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

by

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Dorothy J. Reed*

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SUMMARY

Using synthetic standards, hafnium has been determined in mild steels in concentrations up to 0.200% by X-ray spectrography. It has been established that both Hf Lα (n = 1) and Hf Kα (n = 2) may be used for the determination of hafnium at these levels.

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INTRODUCTION

During the past five years samples of mild steels containing zirconium and niobium have been submitted by the Physical Metallurgy Division for the determination of these elements. Recently, low concentrations of hafnium have been added to mild steels and requests for its determination received.

There are no steel standards available which contain hafnium in the appropriate concentration range. Under similar circumstances, niobium (1) and zirconium (2) were determined successfully in mild steels using synthetic standards prepared from electrolytic iron. The same type of standards were prepared for the determination of hafnium.

PREPARATION OF SYNTHETIC STANDARDS

Eight standards were prepared by dissolving known quantities of electrolytic iron, approximating 10 g, in HCl. To these, aliquots of a solution of hafnium in HCl and HF were added to give a concentration range of the element from 0 to 0.276 per cent. The solutions were taken to dryness and the residues ground in an agate mortar to pass 200 mesh.

The samples, submitted as drillings, were dissolved in HCl, taken to dryness and ground similarly. The same samples were also received in the form of discs 1 3/4 inch in diameter. These were reserved for possible future use as secondary standards.

THE X-RAY SPECTRA OF HAFNIUM

Both the K and L spectra of hafnium are obtainable with the 100 kV spectrograph. The critical potential for the K spectrum is 65.4 kV, that for the L varies from 9.5 to 11.3 kV depending on the L subshell of electrons involved.

The L spectra suffer interference from tungsten spectra which are generated from the target of the X-ray tube. This is evident in Figure 1 which reproduces a scan of one of the synthetic standards. Substitution of the X-ray tube for one with a molybdenum target would not completely remove target interference because second order molybdenum radiation would interfere. The positions of these second order peaks are marked in Figure 1. Moreover, molybdenum is not as efficient in exciting hafnium radiation as is tungsten (3) and a loss in sensitivity would result.

Hf $L\alpha_1$ is the most intense hafnium peak. It occurs on the tail of $WL\alpha_1$, but the contribution from the continuum should be constant and hence eliminated by a blank count or compensated for by the intercept of the reference line.

The hafnium K spectrum has no tungsten interference from the continuum. However, first order Hf K lines occur near the continuum maximum and the resulting high background counts make the few counts from low concentrations of hafnium insignificant, even in a count scan. This is shown in Figure 2a which is a count scan made on one of the discs. First order K radiation can be used only for much higher concentrations of hafnium.

Figure 2b presents a normal chart scan of the same sample for second order K radiation. In the curve using a 6V baseline, the Kα peak is evident while the presence of Kβ is barely indicated. The signal-to-noise ratio for Hf Kα (n=2) might be improved if some of the noise pulses were eliminated by use of a higher baseline voltage. A pulse amplitude distribution curve for this radiation, made using HfO_2, showed that all Hf Kα pulses had an amplitude greater than 48V. Nonetheless, as is also shown in Figure 2b, increasing the baseline had the opposite effect to that expected.

THE DETERMINATION OF HAFNIUM

The synthetic standards and the powders prepared from the samples were counted at Hf $L\alpha_1$ using 80 kV, 20 mA, a baseline of 6V and an amplifier gain of 10. The detector used was the scintillation counter with an applied potential of 900V. Counts were taken at 45.80°2θ LiF for the peak and at 47.50° for the background. A regression line was established which had the equation $Y = 0.001020X - 0.0527$, where Y is the per cent hafnium and X net counts per second. When there is no hafnium in the sample, X is equal to 52 cps from the equation. This may be considered a measure of the tungsten interference. Two blank samples submitted had actual net counts of 52 and 57 cps giving reasonable agreement with the derived figure X. The correlation coefficient for the regression was + 0.9973 and the standard error $\pm$ 0.007.

The steel discs submitted were counted and a line was established to determine the error should these discs be used as secondary standards. In this case the equation was $Y = 0.00060673X - 0.014$, the correlation coefficient + 0.9998 and the standard error $\pm$ 0.002. It gave 23 cps for zero hafnium compared with actual net counts of 22 and 26. The better error and correlation from the discs reflect in part the difficulty in packing the powders uniformly.

The discs were also counted at Hf $K\alpha_1$ (n=2) to check the sensitivity of this peak. In this case 90 kV was used as the accelerating voltage. The other counting conditions were unchanged. Peak counts were taken at 12.54° and background counts at 12.30 and 12.75°2θ LiF. The counts at 12.30° were very consistent, but for some samples they were higher than the peak counts. Therefore the ratios of the counts, rather than net counts, were used as X with a resulting equation $Y = 2.7412X - 0.6714$. The counts at 12.75° varied with the amount of hafnium present. When the background is changed to 13.10° it is consistent and may be used to determine net counts.

