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THE DETERMINATION OF
ZIRCONIUM, NIOBIUM AND
HAFNIUM IN LOW ALLOY STEELS
BY X-RAY SPECTROGRAPHY

DOROTHY J. REED

DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

MINERAL SCIENCES DIVISION

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RESEARCH REPORT

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THE DETERMINATION OF ZIRCONIUM, NIOBIUM AND HAFNIUM
IN LOW ALLOY STEELS BY X-RAY SPECTROGRAPHY

by

Dorothy J. Reed*

ABSTRACT

Zirconium, niobium and hafnium have been determined in mild steels by X-ray spectrography in amounts up to 0.35, 0.30 and 0.20% respectively with errors of less than $\pm 0.01\%$.

Because suitable standards for zirconium and niobium were unavailable and no standards for hafnium existed, it was necessary to use synthetic standards. A number of samples have been set up as Mines Branch secondary standards and the validity of their use has been verified.

Using accelerating potentials of 80 or 90 kV, zirconium and niobium may be determined in the ppm range. The sensitivity for hafnium is 0.01%.

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Direction des mines

Rapport de recherches R 174

LE DOSAGE DU ZIRCONIUM, DU NIOBIUM ET DU HAFNIUM DANS
LES ALLIAGES FERREUX LÉGERS PAR SPECTROGRAPHIE AUX RAYONS-X

par

Dorothy J. Reed*

RÉSUMÉ

Le zirconium, le niobium et le hafnium ont été dosés dans les aciers doux par spectrographie aux rayons-X jusqu'à des quantités de 0.35, 0.30 et 0.20% respectivement avec des erreurs de moins de $\pm 0.01\%$.

Puisque des étalons appropriés pour le zirconium et le niobium étaient indisponibles et qu'aucun étalon n'existait pour le hafnium, il fut nécessaire d'employer des étalons synthétiques. On a établi un certain nombre d'échantillons comme étalons secondaires de la Direction des mines, et la validité de leur emploi a été vérifiée.

En employant des potentiels accélérés de 80 ou 90 kV, le zirconium et le niobium peuvent être dosés pour des teneurs de l'ordre de ppm. La sensibilité pour le hafnium est de 0.01%.

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INTRODUCTION

During the investigation of the effect of minor alloying elements on the properties of mild steels, the determination of small amounts of zirconium, niobium and hafnium was required. In many samples the concentration was too low for precise wet chemical estimation but too high for emission spectrography. X-ray spectrography was recognized as a means of determining major constituents in steels, so it was decided to investigate its application to minor ones.

The determination of zirconium, niobium and hafnium in amounts from a few tenths to a few thousandths of a per cent has proved rapid and precise. For the benefit of those interested in such analyses, the investigations conducted and the methods employed are outlined in this report.

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EQUIPMENT

A Norelco 100-kV X-ray spectrograph equipped with a tungsten X-ray tube and a double detector was used for all determinations. Only the scintillation counter of the detector unit was utilized. Lithium fluoride has been used as the analyzing crystal for most of the work. It was preceded by a 4-inch receiving collimator having nickel plates spaced at 0.005 inch and followed by a 1-inch collimator with 0.02-inch spacing. The pulse height analyzer unit in the counting panel was modified to extend the baseline to 150 V.

A special platinum mask was made to support standards of the National Bureau of Standards, which were $1\frac{1}{4}$ inches in diameter. The 2-inch sample holders of the spectrograph had $1\frac{3}{8}$ inch irradiation ports. The platinum mask, made to fit inside the sample holder, had an opening one inch in diameter.

STANDARDS

National Bureau of Standards

The only standards immediately available were NBS low-alloy steels 1161 to 1168. Of these only four were certified as to their zirconium content, which ranged from 0.01 to 0.20%. There were seven standards with certified niobium values from 0.005 to 0.29%. None contained hafnium. Most of the samples submitted have contained less than 0.1% niobium or zirconium; this reduced the number of standards in the appropriate range.

