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UNION CARBIDE

OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

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ABSTRACT

A method has been developed for the X-ray fluorescence determination of nickel, chromium, manganese, titanium, and silicon in stainless steel. Samples in the form of chips or turnings are melted in an arc furnace and the resulting button analyzed using an automated X-ray fluorescence spectrometer. The method has the advantages of being less time consuming and more precise than the atomic absorption and gravimetric procedures previously used.

CONTENTS

SUMMARY

X-ray fluorescence spectroscopy is shown to be a rapid and precise method for the determination of nickel, chromium, manganese, titanium, and silicon in stainless steel. The steel sample is melted in an arc furnace and the flat surface of the button is ground to a smooth finish. Elements of interest are analyzed on an automated X-ray fluorescence spectrometer and compared with primary and secondary standards. A comparison with the methods previously used indicated that the X-ray fluorescence method has a better precision while, at the same time, being less time consuming.

INTRODUCTION

Atomic absorption has been used successfully for the analysis of nickel, chromium, manganese, and titanium in stainless steel.(1,2) However, determining percentage quantities of metals by atomic absorption will often lead to large dilution errors and poor precision. Silicon in stainless steel is determined gravimetrically.(3) This method, though reasonably precise, is very time consuming and requires considerable skill.

The preparation of metallic buttons for X-ray fluorescence analysis utilizing a vacuum arc furnace has been described by Fahlbusch.(4) Various alloy steels were analyzed for chromium, manganese, molybdenum, nickel, and titanium. X-ray fluorescence has also been successfully used to analyze low-alloy steels and cast irons using solid-phase samples.(5) An extensive study of the interferences encountered when analyzing highly alloyed steels has been presented by Sermin.(6)

Work was undertaken at the Oak Ridge Y-12 Plant(a) to characterize and modify the X-ray fluorescence method to analyze the types of steels encountered in plant operations. Precision, accuracy, and interferences were evaluated using a modern, computer-controlled X-ray fluorescence spectrometer. The method was found to be ideally suited for use in a production control laboratory. Samples are received in the form of chips or turnings and are cleaned and arc melted to form a button. Alternatively, sheet or bar samples can be cut to the appropriate size and analyzed directly. The flat surface of the button is ground and polished to 240 grit. X-ray fluorescence intensities of chromium, manganese, nickel, titanium, and silicon are measured by the automated spectrometer. The percentage of each element present is then computed by direct comparison with primary and secondary standards.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

ANALYSIS BY X-RAY FLUORESCENCE

APPARATUS

To obtain a button for X-ray measurements, the electric arc button furnace (illustrated in Figure 1) was used. As indicated, the furnace consists of a water-cooled copper crucible supported on a jack, and a water-cooled copper housing through which a manually operated carbon electrode can be raised and lowered. The furnace is powered by a DC arc welder. A vacuum pump and argon supply are needed to evacuate and flush the crucible.

