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DETERMINATION OF IRON, CHROMIUM,
AND NICKEL BY X-RAY FLUORESCENCE
AQUEOUS SOLUTION METHOD



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ABSTRACT

The iron, chromium, and nickel content in many types of stainless steels were determined by X-ray fluorescence. The steel samples were dissolved in aqua regia and hydrofluoric acids, fumed with perchloric acid and diluted to volume with water. The fluorescence data were obtained for specific K alpha lines and the intensities were compared to the background intensity reading obtained at 0.6 A, and the values obtained from a standard plot.

The values so obtained were within 3 per cent of the recommended values of NBS samples.

The curves obtained for stainless steels are also applicable to certain chromium-nickel alloys.



I. INTRODUCTION

Methods for the analysis of stainless steel by X-ray fluorescence have been introduced in the past several years. The usual methods utilize solid steel samples with a prescribed surface area and surface finish.¹ However, these methods have not been adaptable to chips, drillings or powders. Many laboratories having the required instrumentation do not have control over the shape of the samples received and as a consequence must resort to the longer wet chemical methods for such materials. The need for an X-ray fluorescence method utilizing these samples is quite evident and this paper proposes an aqueous solution X-ray fluorescence method for the determination of the three important elements in stainless steels.

One of the disadvantages of the solid-sample method has been the interelement effect. In the case of chromium in stainless steels this error may be as much as 25 per cent of the amount of chromium present.¹ This error can be compensated for either by making a mathematical calculation to correct the interelement effect or by making separate working curves for each type of stainless steel alloy.^{2, 3} In the latter case the number of standards needed to make the working curves would be large.

The aqueous solution method would have the following advantages over the solid sample method: no specific surface area or surface finish on the sample would be necessary, the size of the sample could be reduced several hundred times, the addition of internal standards to eliminate any interelement effect or instrumental variations would be simplified, and one standard sample would be sufficient to make a working curve to cover many types of alloys.

The discovery by George Andermann² at Applied Research Laboratories that the scattered radiation at 0.6 A could be used as an internal standard in analyzing fuel stock oils and ores at low concentrations suggested the possibility of using this radiation as our internal standard. This would simplify the method in that the preparation and addition of an internal standard to the sample would not be necessary. The only disadvantage to the solution type of X-ray analysis would be that the physical state of a small amount of sample would be destroyed; however, the solution could be used for further wet analytical tests.



II. APPARATUS AND REAGENTS

The apparatus used in this laboratory consists of a North American Phillips X-ray Spectrograph with a molybdenum target X-ray tube and a lithium fluoride analyzing crystal. The X-ray tube was operated at 46 kv and 38 ma. An argon-filled Geiger tube was used to record the counts. The solution cell⁴ was of our own design and the window used was acetate Scotch tape. The Scotch tape was used because of the ease with which it could be placed on the cell and stripped off, and because it was readily available. This window has a transparency to X-rays equivalent to a 0.008-inch Mylar film.

Reagent grades of hydrochloric, hydrofluoric, nitric, and perchloric acids were used to dissolve the samples.

III. EXPERIMENTAL PROCEDURE

A. STANDARD WORKING CURVE

Perchloric acid solutions of NBS steel samples in known concentrations were prepared. The time to record 25,600 count was measured for the K alpha lines of iron, chromium, nickel, and for the background at 0.6 A. The ratio of each element to background was calculated. The respective ratios were plotted against the concentrations (mg/ml) to form the working curves for the chromium, iron, and nickel.

B. SAMPLE PREPARATION

The sample of stainless steel weighing one-half gram was dissolved in 10 ml of a mixture of nitric and hydrochloric acids. Several drops of hydrofluoric acid and 8 ml of perchloric acid were added and the solution was evaporated until dense fumes of perchloric acid were given off. The solution was cooled and diluted to 100 ml with water. Approximately 10 ml of the solution were used to fill the solution cell.⁴ The time to record 25,600 counts was measured for the K alpha lines of the iron, the chromium, the nickel and the background at 0.6 A. The ratio of the element to background was calculated and the milligrams of the element were obtained from the previously prepared working curves.



IV. RESULTS

Stainless steels are customarily dissolved in a mixture of nitric and hydrochloric acids, but when solutions were prepared in this manner the results obtained by X-ray fluorescence for iron, chromium, and nickel were not consistent.

A study of the change in concentration of selected acids was then made to determine the effect on background intensities (Fig. 1).