The zirconium, niobium and molybdenum concentrations in the seven standards are shown in Table 1. Zirconium and niobium suffer mutual interference in X-ray spectrography. Molybdenum must be considered because it affects the background determination and interferes with $ZrK\beta$ and, in the higher concentrations, with $NbK\alpha$ radiation. A count scan of two of these standards is shown in Figure 1. By counting at intervals of 0.05° over the region of interest, small peaks may be found that normally are lost in the excursion of the pen of a chart recorder. The

TABLE 1

Composition of NBS Low Alloy Steel Standards

No.	% Zr	% Nb	% Mo
1161	-	0.001	0.300
1162	0.063	0.096	0.080
1163	0.200	0.195	0.120
1164	0.010	0.037	0.029
1166	-	0.005	0.011
1167	0.094	0.290	0.021
1168	-	0.006	0.200

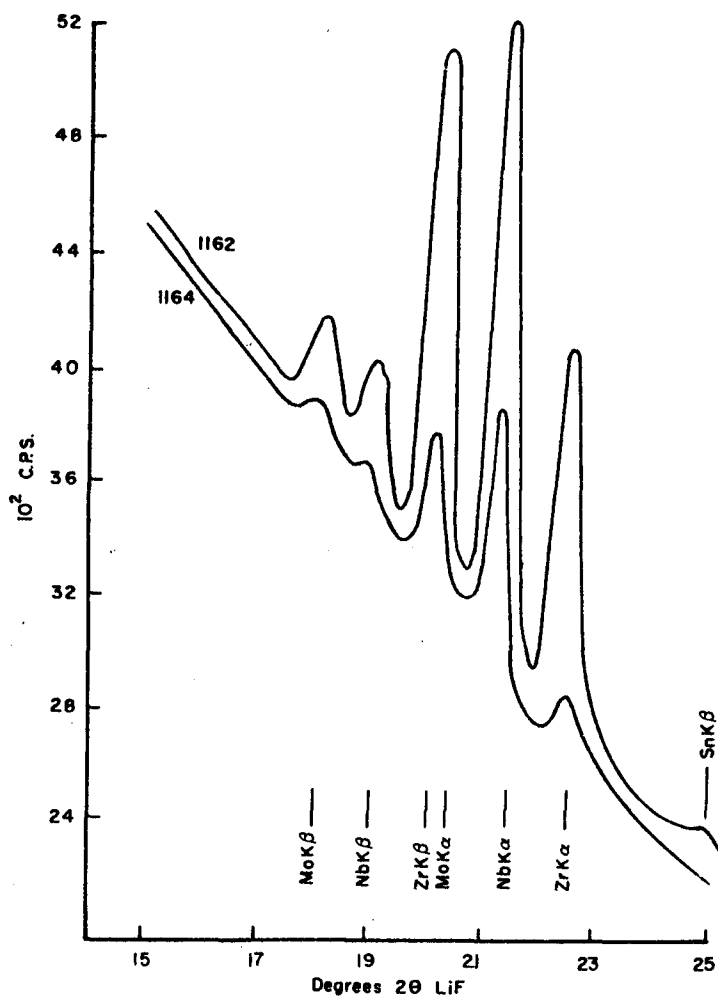


Figure 1. Count scan of NBS standards at 70 kV.

characteristic radiation of the elements is superimposed on the continuum from the X-ray tube, which in this region is approaching its maximum. Complete separation of the peaks is impossible when lithium fluoride is used as the analyzing crystal. The use of a quartz crystal was considered unsuitable for such low concentrations, because of its poor reflectivity.

In addition to the above interferences, it was possible, though not probable, that the large number of other elements in the standards, although present in amounts mostly less than 1%, might affect the radiation to be measured. The samples, which were received in the form of discs approximately 2 inches in diameter, usually had only one element added to the steel.