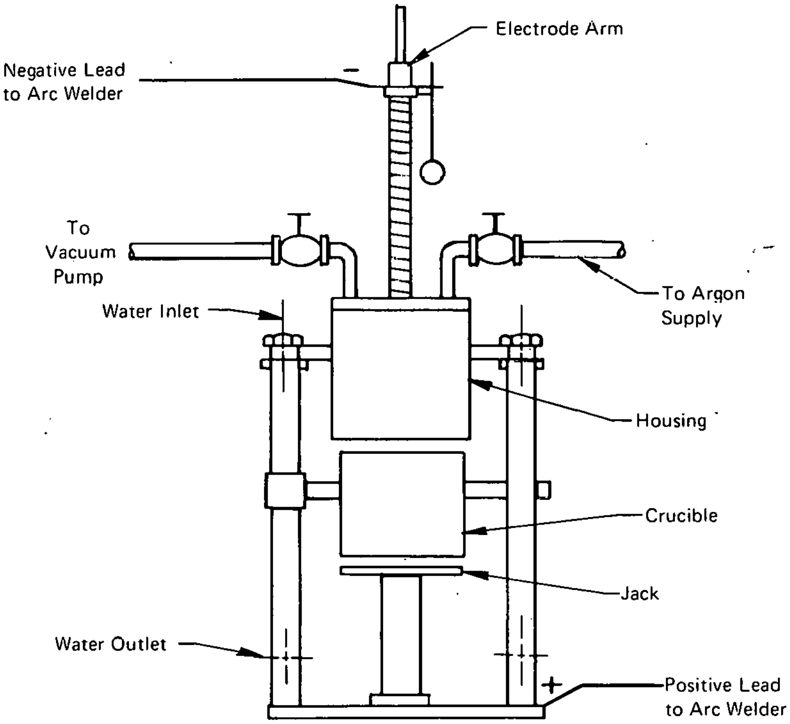

Figure 1. COMPONENTS OF THE ELECTRIC-ARC BUTTON FURNACE.

Belt sanders equipped with 60 and 100-grit aluminum oxide belts were used to grind the buttons. Final polishing was done with 240-grit aluminum oxide grit cloth.

All X-ray fluorescence measurements were made with an evacuable, automated X-ray spectrometer equipped with a ten-position sample changer, four analyzing crystals, 0.15 and 0.40-mm collimators, a wide-range goniometer, flow and scintillation detectors, and a measuring unit with a pulse height analyzer. The excitation source was a gold-target X-ray tube powered by a constant-potential X-ray generator. The automatic counting was controlled by a one-address, 12-bit, fixed-word-length, parallel computer with a teletypewriter printout.

PREPARATION OF STANDARDS

Primary Standards

Table 1 lists the primary stainless steel standards obtained from the National Bureau of Standards.

Standard D 847 was received with a deep fissure across the analyzing surface, but it was arc melted, ground, and polished to 240 grit. The remaining standards were polished to 240 grit.

Table 1

PRIMARY STAINLESS STEEL STANDARDS

Standard	Element Concentration (%)				
	Cr	Mn	Ni	Si	Ti
D 845	13.31	0.77	0.28	0.52	0.03
D 846	18.35	0.53	9.11	1.19	0.34
D 847	23.72	0.23	13.26	0.37	0.02
D 848	9.09	2.13	0.52	1.25	0.23
D 849	5.48	1.63	6.62	0.68	0.11
D 850	2.99	-	24.8	0.12	0.05

Secondary Standards

To extend the useful range on titanium and to check the calibration curves, two secondary standards were prepared by melting National Bureau of Standards standard-reference-material (SRM) steels. Table 2 lists the compositions of the SRM steels.

These standards were also ground and polished to 240 grit.

Table 2

SECONDARY STAINLESS STEEL STANDARDS

Standard	Element Concentration (%)				
	Cr	Mn	Ni	Si	Ti
SRM 101e	17.98	1.77	9.48	0.43	-
SRM 121c	17.58	1.31	10.51	0.64	0.42

OPTIMUM OPERATING CONDITIONS

Instrumental conditions were selected to minimize spectral and interelement interferences and to yield linear calibration curves. Since the method is based on direct-intensity comparisons between standard and sample, the X-ray fluorescence must be a linear function of the metal concentration and be independent of the steel type. The instrumental conditions in Table 3 were found to yield optimum analytical results. In each case, the base line/window adjustment was made as necessary.

Table 3

TYPICAL INSTRUMENT SETTINGS

Line	kV/mA	Crystal	Angle (deg)	Detector	Collimator (mm)
Mn Kα	35/20	$\text{LiF}^{(200)}$	62.970	Flow	0.15
Ni Kα	35/20	$\text{LiF}^{(220)}$	71.460	Flow	0.15
Cr Kα	35/20	$\text{LiF}^{(220)}$	107.360	Scintillation	0.15
Ti Kα	35/20	Pet	36.722	Flow	0.15
Si Kα	50/50	Pet	109.160	Flow	0.40

The $\text{LiF}^{(220)}$ (2d = 2.848) analyzing crystal was used for nickel and chromium to prevent detector flooding with possible coincidence errors. The scintillation detector was used for chromium for the same reason.