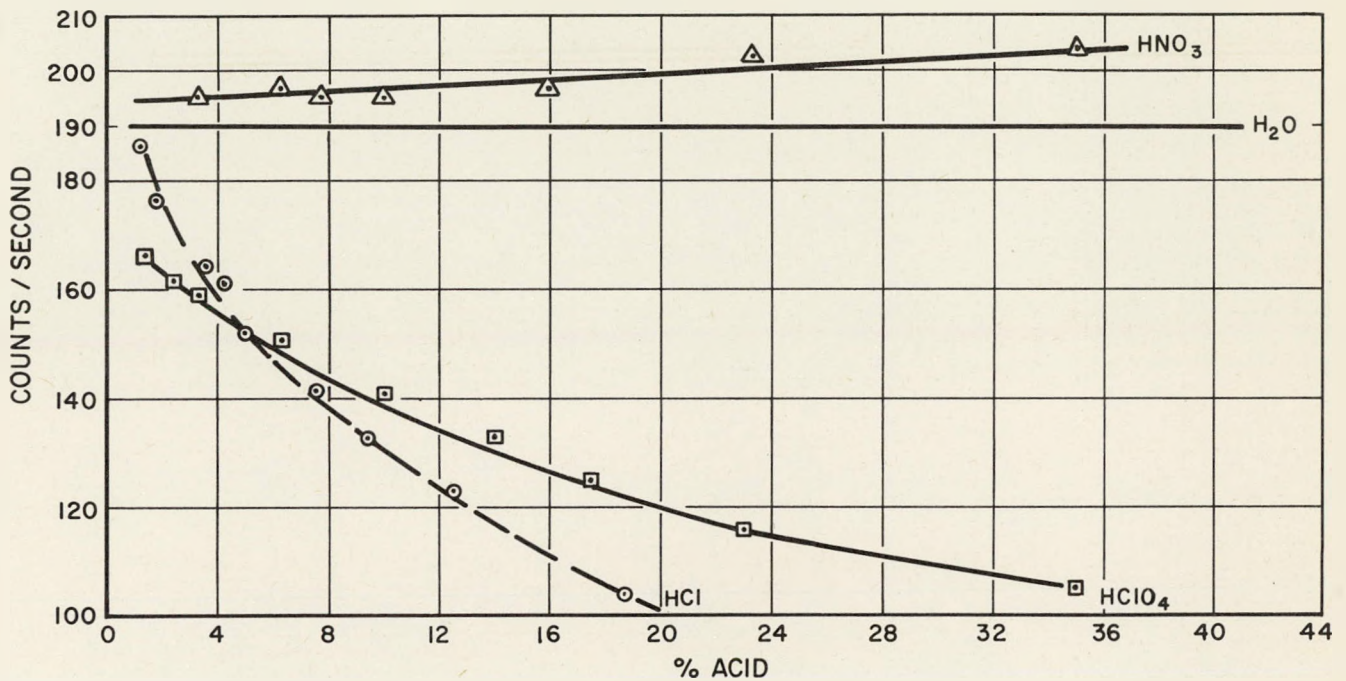


Fig. 1. Variation of Background with Concentration of Acid at 0.6 A

Nitric acid appeared to be the ideal solution acid to use as there were practically no changes in background intensities with large changes in acid concentration. Unfortunately, nitric acid alone will not dissolve the stainless steel. Hydrochloric acid alone will not dissolve the carbides present in the steel and small changes in hydrochloric acid concentration made large changes in the background intensities. The changes in background intensities with changes in perchloric acid concentration



were about one half that for hydrochloric acid. However, after the higher-boiling perchloric acid has been used to volatilize the other two acids from the solution, the ratio of the intensities of the elements to the intensity of the background remained constant.

Typical working curves for iron, chromium and nickel are shown in Fig. 2, 3, and 4.

