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MINES BRANCH INVESTIGATION REPORT IR 63-36

THE DETERMINATION OF SMALL AMOUNTS OF NIOBIUM IN MILD STEELS BY X-RAY SPECTROGRAPHY

by

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Dorothy J. Reed*

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INTRODUCTION

This report is a successor to Mines Branch Investigation Report IR 61-14, which dealt with the determination of Zr as a minor constituent in mild steels. The problems in the determination of Nb are essentially the same as those of Zr, but additional counting techniques have been tested. Mines Branch secondary steel standards have been established for both elements.

DISCUSSION

As mentioned in the previous report, the size of NBS low alloy steel standards made the use of a Pt mask necessary. The irradiated area of the samples was reduced, thus decreasing the intensity of the secondary X-rays and raising the lower limit of detection. By off-centering the hole in the mask and positioning it and the sample in the sample holder with care, the effect of the mask was kept to a minimum.

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Most of the samples submitted were polished discs of two-inch diameter that could be used without a mask. It was therefore decided to try to establish a number of these discs as secondary standards and, using them, determine the limit of detection of Nb in mild steel and the accuracy of its determination.

The use of such secondary standards would have additional advantages for general analyses. The absence of Zr and Mo would eliminate any effect their presence in NBS standards might have on Nb radiation (see IR 61-14). The determination of background intensity would be simpler and more accurate with neighbouring elements absent.

THE DETERMINATION OF NIOBIUM

a) Interpolated Background

For ready reference, Figure 1 of the earlier report is included as Figure 1 of the present one. It shows scans of two NBS standards and illustrates the difficulty of obtaining a background count, except by interpolation from counts taken at not less than three carefully chosen points.

Figure 2 presents the scan of a mild steel containing 0.036% Nb at two excitation potentials. The slope of the continuum and the factors affecting it were discussed previously. Even in the absence of neighbouring elements (a minute amount of Mo is indicated in the 90 kV scan) interpolation is necessary for the background. The straighter slope from the higher potential makes a better estimation possible. A regression line was established using NBS standards measuring the background at 19.50, 23.50 and 24.00° 2θ LiF with 90 kV and 20 mA excitation. NbK_α was counted at 21.35°. With Mines Branch samples, a fourth background count may be taken at 22.00°, but ZrK_α interferes in the case of the standards. The equation of the line was $Y = 0.00010302X - 0.0048$ where Y is % Nb and X net cps. The correlation coefficient was +0.9996 and the standard error of prediction $\pm$ 0.0023, making the CV of the mean of y 3.35%.

b) Scan Count

It seemed possible that variation in the continuum slope might be compensated for by taking a count as the goniometer scanned the sample from the point below the Nb peak on the 2θ scale where Nb radiation emerges from the background to a point an equal distance above it. This would estimate the total area under the Nb peak. The background would be the mean of the counts at the two limiting points. This procedure would reduce the sensitivity as the intensity of the radiation in cps would be measured over its full Gaussian spread, not just at its maximum, but it might result in a more reproducible net count.

The Norelco counting panel can be set to count for a number of preset times. The maximum is 64 seconds making it possible to scan 0.53° 2θ each side of a peak with the goniometer moving at 1°/min. The total 2θ angle of 1.06° matched the spread of the Nb radiation under the conditions used. Scan counts were made from 20.82 to 21.88° 2θ at 90 kV and 20 mA and the background counted at these two angles. Standards high in Mo and Zr had to be omitted because of interference. The equation of the line was $Y = 0.0002978X - 0.0026$. A correlation coefficient of + 0.9996 was found and a standard error of $\pm$ 0.00147 giving a CV of 3.29%.

c) Counted Background

If there are no intervening peaks, it is customary to take background counts at points a degree or two removed from the peak in question, where the background has reached a constant value. Figure 2 shows that this is impossible in the case of small amounts of Nb in steels. The backgrounds measured for the scan counts were remarkably constant from sample to sample, and it was, therefore, practicable to measure the background just where the Nb peak emerged from it. Scans of a number of samples indicated that 20.60 and 22.20° 2θ LiF would be satisfactory positions. This technique can be used when Mo and Zr are absent or are present in minute amounts - 0.005% or less.

Determinations by the three methods were made using a scintillation counter with 900 V applied emf, an amplifier gain of 90 and a baseline of 18 V. Pulse height discrimination curves and scans under varying conditions indicated that these conditions gave the best peak-to-background ratio and continuum slope.

MINES BRANCH SECONDARY STANDARDS

From samples submitted and analysed by the first method, a number were chosen that gave a representative coverage. These were again analysed by the first method, then by scan count in duplicate against the NBS standards. Results differed by $\pm$ 0.002% at most. The mean was taken as the Nb content of these secondary standards. It varied from 0.012 to 0.045%. This range will be extended as circumstances permit.

