0.001 percent of manganese. Similar straight-line curves are obtained with the standards for copper, nickel, chromium, and vanadium. If the concentration ranges are extended beyond those considered in this investigation, interferences may be observed. For example, chromium at higher concentrations will interfere in the determination of manganese [5].

<sup>2</sup> The standards are described in NBS Circ. 552, Standard Materials Issued by the National Bureau of Standards. This Circular may be obtained from the Superintendent of Documents, U.S. Government Printing Office, Washington 25, D.C., for 35 cents. Supplementary inserts are available from the National Bureau of Standards upon request.

<sup>3</sup> Sample designation is denoted on figures 1 through 8 by numbers or letters.

TABLE 2. Provisional certificate of analysis

(Revised—November 25, 1959)

Spectrographic ingot iron and low-alloy steel standards

NBS No. <sup>a</sup>	461 1161	462 1162	463 1163	464 1164	465 1165	466 1166	467 1167	468 1168
Designation	Low-alloy steel A	Low-alloy steel B	Low-alloy steel C	Low-alloy steel D	Ingot iron E	Ingot iron F	Low-alloy steel G	Low-alloy steel H
Element	%	%	%	%	%	%	%	%
C	0.15	0.40	0.19	0.54	0.037	0.065	0.11	0.26
Mn	.36	.94	1.15	1.32	.032	.11 <sub>3</sub>	.27 <sub>5</sub>	.47
P	.053	.045	0.031	0.017	.008	.012	.033	.023
S	(.02) <sup>b</sup>	(.02)	(.02)	(.02)	(.01)	(.01)	(.01)	(.02)
Si	.047	.28	.41	.48	.029	.025	.26	.075
Cu	.34	.20	.47	.094	.019	.033	.067	.26
Ni	1.73	.70	.39	.13 <sub>5</sub>	.026	.051	.088	1.03
Cr	0.13	.74	.26	.078	.004	.011	.036	0.54
V	.024	.058	.10	.29 <sub>5</sub>	.002	.007	.041	.17
Mo	.30	.080	.12	.029	.005	.011	.021	.20
Sn	.022	.066	.013	.043	.001	.005	.10	.009
Ti	(.01)	.037	.010	.004	.20	.057	.26	.011
B	.000 <sub>2</sub>	.000 <sub>5</sub>	.001 <sub>2</sub>	.005	.000 <sub>1</sub>	(.000 <sub>2</sub> )	(.000 <sub>2</sub> )	.009
As	.028	.046	.10	.018	.010	.014	.14	.008
W	.012	.053	.10 <sub>5</sub>	.022	(.001)	(.006)	.20	.077
Zr	(<.005)	.063	.20	.010	(.002)	(<.005)	.094	(<.005)
Nb	.011	.096	.19 <sub>5</sub>	.037	(.001)	.005	.29	.006
Ta	.002	.036	.15	.069	.001	.002	.23	.005
Al	(.005)	.02 <sub>3</sub>	.02 <sub>7</sub>	.005	.19	.01 <sub>5</sub>	.16	.04 <sub>2</sub>
Co	.26	.11	.01 <sub>3</sub>	.02 <sub>8</sub>	.008	.04 <sub>6</sub>	.07 <sub>4</sub>	.16
Pb	(.003)	.006	.012	.020	(<.0005)	(.001 <sub>3</sub> )	.000 <sub>6</sub>	(<.0005)
Ag	(.001 <sub>5</sub> )	(<.0002)	(<.0002)	(.003 <sub>0</sub> )	(.0002 <sub>5</sub> )	(.0004 <sub>5</sub> )	(.004 <sub>0</sub> )	(<.0002)
Ge	(.001 <sub>5</sub> )	(.003 <sub>0</sub> )	(.002 <sub>5</sub> )	(.001 <sub>5</sub> )	(.003 <sub>5</sub> )	(.003 <sub>0</sub> )	(.003 <sub>0</sub> )	(.001 <sub>0</sub> )
O	(.02 <sub>0</sub> )	(.006)	(.007)	(.006)	(.003)	(.005)	(.004)	(.004)
N	(.00 <sub>6</sub> )	(.00 <sub>8</sub> )	(.00 <sub>6</sub> )	(.00 <sub>7</sub> )	(.00 <sub>5</sub> )	(.00 <sub>6</sub> )	(.00 <sub>4</sub> )	(.00 <sub>6</sub> )

<sup>a</sup> Sizes: 400 series, rods 7/8 in. in diameter and 4 in. long.

1100 series, disks 1 1/4 in. in diameter and 3/4 in. thick.

<sup>b</sup> Values in parenthesis are not certified, but are given for information on the composition.