PROCEDURE

To properly prepare the sample, it is cleaned and degreased. Approximately 40 grams of the sample are placed in the furnace crucible and tamped, then the crucible is swung under the furnace housing and raised firmly against the housing by means of the hand-operated jack. Next, the crucible is evacuated and flushed twice. With the argon flow on, the arc welder is turned on and the electrode lowered until an arc is struck. As the metal melts and falls to the bottom of the crucible, the electrode is lowered to insure complete melting and homogeneous mixing of the melt. Finally, the arc welder is turned off and the button allowed to cool before removal from the crucible. Between each melting, the crucible is cleaned of excess carbon and the electrode replaced as necessary. Surface irregularities are removed from the flat surface of the button by the 60 and 100-grit belt sanders; final polishing is done with 240-grit cloth and the surface is wiped clean. The sample is loaded into the sample chamber along with the appropriate primary and secondary standards, then the computer is programmed to automatically select the correct crystal, angle, collimator, and detector for each element. An intensity measurement is made at each position for one element and printed out on the teletypewriter. The settings for the next element are made by the computer and the counting sequence repeated. (A 40-second count is normally taken.) Percent concentrations of all the elements are calculated by comparing the intensity measurements of the sample with those of the standards.

RESULTS AND DISCUSSION

A scan of a typical stainless steel button using a $\mathrm{LiF}^{(200)}$ (2d = 4.0267) analyzing crystal is presented in Figure 2. Note that the Mn Kα line is not completely resolved from the Cr Kβ line, one very obvious example of a possible spectral interference in the X-ray fluorescence measurements. Spectral and matrix interferences must be minimal, or nonlinear plots of intensity as a function of percent metal will result. This method can only be useful if the calibration curves for all the elements are linear over a sufficiently wide range of

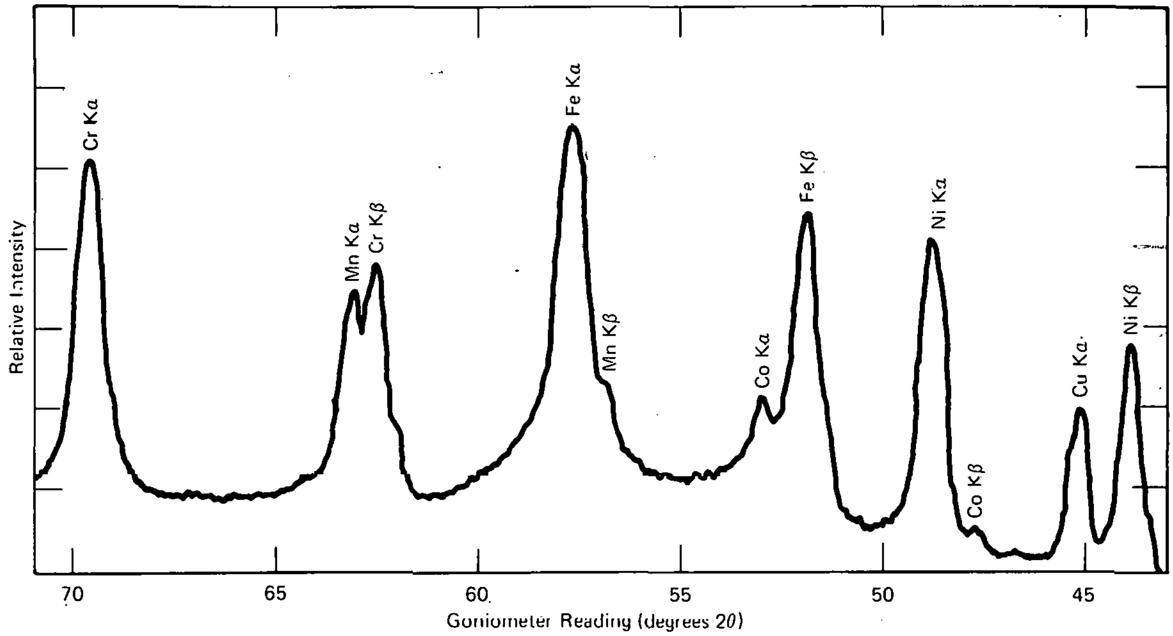

Figure 2. X-RAY FLUORESCENCE SPECTRUM OF A TYPE 304L STAINLESS STEEL BUTTON.