Counted in triplicate by method (c), these secondary standards gave a line having the equation $Y = 0.00007466\,X - 0.00026$ with a correlation coefficient of + 0.9992. The standard error of prediction was $\pm$ 0.000513, which made the CV of the mean of y $\pm$ 1.79%. The small value for "a" in the equation indicates that estimation of the background by counting at the limits of the peak spread is extremely good. A net of 10 cps, which can be made significant by counting for a sufficiently long time, is equivalent to 0.0005% Nb.

Secondary Zr standards containing from 0.001 to 0.07%, have also been established.

LIMITS OF THE INVESTIGATION

In this investigation, NBS standards containing up to 0.195% Nb were used, and the determination of Nb in mild steels is thus, at present, limited to 0.2% of the element. If larger concentrations are to be determined, powdered synthetic standards, such as were used for Zr in the previous work, will have to be prepared.

CONCLUSIONS

Nb in mild steel may be estimated within 2% of the amount present, if Zr and Mo are not present in significant amounts. In the presence of these elements the error of the determination is almost doubled.

With the 100 kV spectrograph the limit of quantitative determination is 5 ppm.

Several counting techniques for the determination of Nb as a minor constituent in steels have been tested and found satisfactory. In deciding the technique to be employed, consideration must be given not only to the nature of the samples submitted and of the available standards, but also to their composition and size.

