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THE USE OF SYNTHETIC STANDARDS IN THE DETERMINATION OF MINOR CONSTITUENTS IN MILD STEELS BY X-RAY SPECTROGRAPHY

by

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SUMMARY

The use of Mines Branch secondary standards for the determination of niobium and zirconium in mild steels has been evaluated. Their acceptance has, in turn, validated the preparation of synthetic standards from electrolytic iron and the alloying metal in question.

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INTRODUCTION

X-ray spectrography, like emission spectrography, suffers from a lack of standards for non-routine, investigational analysis. In the Mineral Sciences Division this has resulted in the use of synthetic standards for the determination of minor constituents in mild steels. Investigation reports have been issued regarding the determination of 3 elements on this basis, specifically: Zr (1), Nb (2) and Hf (3).

Recently, the validity of the use of synthetic standards in the determination of Nb and Zr has been further investigated. This report contains the results of this investigation.

STANDARDS AVAILABLE

A number of low alloy steel standards, $1\frac{1}{4}$ inches in diameter, have been prepared for spectrographic use by the National Bureau of Standards, Washington, D.C. The concentration of Mo, Nb and Zr in them is shown in Table 1. It is necessary to consider the Mo in these standards, as it affects the determination of background counts, interferes with ZrKβ radiation and, in the higher concentrations, with NbKα.

It has been shown elsewhere (1) that for some of these standards, complete separation of the characteristic X-radiation of the 3 elements is impossible. In addition, because early groups of samples received for Nb and Zr determination contained much less than 0.10 per cent of these elements, there was an insufficient number of NBS standards in the appropriate concentration range. To meet the need an adequate number of synthetic standards were prepared.

SYNTHETIC STANDARDS

The synthetic standards were prepared from electrolytic iron with additions of the element in question (1, 3). The preparation of these standards was tedious and the grinding quite unpleasant. To reduce the grinding time by reducing the weight of the electrolytic iron would have greatly increased the weighing or dilution errors of the additions.

Portions of the samples had also to be dissolved, dried and ground for comparison with the standards.

SECONDARY STANDARDS

Samples have been submitted in the form of discs approximately 2 inches in diameter. The use of such samples as secondary standards, when their composition is well established, would greatly reduce the time required for the analysis of unknowns and eliminate the distasteful grinding. For these reasons, it was decided to establish secondary standards.

From the earliest groups of samples analyzed a number were chosen which formed an appropriate concentration series. Powders prepared from them were analyzed several times on different days and the mean value of the analyses was assigned to the corresponding discs. Then the discs were counted and a regression equation was calculated.

Once secondary standards were available, all samples were analyzed by comparison with them. As new samples presented a wider range of concentration, selected ones were analyzed several times and used as additional secondary standards. This had led to extrapolation beyond the original standard range and concern has been felt that any error in the original secondary values could have been compounded as the newer standards have been added.

NIOBIUM SECONDARY STANDARDS

Recently steels were received for the determination of Nb in which the expected concentration was more than double that of the secondary standards. It was decided to use a mixture of NBS and secondary standards for these samples rather than prepare synthetic standards of corresponding concentration. This would be a simpler operation and would also resolve any doubts about the secondary standards.

Three NBS and 4 Mines Branch secondary standards were chosen. Because of the presence of Zr and Mo in the NBS standards the background had to be determined by interpolation from counts at 4 points. The results, in duplicate, are shown in Figure 1 with the resultant standard line. The standards were all counted once and then the counts repeated. The variables affecting the difference in the counts between duplicates were: sample area exposed, sample positioning, goniometer positioning and voltage fluctuation. There is, as well, greater error in estimating the background by interpolation than by 2 counts equidistant from the peak - the procedure when secondary standards alone are used.

ZIRCONIUM SECONDARY STANDARDS

As a further check, some Zr secondary standards were compared with NBS standards. Again the background was estimated by interpolation, but its estimation was more complex than for Nb. Four points were used for the secondary standards but only 3 of these could be used for NBS standards due to the presence of Nb. The results which are presented in Figure 2 show a greater scatter than the Nb counts.

The NBS standards of themselves do not give a straight line. This is an effect of the Nb which is present in these standards in equivalent or greater concentrations than Zr and has contributed to the Zr peak. In this instance, the secondary standards give a better line.

CONCLUSIONS

The use of synthetic standards for the determination of minor components in mild steels and the establishment of secondary standards based on results so obtained are justified if sufficient care is exercised in preparing the synthetic standards.