concentrations to accommodate many different types of stainless steel. Plots of fluorescence intensity versus percent metal for nickel, chromium, manganese, titanium, and silicon obtained with the instrument settings in Table 3 are given in Figures 3 through 7. The curves show that the fluorescence intensity is a linear function of percent metal and independent of the type of steel.

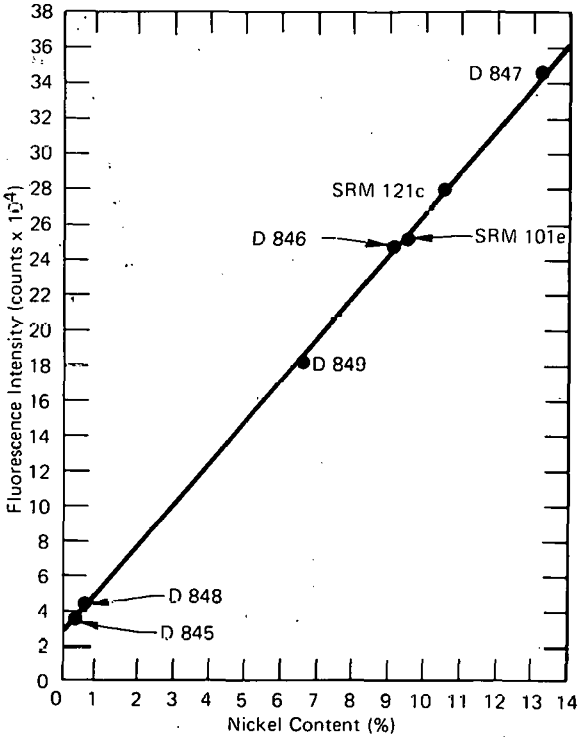

Figure 3. X-RAY FLUORESCENCE INTENSITY VERSUS THE PERCENT NICKEL.

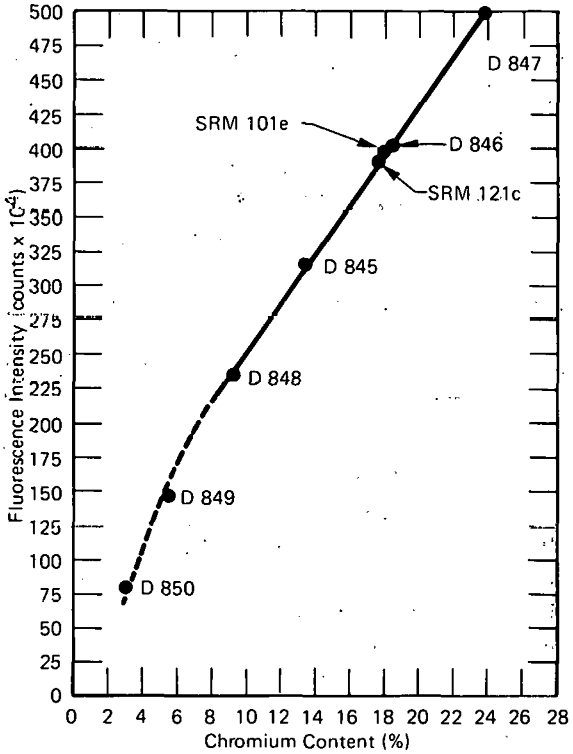

Figure 4. X-RAY FLUORESCENCE INTENSITY VERSUS THE PERCENT CHROMIUM.