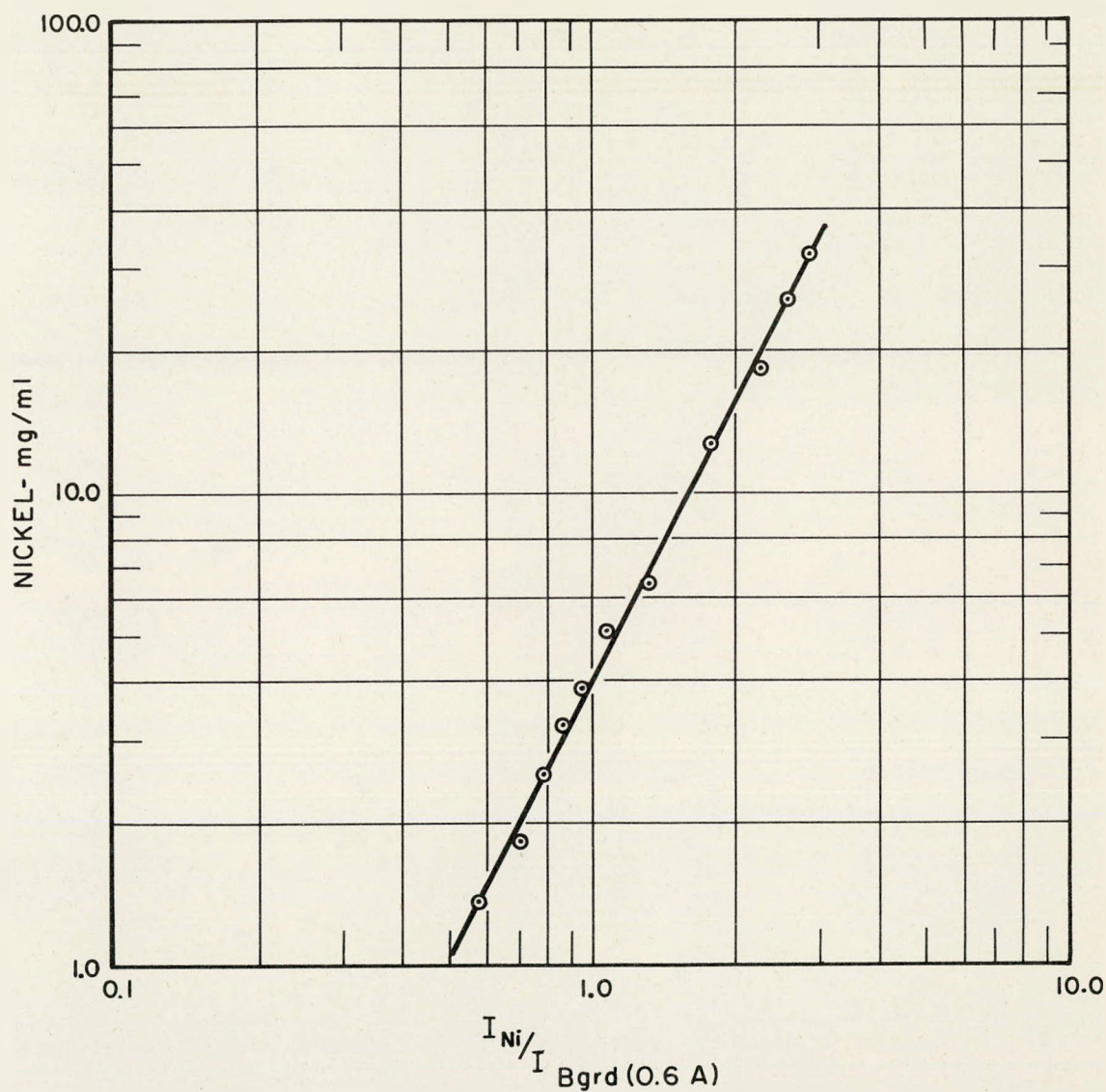


Fig. 2. Nickel in Ferrous Alloys - Perchloric Acid Solution Method (Range 1 to 32 mg/ml)