Hafnium is readily determined by neutron activation. Rods of the size required for this technique were poured. Because no similar standards were available, it was possible to obtain only ratios of the counts from the samples. The counts from the sample containing the most hafnium were taken as unity and those from the other samples were related to it.

RESULTS

The results obtained on 4 samples are shown in Table 1. Included are the per cent hafnium determined on the drillings using the synthetic samples, the net counts on the discs and the ratios obtained by neutron activation on sample rods. The results show satisfactory agreement, especially when it is considered that three samplings are involved.

It is noteworthy that the second order K radiation of an element as heavy as hafnium offers sufficient sensitivity for the determination of the small concentrations occurring in these samples.

CONCLUSIONS

Using synthetic standards, hafnium may be determined by X-ray spectrography in mild steels in concentrations up to 0.28 per cent with an error of $\pm$0.007 per cent.

When secondary Mines Branch standards are established, it should be possible to reduce this error to $\pm$0.002 per cent.

Both the K and L spectra of hafnium may be used if a 100 kV spectrograph is available.

ACKNOWLEDGEMENT

The neutron activation ratios were obtained by Dr. H.P. Dibbs.

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DJR:ST

TABLE 1

Results Obtained on Mild Steel Samples

Sample	% Hf	Net cps on discs		Neutron Ratio
		Lα(n=1)	Kα(n=2)	
A	0.200	332	240	1.00
B	0.154	242	174	0.75
C	0.080	132	103	0.42
D	0.035	60	28	0.17

