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ON

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MINERAL SCIENCES DIVISION

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X-Ray Spectrographic Analysis at Low Two-Theta Angles

by Dorothy J. Reed*

Résumé

A des angles 2θ petits, les radiations non différenciées ont été éliminées par l'introduction d'un écran de plomb à l'extrémité du collimateur récepteur. L'écran est placé de façon à éliminer le tiers supérieur du faisceau collimé de Rayons-X avant qu'il ne frappe le cristal analyseur. L'élimination de cette radiation ne réduit pas la sensitivité analytique, malgré une légère diminution du taux de comptage. On présente les résultats obtenus pour la détermination du tungstène et de l'hafmium dans l'acier ainsi que du tantale dans des alliages à haute résistance thermique.

Abstract

Undifferentiated radiation has been removed from the continuum at low 2θ angles by inserting a lead shield at the end of the receiving collimator to remove the upper third of the collimated X-ray beam before it strikes the analyzing crystal. The removal of this radiation caused no decrease in analytical sensitivity although counting rates were reduced. Results are presented for the determination of tungsten and hafnium in steels and tantalum in high temperature alloys.

Introduction

In the Mineral Sciences Division of the Mines Branch K lines are used for the X-ray spectrographic determination of the heavy elements for several reasons:

When L lines are used they may be subject to interference from second and third order K lines of the heavier elements that may be present in the samples and those of the first order of the lighter elements. In the determination of tantalum in ores, second order molybdenum and first order copper and zinc K lines have been found to interfere with tantalum L radiations.

For many of the alloy samples and all of the ore fractions submitted for analysis no standards are available. When standards are available, compensation may be made for interferences. Without standards, or with simple synthetic ones, it is preferable to make determinations where there is no interference, if it is possible to do so.

K lines may give better net intensities. For example, in the recent determination of small amounts of tungsten in ore tailings, the K_{α_1} line gave net counts of an order of magnitude greater than those obtained with the L_{γ_1} line, which was the most intense of the L lines free of interference. The intensity of this L line had to be corrected for the contribution from the X-ray tube. This is not a simple matter when the matrix variation in the samples is great.

There are no tungsten K lines present in the tube continuum so tungsten and tantalum may be determined without such intereference using a tungsten tube. When the L lines are used, there is interference from a tungsten tube with all the characteristic L lines of these elements and from a molybdenum tube with the principal $L\beta$ lines.

One of the major difficulties in the determination of heavy elements by X-ray spectrography using their K radiation is the presence of a high continuum at the low angles to which the characteristic K radiation is reflected by analysing crystals. An intense signal is necessary if a good signal-to-noise ratio is to be achieved.

The continuum at low two-theta angles may be divided into two components: that which is of the same energy as the radiation to be measured and has been reflected to the same angle by the crystal, and that which is undifferentiated and consists of radiation of all the energies produced by the X-ray tube that have not been absorbed in their passage along the optical path of the spectrograph. This portion has passed through the goniometer without striking the crystal. Pulse height discrimination is not satisfactory for its removal because there is at the same time a significant loss of signal due to the wide energy spectrum of the characteristic radiation and its escape peak.

By a simple lead shield the undifferentiated radiation has been eliminated from the continuum at low angles. The effect of this shielding on analytical results is presented here.

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Continuum Reduction

Figure 1a shows the optical path of our 100kV spectrograph when the goniometer is set at 6°2θ. The instrument is equipped with a double detector — a flow counter (FC) lies immediately behind collimator B and in front of the scintillation counter (SC). It is readily seen that the radiation leaving collimator A may be divided into three almost equal parts at this angle. One third of it overshoots the crystal and most of this portion is received directly by the scintillation counter. Another third is separated into its component energies by the crystal and reflected into the counters. The final third undershoots the crystal and is lost. Only when the goniometer reaches 12°2θ does no portion of the undifferentiated radiation impinge upon the scintillation counter. At approximately 24° all the radiation is intercepted by the crystal and reflected into the counters — in agreement with the calculations of Jenkins and de Vries[1].