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DJR/DV

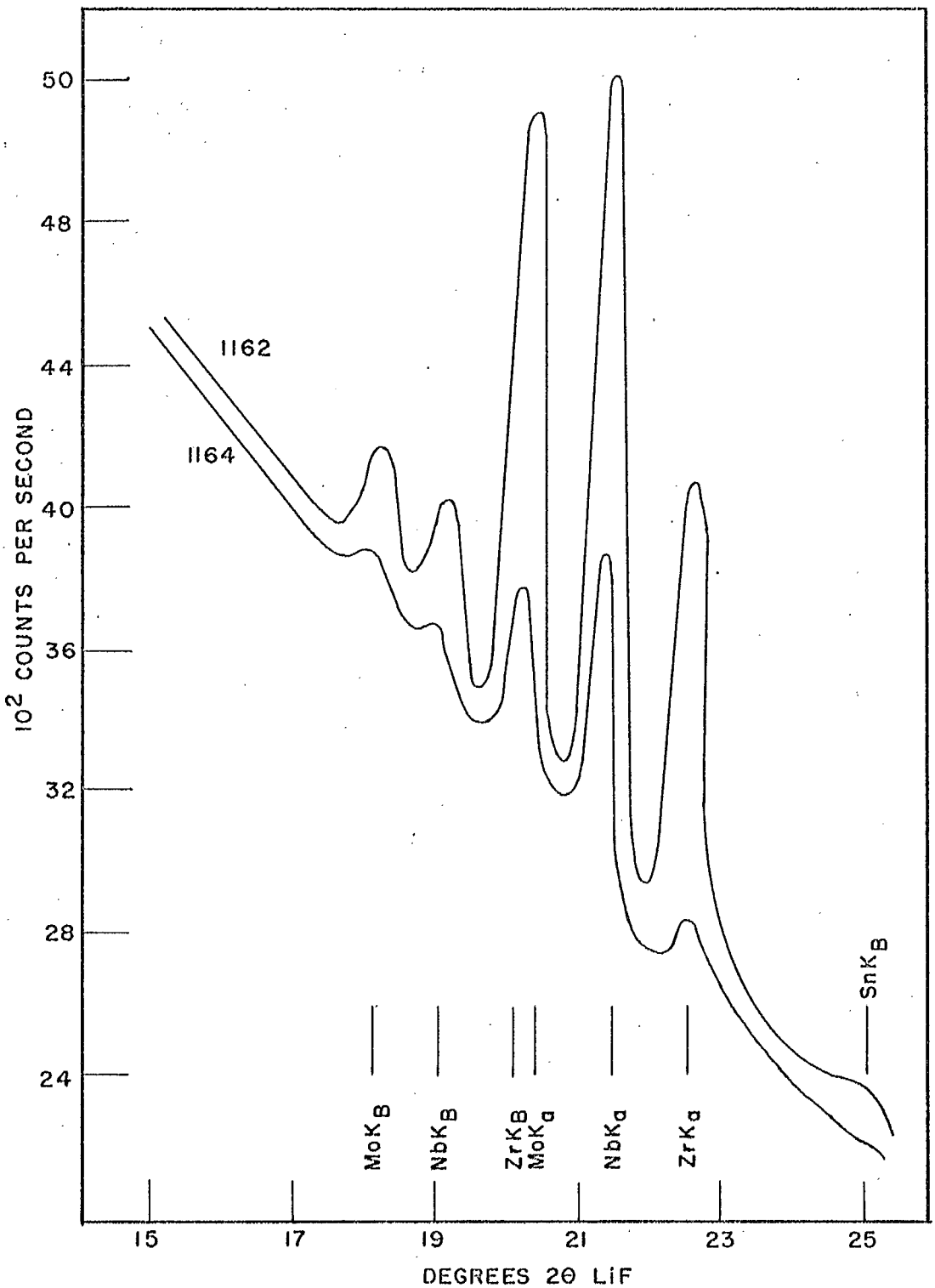

Figure 1. Count Scan of Low Alloy NBS Steel Standards.

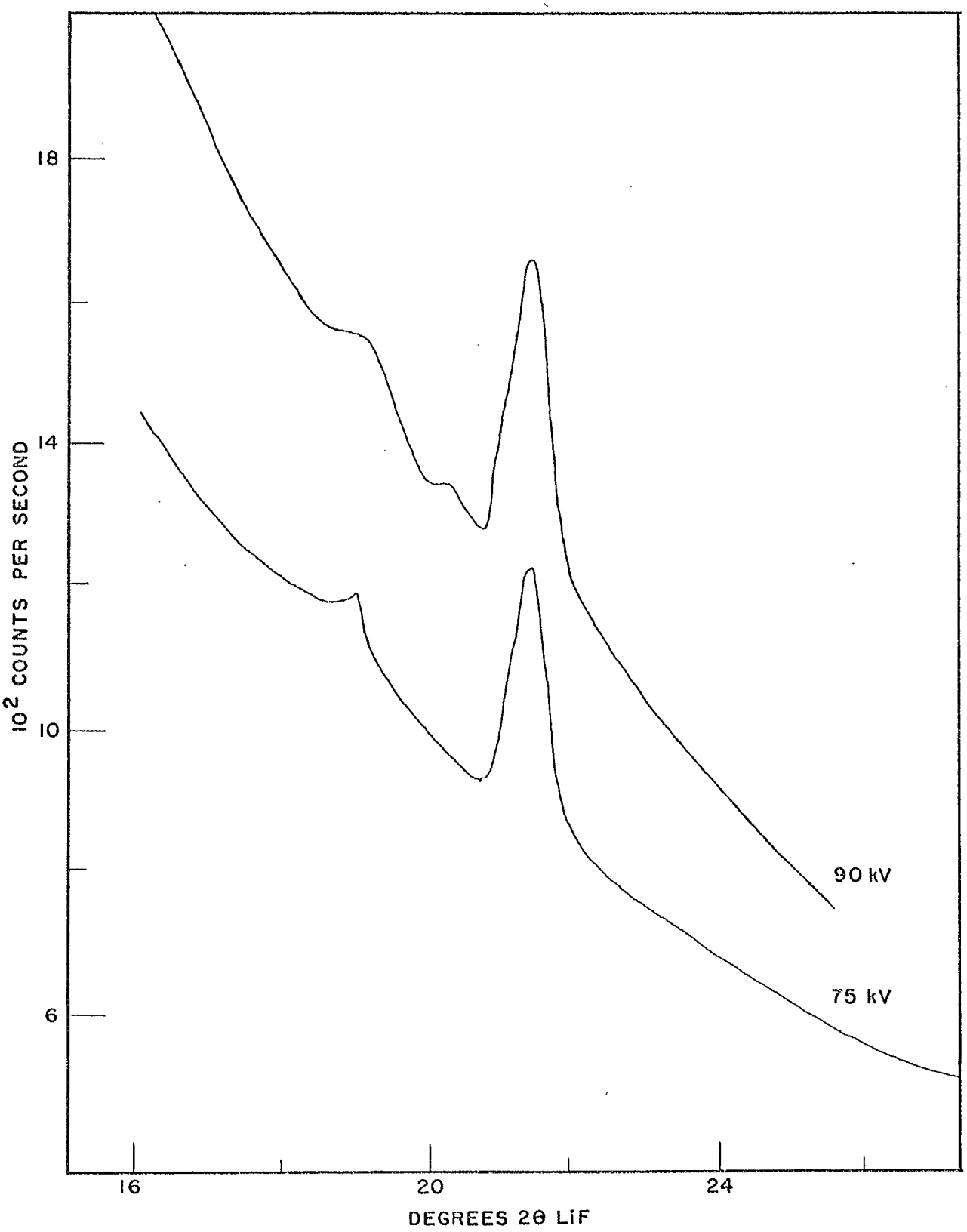

Figure 2. Scans of a Mild Steel Containing 0.036% Niobium.