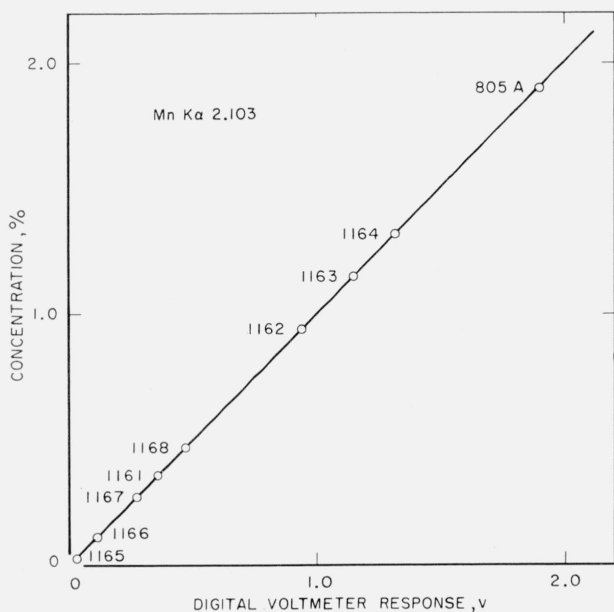


FIGURE 1. Analytical curve for manganese in steel.

The analytical curve for the molybdenum  $K_{\alpha}$  line at 0.711 Å is shown in figure 2; some of the points of this curve exhibit interference caused by the zirconium  $K_{\beta}$  line at 0.702 Å. For interference of this

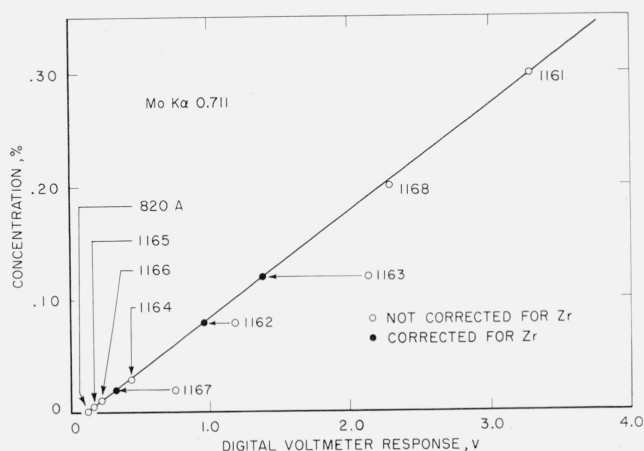


FIGURE 2. Analytical curve for molybdenum  $K_{\alpha}$  line, showing correction for interference by zirconium.

type, a correction curve can be established by the use of standard samples to relate the apparent increase in molybdenum content to the zirconium content. The relationship is linear for the ranges of concentration usually covered. The corrected values, which are obtained from a separate correction curve, are indicated by the black dots. To determine molybdenum with the most sensitive  $K_{\alpha}$  line, either the zirconium content of the samples to be analyzed must be known to be below about 0.02 percent, or the zirconium content must be determined and a correction made. An alternative procedure is to choose a higher diffraction order of the same line to achieve separation from the interference line; however, this usually results in a severe loss in intensity. Another alternative is to use another line of the same series or another series; either choice results in a loss of intensity, the magnitude of which depends on the line chosen.

The analytical curve for the molybdenum  $K_{\beta}$  line, figure 3, clearly shows the absence of zirconium interference. In contrast to a 1-min integration time with the  $K_{\alpha}$  line, a 4-min time is necessary with the  $K_{\beta}$  line for suitable detectability and for the precise determination of molybdenum at an alloy concentration of about 0.2 percent.

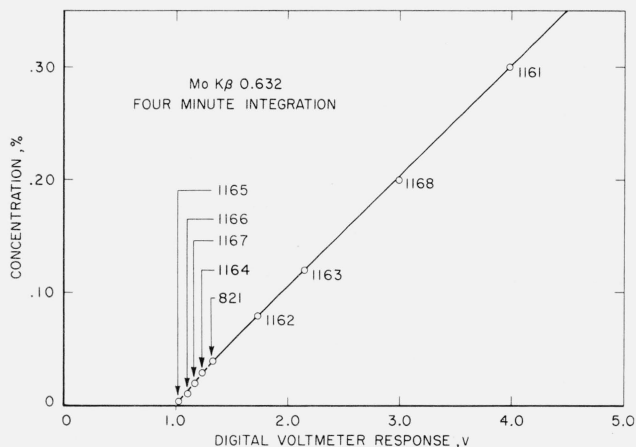


FIGURE 3. Analytical curve for molybdenum  $K_{\beta}$  line, showing absence of interference by zirconium.