It was decided to remove the radiation that overshoots the crystal by means of a lead shield and determine the effect on analytical results. The shield would remove one half of the radiation that reaches the counter at 6°2θ and a significant reduction in counting rate was expected.

At the exit end of collimator A in our equipment, there is a lead mask one eighth of an inch thick with a window five sixteenths of an inch square. It was a simple matter to replace this mask by another having the window two-thirds the height of the original one.

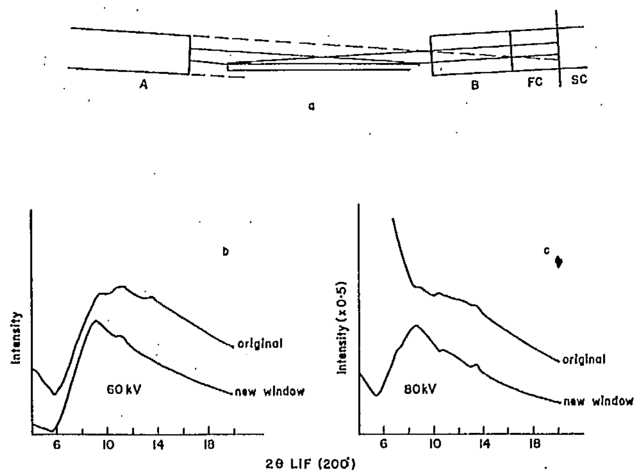

Figure 1: Elimination of Undifferentiated Radiation:
a) goniometer at 6°2θ
b) continuum at 60kV using two collimator windows
c) continuum at 80kV using two windows.

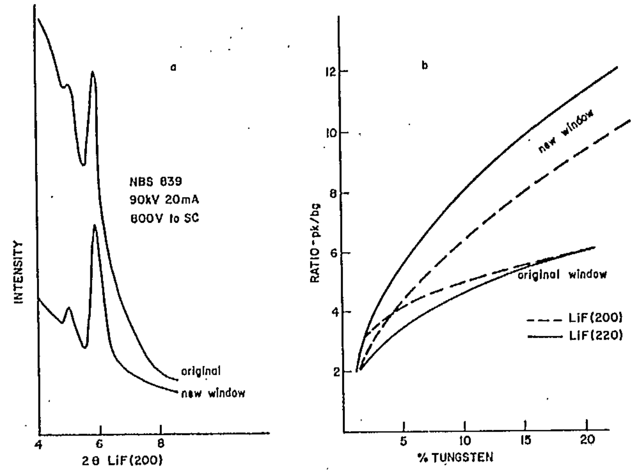

Figure 2: Determination of Tungsten in Tool Steels
a) first order WK radiation using different windows
b) reference lines using peak-to-background ratios with two crystals and two windows

The effect of the new window on the continuum reflected from sheet aluminum at two tube potentials is shown in Figures 1b and c. For both potentials, the curve using the new window has less intensity, as would be expected. At 60kV, the continuum maximum is less extensive with the new window. With the original one, the 80kV curve shows that the undifferentiated radiation begins to reach the scintillation counter in significant amounts at 8°2θ. At lower angles the continuum rises markedly. With the new window, the continuum reaches a maximum at 8.60°, then decreases until the angle 5.50° is reached. Here, it begins to rise again indicating that at this angle the radiation that overshoots the crystal is again reaching the counter.

Analytical Results

For the determination of tungsten in amounts from 1.7 to 18.5% in tool steels (NBS series 836-841), with the old and new windows the lines using net counts were almost identical over most of the range. However, the lines were entirely different when peak-to-background ratios were used. Figure 2b shows the lines obtained using two LiF crystals. The difference was more pronounced when LiF(220) was used. A scan of standard 839, Figure 2a, shows the improved background obtained with the new window and LiF(200).