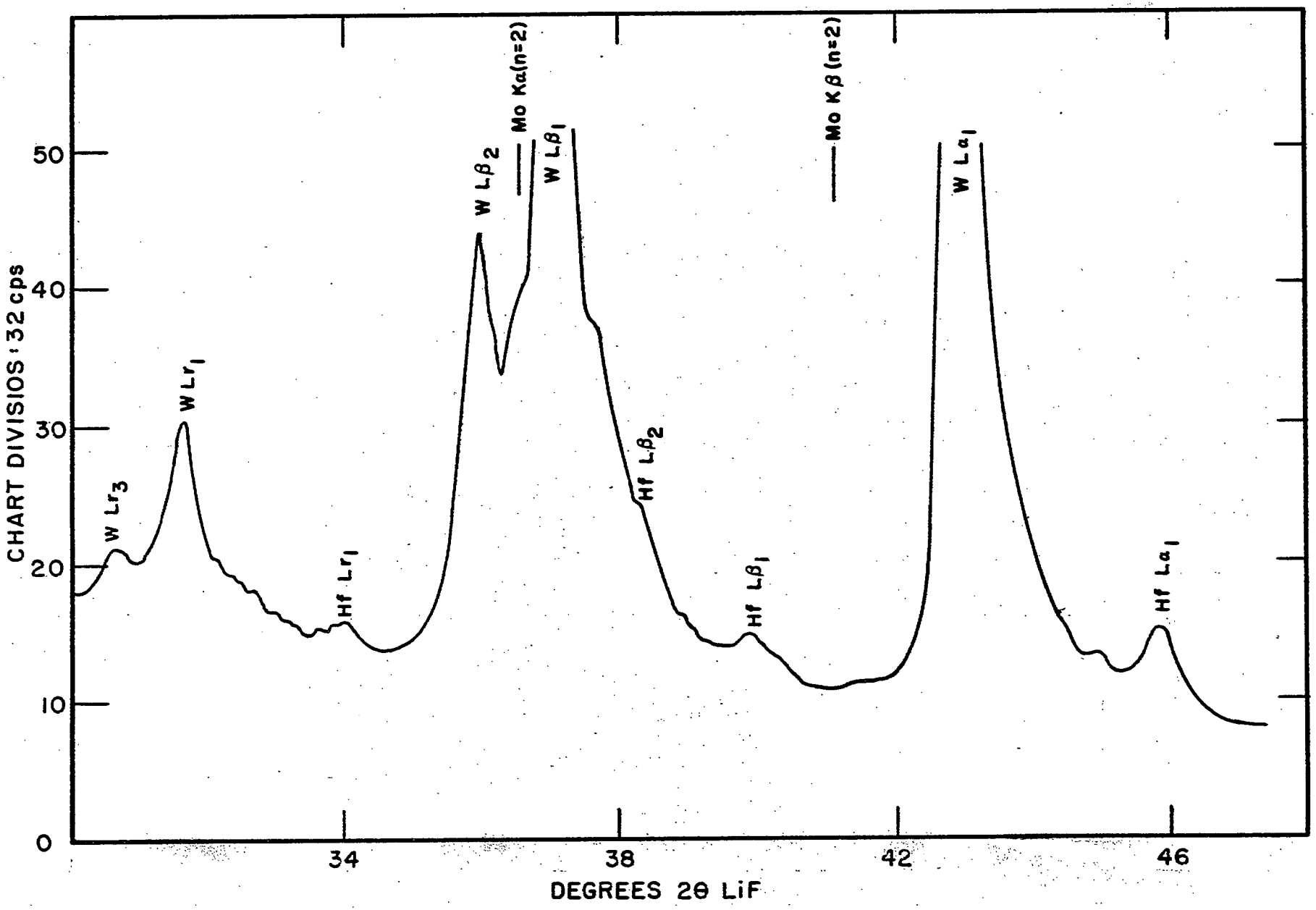

FIGURE I SCAN OF SYNTHETIC STANDARD 0.276 % Hf.

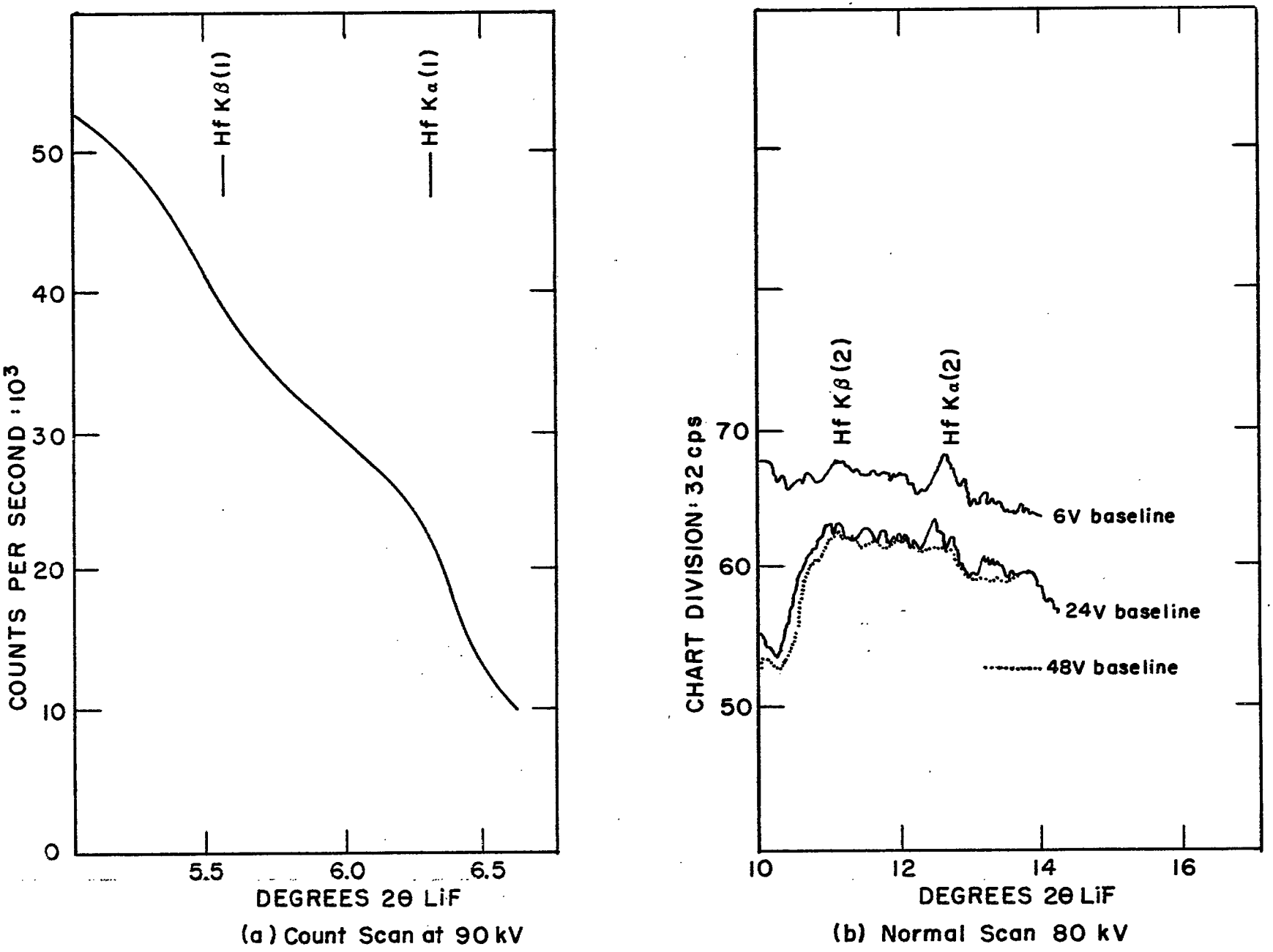

FIGURE 2 SCANS OF STEEL DISC CONTAINING 0.20 % Hf.