These results disagree with Sermin(6) who indicated that the fluorescence intensity of chromium and titanium are dependent upon the steel type. The slight deviation of the chromium curve from linearity at low concentrations can be ignored since all the steels analyzed have greater than 10 percent chromium.

Before X-ray fluorescence was accepted as a satisfactory substitute for the atomic absorption and gravimetric methods, a methods comparison was conducted using a Type 304L steel control. The results are summarized in Table 4. The limit of error of the mean (LE) is defined as:

$$\text{LE mean} = tS/\sqrt{n}, \tag{1}$$

where:

S represents the standard deviation of the result,
t the "t" statistic at the 95 percent confidence limit, and
n the number of measurements made.

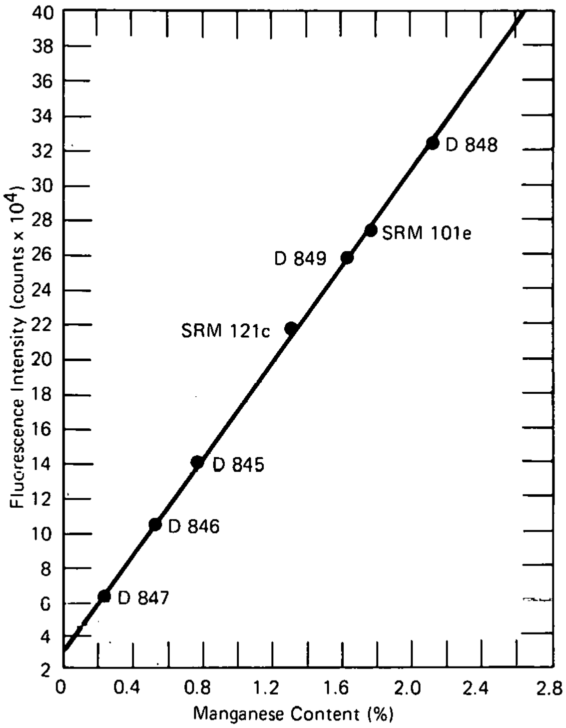

Figure 5. X-RAY FLUORESCENCE INTENSITY VERSUS THE PERCENT MANGANESE.

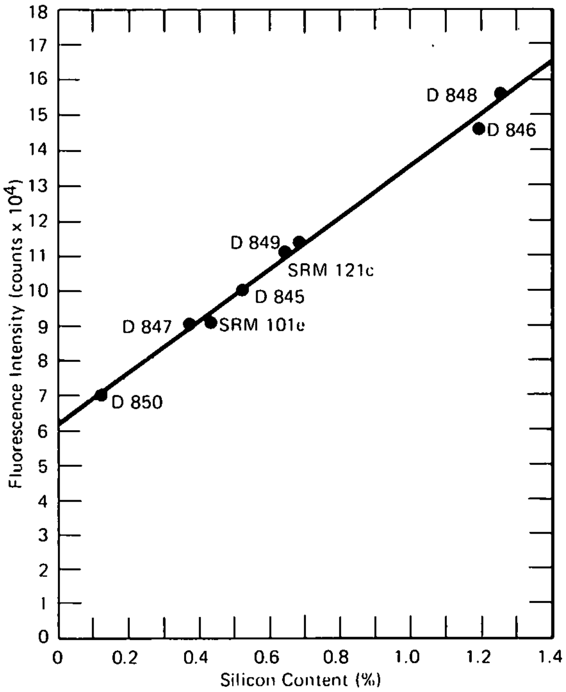

Figure 6. X-RAY FLUORESCENCE INTENSITY VERSUS THE PERCENT SILICON.