When minor constituents were determined, as represented by 0.1 to 0.7% tantalum in high temperature alloys (NBS series 1187-1205), there was a significant difference in sensitivity for both net counts and peak-to-background ratios between

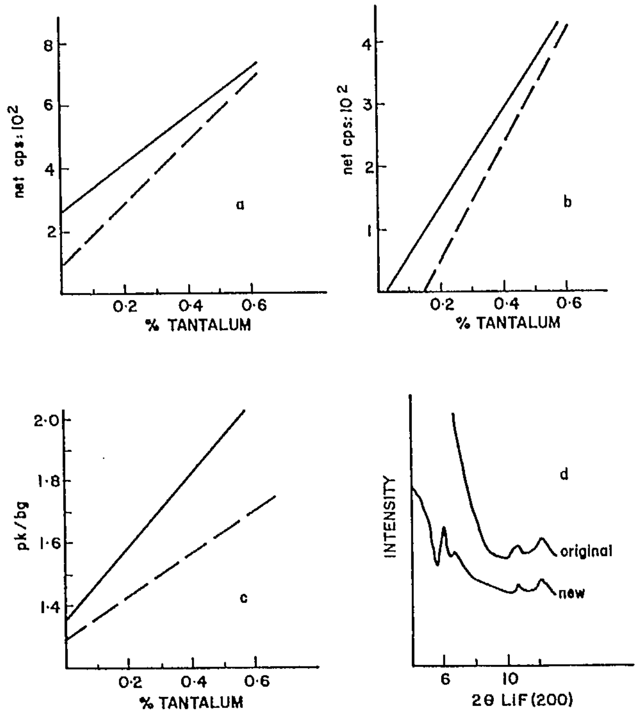

Figure 3: Determination of Tantalum in High Temperature Alloys:
a) net counts per second using background to low energy side of $K\alpha$
b) net counts per second using true background
c) peak-to-background ratios, ——— new and - - - old window
d) scan of standard 1205 with different windows.

the two windows. As shown in Figure 3d for standard 1205, it was not possible to use first order tantalum K lines from LiF(200). However, it was possible to use them when LiF(220) was the crystal used. Figure 3a shows the lines obtained from net counts and Figure 3c those for peak-to-background ratios with the latter crystal, using $TaK\alpha$ and counting the background at 10.60°. The dashed lines were obtained with the old window in place. None of the lines were satisfactory with regard to intercept because of the difference in the continuum intensity at the peak and background angles. When the true background directly under the peak was obtained by a ratio technique, a good line resulted using the smaller window — Figure 3b. The true background was measured by determining the ratio between counts taken at the peak angle and at 14° on standards containing no tantalum and using this ratio to determine the counts under the peak from those taken at 14° on the standards containing the element. Using second order radiation and LiF(200) a line with a satisfactory intercept was obtained for tantalum from the net counts. It had the equation $Y = 0.001927X + 0.0700$, X representing the counts and Y the per cent of tantalum.

In the determination of still smaller quantities of an element, hafnium from 0.035 to 0.20% in mild steels[2], it was again necessary to use second order radiation for LiF(200), when the original window was in place, because first order $HfK\alpha$ could not be counted above the high continuum. With the second order radiation, there was little difference in the standard lines with the two windows: for the original window a regression line $Y = 0.001243X + 0.0078$ was calculated, while the corresponding equation with the new window was $Y = 0.001693X - 0.01398$. The latter equation represents a slight decrease in sensitivity. The use of first order radiation, which was possible with the smaller window, increased the sensitivity by a factor of three resulting in an equation $Y = 0.0004829X - 0.0792$. When LiF (220) was used as the analysing crystal, first order $HfK\alpha$ could be used with both windows. There was no loss in sensitivity with the new one which gave an equation $Y = 0.0007897X + 0.0068$ as compared with $Y = 0.0007568X + 0.0181$ for the larger window.

Conclusion

The radiation that overshoots the crystal in flat-crystal spectrographs at low two-theta angles (<12° for our spectrograph) may be removed from the X-ray beam by a simple lead mask. The removal causes no significant decrease in analytical sensitivity and, in certain cases, may increase it.

References

1. Jenkins, R. and de Vries, J. L.: Analyst 94, 447 (1969).
2. Reed, D. J.: Mines Branch Res. Rept. R174, (1965).