REFERENCES

1. Reed, D.J., "The Determination of Small Amounts of Zirconium in Steels by X-ray Spectrography". Mines Branch Investigation Report IR 61-14, February 17, 1961.

2. Reed, D.J., "The Determination of Small Amounts of Niobium in Mild Steels by X-ray Spectrography". Mines Branch Investigation Report IR 63-36, March 18, 1963.

3. Reed, D.J., "The Determination of Small Amounts of Hafnium in Mild Steels by X-ray Spectrography". Mines Branch Investigation Report IR 65-23.

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DJR:ST

TABLE 1

Concentration of Three Components in NBS Low Alloy Steels

Sample	% Mo	% Zr	% Nb
1161	0.300	< 0.005*	0.011
1162	0.080	0.063	0.096
1163	0.120	0.200	0.195
1164	0.029	0.010	0.037
1165	0.005	0.002*	0.001*
1166	0.011	< 0.005	0.005
1167	0.021	0.094	0.290
1168	0.200	< 0.005*	0.006

* values not certified

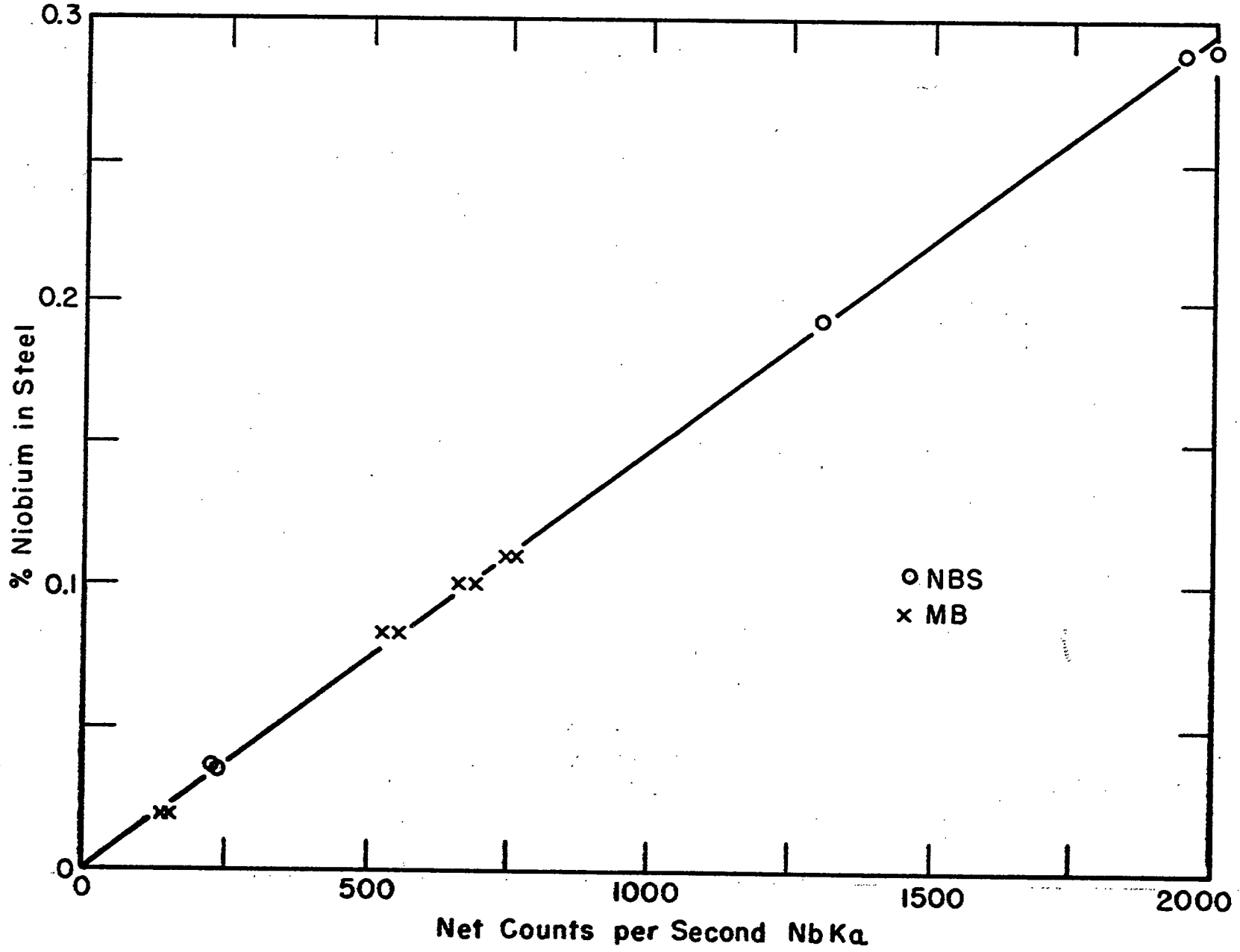

FIGURE I COMPARISON OF NBS AND MINES BRANCH STANDARDS FOR Nb.