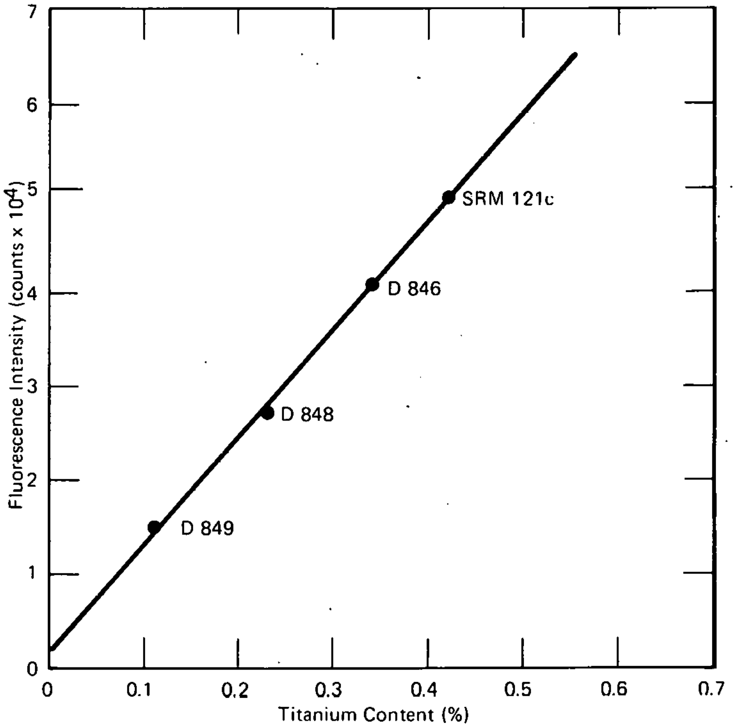

Figure 7. X-RAY FLUORESCENCE INTENSITY VERSUS THE PERCENT TITANIUM.

Table 4

METHODS COMPARISON OF STEEL CONTROL

Element	Number of Comparisons	X-ray Fluorescence		Atomic Absorption/Gravimetric(1)	
		Mean Weight Percent, ± LE Mean	Relative LE (%)	Mean Weight Percent, ± LE Mean	Relative LE (%)
Ni	10	9.264 ± 0.019	± 0.65	9.38 ± 0.21	± 8.0
Mn	10	1.690 ± 0.011	± 2.0	1.654 ± 0.022	± 4.5
Cr	10	18.581 ± 0.074	± 1.3	18.43 ± 0.17	± 3.2
Si	19	0.516 ± 0.016	± 13.8	0.519 ± 0.011	± 9.1

(1) Ni, Mn, and Cr by atomic absorption; Si by gravimetric.

The relative percent limit of error is defined as:

$$\text{Relative LE} = (tS/\bar{x})\,100\,, \tag{2}$$

where $\bar{x}$ represents the mean of the results.

Thus, the limit of error expected for a single analysis can be found from:

$$\text{LE single} = \text{LE mean} \times \sqrt{n}\,. \tag{3}$$

After the analysis of stainless steel by X-ray fluorescence was put on a routine basis, another comparison of precision was made for the laboratory steel control covering three-month periods. The relative limits of error (0.95) for routine analysis are presented in Table 5.

Table 5

METHODS COMPARISON OF ROUTINE
STEEL CONTROL

Element	X-Ray Fluorescence, Relative LE (%)	Atomic Absorption/Gravimetric, Relative LE (%)
	January - March 1972	January - March 1971
Ni	± 1.7	± 8.0
Mn	± 2.9	± 4.5
Cr	± 1.4	± 3.2
	April - June 1972	October - December 1971
Si	± 10.4	± 12

The data given in the preceding tables represent an average of duplicate aliquots for the atomic absorption and gravimetric methods, while only one aliquot was analyzed by X-ray fluorescence. Thus, the precision obtained by the X-ray fluorescence method on a single aliquot is equivalent to or better than the precision obtained on duplicate aliquots by the atomic absorption and gravimetric methods. It has been estimated that 1.5 hours of analysis time per sample have been saved by the X-ray fluorescence analysis of stainless steel. Additional savings can be obtained for the analysis of any other elements for which the standards are certified, since all analyses are done on a single button. The only serious disadvantage of the method is the large amount of sample required.

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