Only preliminary results are available for the determination of silicon in low-alloy steel. Figure 4 shows the curve covering the range from about 0.1 to 0.8 percent of silicon and indicates the feasibility of the determinations. Even with 4-min integrations, however, rather poor detectability is observed and additional work on the determination of this element is necessary including possible changes in detector, crystal and slit width. Additional work on a set of proposed NBS white cast-iron spectrometric standards has demonstrated the suitability of the X-ray method for the determination of silicon over the concentration range of 0.5 to 3.5 percent. In this investigation, it was observed that deviations from the analytical curve may occur as a result of

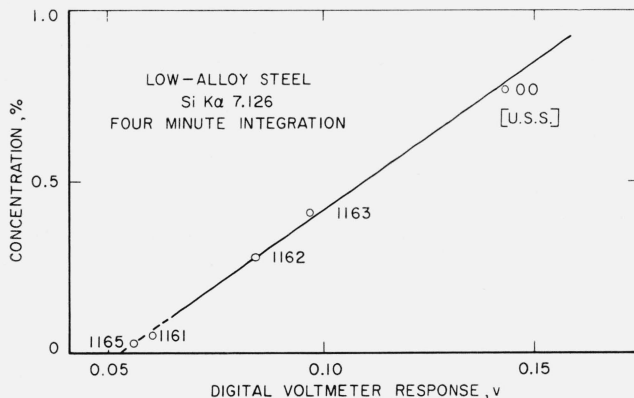


FIGURE 4. Preliminary analytical curve for silicon in steel. Point 00 represents a reference sample from the United States Steel Corporation.

different casting conditions and surface preparations of samples and standards; these variables should be controlled carefully.

#### 4.2. Analytical Curves for Elements Not Commonly Determined

The determination of boron in steel unfortunately cannot be done with the X-ray spectroscopic equipment now available; hence, optical emission has the advantage for this element. By contrast, selenium determinations cannot be made by conventional optical emission spectroscopy, but may be made readily by X-ray spectrometry. Since samples of low-alloy steel containing selenium were not available, analyzed samples of free-machining stainless steel of the 18-chromium—8 nickel type were used.<sup>4</sup> The results for selenium are shown in the analytical curve in figure 5.

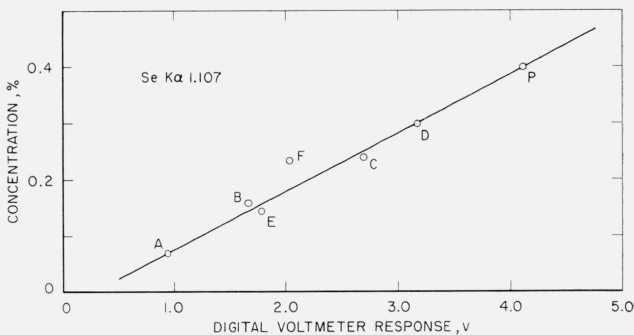


FIGURE 5. Analytical curve for selenium in free-machining stainless steel.

Arsenic also is difficult to determine in steel by conventional optical emission spectroscopy. The analytical curve obtained by X-ray spectroscopy is given in figure 6. A correction for amounts of lead above about 0.005 percent was found necessary, since the  $L_{\alpha 1}$  line of lead is coincident with the  $K_{\alpha}$  line of arsenic. The analytical points for arsenic, after making linear corrections for lead, are shown by black dots.

<sup>4</sup> The samples were provided by courtesy of the Baltimore Works of the Armeo Steel Corp.

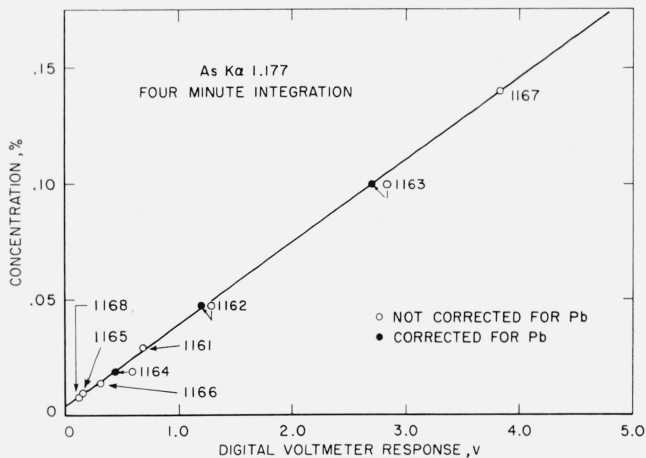


FIGURE 6. Analytical curve for arsenic in steel.