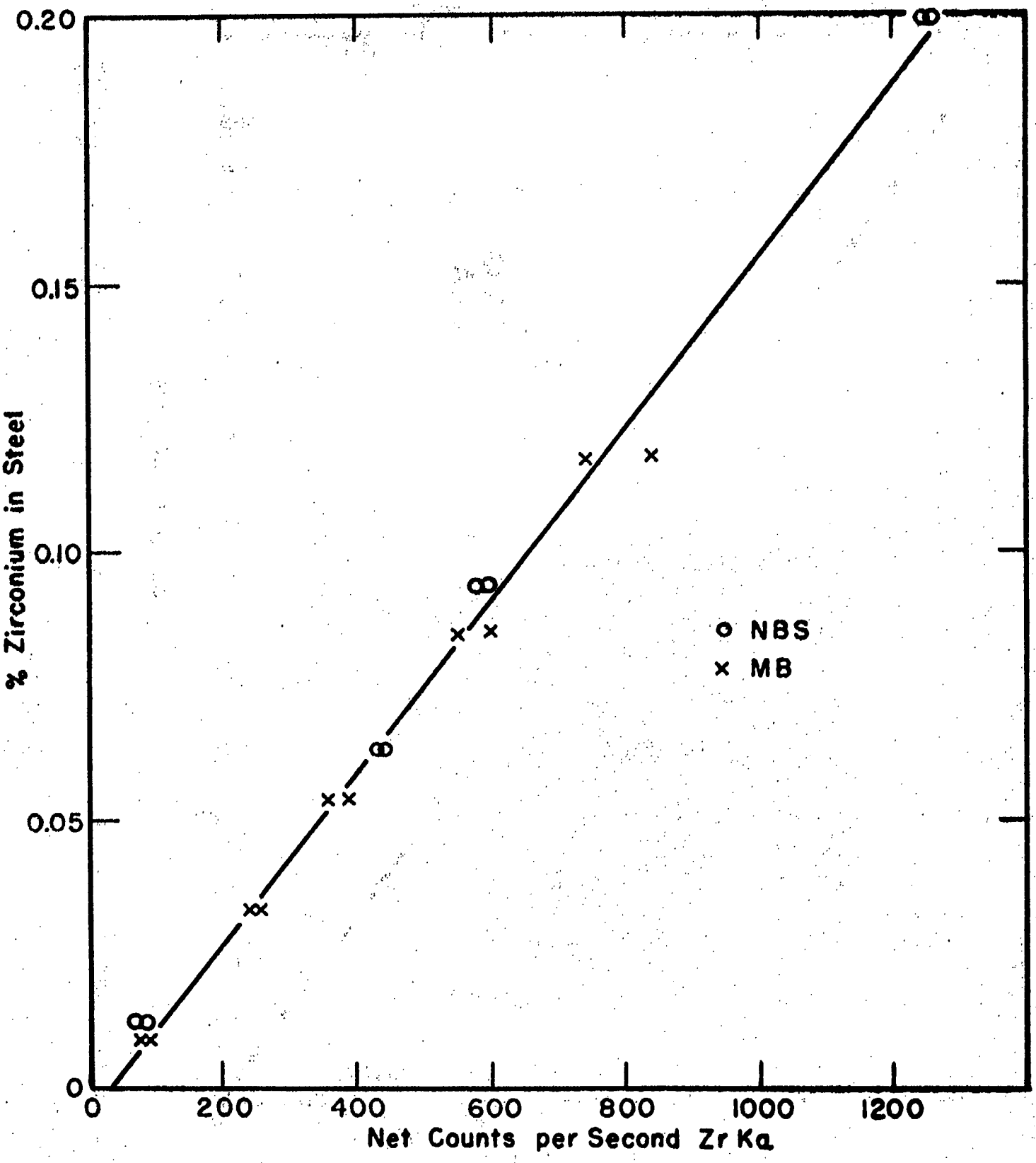

FIGURE 2 COMPARISON OF NBS AND MINES BRANCH STANDARDS FOR Zr.