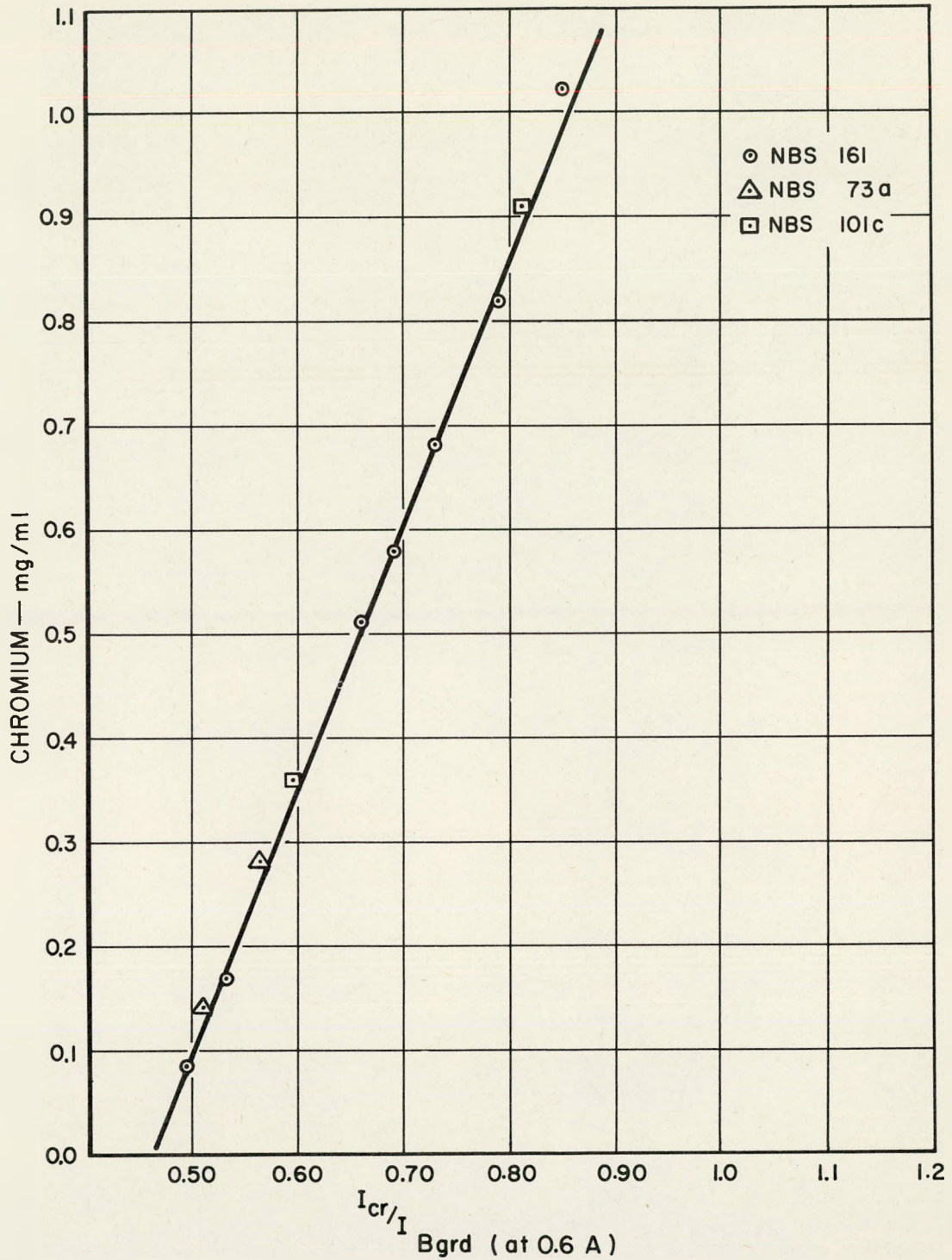


Fig. 3. Chromium in Ferrous Alloys - Perchloric Acid Solution Method (Range 0 to 1.0 mg/ml)