The analytical curve for zirconium is presented in figure 7. This curve is useful not only for determining zirconium but also for correcting results obtained when using the most sensitive molybdenum  $K\alpha$  line (see fig. 2), provided the relationship of the zirconium content to the apparent increase in molybdenum content is established. Linear analytical curves similar to that of zirconium are obtained with  $K$  radiation for titanium, cobalt, niobium, silver, and tin. Interferences are not observed. Because of the limitation in maximum voltage (60 kv) with this X-ray tube, L-series radiation must be used for the determination of some elements having large atomic numbers. The elements in this class include tantalum, tungsten, and lead. The intensities of the L spectra relative to the  $K$  spectra are low; this can generally be compensated by increasing the integration time from 1 to 4 min. Interferences are not detected for tantalum and tungsten. For lead, which exhibits interference from arsenic, the  $L\alpha_1$  line can be used providing either the arsenic content is low, or a correction is made for the coincident  $K\alpha$  line of arsenic. As an alternative, the  $L\beta$  line for lead can be used with little loss in sensitivity.

The results of preliminary data for sulfur, which is present in eight proposed NBS white cast-iron standards, are presented in figure 8. A linear

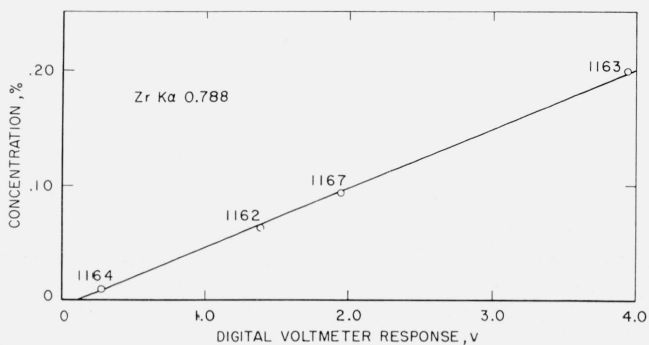


FIGURE 7. Analytical curve for zirconium in steel.

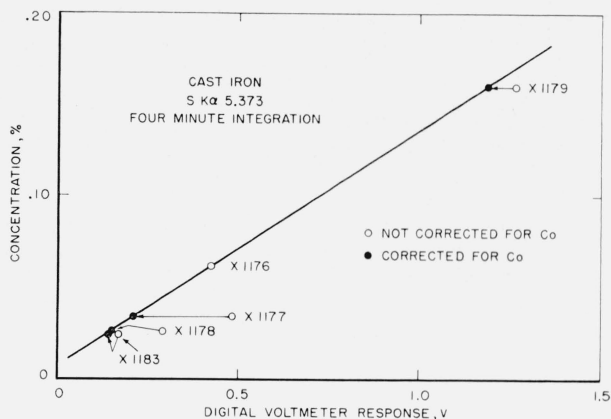


FIGURE 8. Preliminary analytical curve for sulfur in cast-iron showing correction for interference by cobalt.

correction for the cobalt content was found necessary because the cobalt  $K\alpha$  line at 1.791 A in the third order (5.373 A) interferes with the sulfur  $K\alpha$  line at 5.373 A. With the corrected data, a good fit of the analytical points to a straight line is observed for six of the eight standards. The other two show some deviation from the curve and are under further investigation. Similarly to silicon, a bias may be exhibited in the X-ray determination of sulfur because of different casting conditions and surface preparations of samples and standards.

### 4.3. Detectability

Results of the investigation for elements commonly determined in low-alloy steel are shown in table 3. Attention is called first to the detectability, which is defined here as that concentration at which the coefficient of variation is equal to 100 percent; and second, to the coefficient of variation at an alloy concentration for each element. With the possible exception of silicon, the data appear to be acceptable for control analyses of steel for these elements.

The results of the investigation for elements not commonly determined in steel is presented in table 4.

TABLE 3. Results for elements commonly determined in low-alloy steel

Element	Wave-length	Integra-tion time	Detecta-bility	Precision		
				Concen-tration	Coeffi-cient of variation	Interfer-ence
	<i>A</i>	<i>min</i>	<i>%</i>	<i>%</i>		
Mn	$K\alpha$ 2.103	1	0.003	1.00	0.3	None
Si	$K\alpha$ 7.126	4	.05	0.30	16.3	Do.
Si <sup>a</sup>	$K\alpha$ 7.126	4		2.00	2.2	Do.
Cu	$K\alpha$ 1.542	1	.005	0.25	2.0	Do.
Ni	$K\alpha$ 1.659	1	.004	1.00	0.4	Do.
Cr	$K\alpha$ 2.292	1	.005	1.00	.5	Do.
V	$K\alpha$ 2.505	1	.007	0.25	2.7	Do.
Mo	$K\alpha$ 0.711	1	.001	.25	0.4	Zr
Mo	$K\beta$ 0.632	4	.002	.25	.8	None

<sup>a</sup> Cast iron.



TABLE 4. Results for elements not commonly determined in low-alloy steel

Element	Wavelength	Integrat- ion time	Detecta- bility	Interfer- ence
	A	min	%	
S	K <sub>α</sub> 5.373	4	0.002	Co
Ti	K <sub>α</sub> 2.750	1	.015	None
Ti <sup>a</sup>	K <sub>α</sub> 2.750	1	.007	Do.
Co	K <sub>α</sub> 1.791	1	.002	Do.
Ge	K <sub>α</sub> 1.256	4	.003?	?
As	K <sub>α</sub> 1.177	4	.0007	Pb
Se	K <sub>α</sub> 1.107	1	.006	None
Zr	K <sub>α</sub> 0.788	1	.0006	Do.
Nb	K <sub>α</sub> 0.749	1	.002	Do.
Ag	K <sub>α</sub> 0.562	1	.0009	Do.
Sn	K <sub>α</sub> 0.493	1	.004	Do.
Ta	L <sub>α<sub>1</sub></sub> 1.522	4	.009	Do.
W	L <sub>α<sub>1</sub></sub> 1.476	4	.003	Do.
Pb	L <sub>α<sub>1</sub></sub> 1.175	4	.004	As
Pb	L <sub>β</sub> 0.982	4	.005	None

<sup>a</sup> Geiger tube; the detectors for other elements are listed in table 1.

Acceptable detectabilities have been obtained for most of the elements. Specifically, the observed detectability for sulfur in the cast irons, 0.002 percent, indicates that this element can be determined successfully in most steels and cast irons. Note that for titanium, a two-fold improvement in detectability was realized by the substitution of a Geiger for a proportional counter. Although not normally required, considerable additional improvement for titanium (and vanadium as well) could be realized by employing helium or a vacuum rather than an air path. Samples containing more than about 0.003 percent of germanium were not available for further study of this element.

## 5. Discussion

It is of interest to compare the X-ray spectroscopic method of analysis for low-alloy steels to the conventional optical emission method with respect to detectability, precision, and speed. Although X-ray spectroscopy has gained widespread use primarily in the determinations of major and some minor constituents, the observed detectabilities for the minor and trace elements contained in low-alloy steels show that the method can be extended satisfactorily to this application. For the majority of elements, however, the optical emission method offers a marked advantage in detectability.

(Paper 65C1-57)

It is difficult to compare the precision of the two methods without specific reference to the element, concentration, exposure time, and sample. For most elements and with normal exposure times, optical emission will provide better precision below 0.1-percent concentration; the precision of the methods are about equal for concentrations of 0.1 to 1.0 percent, while the X-ray method is superior for concentrations above 1.0 percent. A statement as to the accuracy of the two methods would be similar to that for precision, except that X-ray spectroscopy may provide an advantage, at least for the heavier elements, in the analysis of samples having different metallurgical history. This results from the fact that the chemical combination of the elements has little or no effect on X-ray spectroscopy, but may have a marked effect on volatilization in optical emission analysis.

The exposure time required for optical emission analysis of a sample of low-alloy steel for the elements manganese, silicon, copper, nickel, chromium, and molybdenum is about 30 sec. With the exception of silicon, the same analysis by X-ray spectroscopy requires about 1 min (although this time may be reduced to 30 sec providing the concentration of each element is above 0.1 percent). To include the silicon determination by X-ray spectroscopy would require a minimum of 4 min (but at the same time sulfur also could be determined). The use of a vacuum instead of a helium path, improvements in crystals and detectors, and shorter path length may reduce considerably the time required for the silicon determination or for other determinations that now require long integration times. It may be noted that while boron cannot be determined with available X-ray spectroscopy equipment, selenium and sulfur cannot be determined with conventional optical emission instrumentation.

With respect to standard samples, the investigation has shown that the set of eight NBS Ingot Iron and Low-Alloy Steel Standards (Nos. 1161 to 1168) can be applied to develop suitable analytical curves for the X-ray determination of As, Co, Cr, Cu, Mn, Mo, Nb, Ni, S, Si, Sn, Ta, Ti, V, W, and Zr. For the determination of Ag, Ge, Pb, and Se, additional standard samples are required.

## 6. References

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