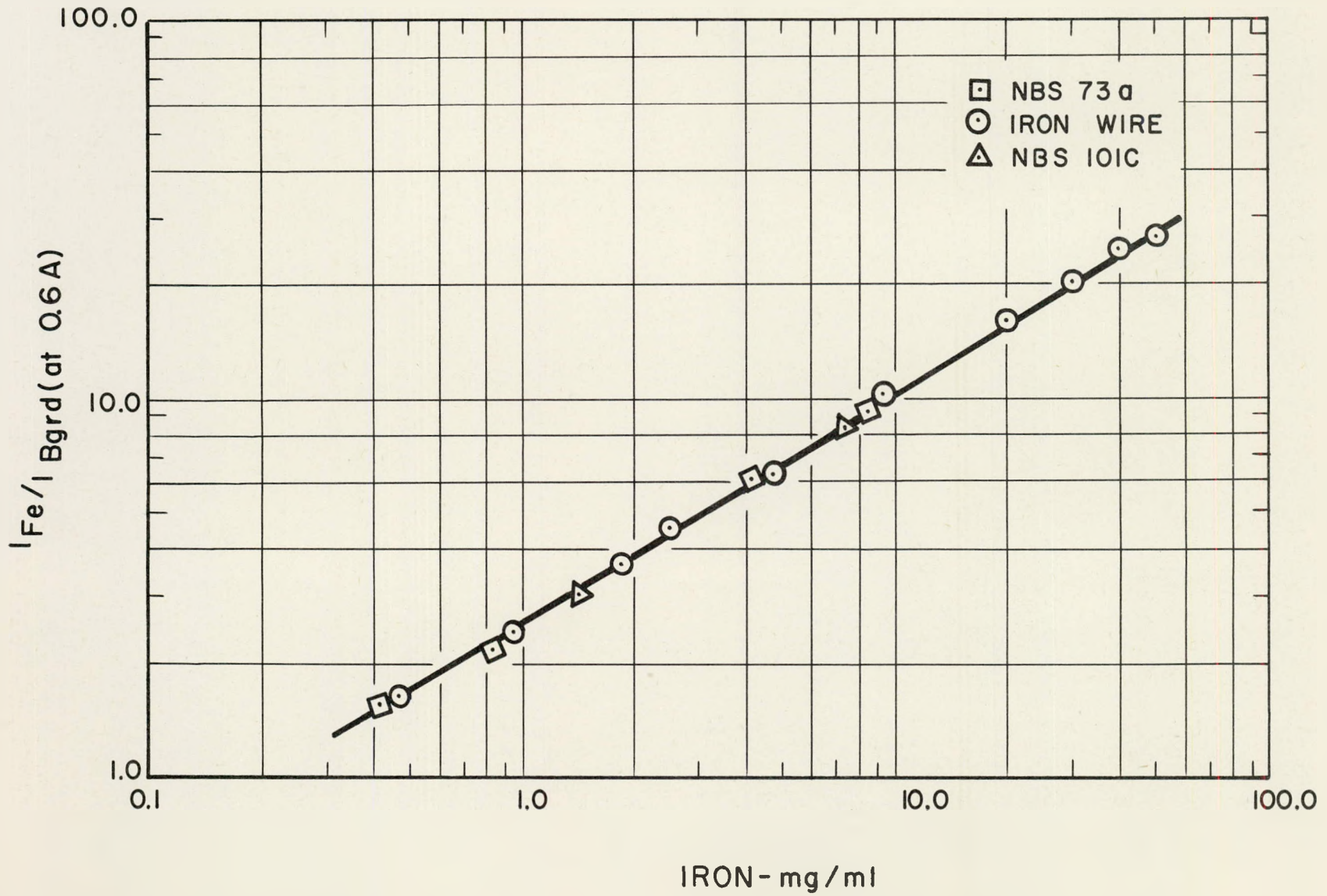


Fig. 4. Iron in Ferrous Alloys - Perchloric Acid Solution Method
(Range 0.4 to 50.0 mg/ml)





The possibility of using these curves for alloys other than stainless steels was suggested by the receipt of two samples of chromel. Upon analyzing these samples for nickel by the X-ray method the results of 76 and 78 per cent respectively were obtained. The results were confirmed by wet chemical methods.

In Table 1 the different types of alloys successfully analyzed by this method are shown. Sample NBS 134 is of particular interest in that it contains 8.68 per cent molybdenum and 1.82 per cent tungsten. These two elements precipitate in a perchloric acid solution. Intensities for the iron, chromium, nickel and background were taken while the molybdenum and tungsten were in suspension. The solution was then allowed to stand for 24 hours so that all of the precipitate would settle out of the solution. The supernatant liquid was then analyzed and no change in the ratio of element to background was noted between this and the original suspension.

V. DISCUSSION

The interelement effect is not observed in the solution method. This can be attributed to the fact that the elements present in the steel have been diluted by a factor of 200 in the test solutions. The use of an internal standard could also eliminate this effect. In Table II the range and accuracy of the method is shown. The limit of detection is 0.1 mg/ml of solution. The working curves are straight lines up to 32 mg/ml for chromium, and nickel and up to 50 mg/ml for iron. The method was not carried beyond these limits. The accuracy of the method is 3 per cent of the element present over the entire range of concentration.

The X-ray fluorescence method has application because of its simplicity and speed, as described in the procedure. The use is obvious when a sample of stainless steel is to be identified as to type by its iron-chromium-nickel content.



TABLE I
COMPOSITION OF STANDARDS

NBS Samples	Iron %	Chromium %	Nickel %
73a	84.5	14.1	0.16
101c	70.8	18.2	9.3
135	93.1	5.5	0.08
106a	96.9	1.15	0.28
134	83.1	3.73	0.08
161	15.3	16.9	64.3
Iron Wire	99.98		

TABLE II
EXPERIMENTAL RESULTS

Element	Number of Samples	Range mg/ml	Accuracy
Nickel (0-64%)	24	0.1-32.0	~ 3%
Chromium (1-25%)	24	0.1-32.0	~ 3%
Iron (0-100%)	30	0.1-50.0	~ 3%



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