Synthetic Standards

The lack of a sufficient number of appropriate standards, and the possible effect of the other elements present, made the use of synthetic standards necessary. These were prepared by adding zirconium, niobium or hafnium to 10-gram portions of electrolytic iron to give the desired concentration. The combined metals were dissolved in hydrochloric and fluoboric acids and the solutions taken to dryness. The residues were baked on a hotplate approximately 30 minutes, then ground to pass 200 mesh. Three of the first group prepared showed the presence of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$, FeOCl and Fe_2O_3 by X-ray diffraction analysis.

Drillings from the samples were also dissolved, dried, and ground for comparison with these standards.

Secondary Standards

By eliminating the platinum mask used to support the NBS standards, the sample area irradiated, and hence the sensitivity, was increased. It was decided, therefore, to select a suitable range of disc samples as secondary standards. Such standards would have a composition similar to the samples, and the absence of other elements would simplify background measurement.

From the samples submitted, those giving a suitable range of values on first analysis were counted on successive days under different conditions in disc form against the NBS standards and as powders against the synthetic standards. The mean of the results obtained was assigned to the selected samples as secondary standards. The range of these standards was extended as sample variation permitted.

THE DETERMINATION OF ZIRCONIUM

General

From Figure 1 it is readily seen that the presence of molybdenum made the use of ZrK α mandatory for NBS standards. The slope of the continuum and the proximity of neighbouring peaks made the usual practice of taking background counts close to the peak and on both sides of it impossible. During early investigations, the background was estimated by interpolation from counts taken at three or four points on one or both sides of the K α peak. Accelerating potentials of from 60 to 90 kV were used

and the amplifier gain, counter voltage and baseline were adjusted to give a straight continuum when possible. For example, counts for background interpolation were taken variously at 16, 17, 23.5, 24 and 24.5 θ LiF, while the threshold was varied from 6 to 18V and the amplifier gain from 10 to 90. The voltage applied to the scintillation counter varied from 850 to 1100V -- the wide range being partly due to the use of two photomultipliers.

Sample discs were counted against NBS standards, and powders from turnings against synthetic standards. All conditions gave excellent correlation, and results from replicated counts agreed within $\pm 0.002\%$. A typical regression equation from the four NBS standards, counted in duplicate, was that obtained at 90 kV: $Y = 0.000041X - 0.0097$. The correlation coefficient was $+ 0.9993$ and the standard error ± 0.004 . Synthetic standards counted on two successive days gave an equation $Y = 0.000114X - 0.009$, with a correlation of $+ 0.9994$ and an error of ± 0.006 . The larger error in the latter case reflects the difficulty in packing powders uniformly. Results obtained from these two lines are shown in Table 2 along with results of analysis of the discs by emission spectrography using NBS standards. Allowing for the calculated errors, the results show satisfactory agreement.

TABLE 2

Zirconium in Mild Steels

Sample	% Zirconium		
	Solids (NBS)	Powders (Synthetic)	Emission Spectrography
19	-	-	0.001
19A	0.025	0.015	0.015
23A	0.086	0.071	0.071
23B	0.010	0.009	0.004
23BN	0.007	0.002	0.002
24A	0.042	0.035	0.032
24AN	0.040	0.028	0.019

Secondary Standards

When secondary standards were established, counts were taken approximately $\pm 0.70^\circ 2\theta$ from the ZrKa peak. By this time, niobium determinations had indicated this method to be successful with such standards containing only one alloying element. A line established in this manner, using an accelerating potential of 90kV, had the equation $Y = 0.00010344X - 0.0093$ with a correlation of $+ 0.99992$ and an error of ± 0.0015 . The improved precision of this line, in comparison with that of the NBS standards above, is due to the larger sample area exposed and to better background estimation.

The reproducibility of zirconium counts under these conditions may be judged by that of the background. The mild alloy steel samples were made from the same base with different amounts of zirconium added,

so they may be regarded as replicates of a single sample for background measurement. The standard deviation of the counting rate includes errors of positioning and goniometer setting and the differences in surfaces and in sample area exposed. With five standards and fifteen samples counted in rotation in duplicate, the background at 23.25 2 θ LiF had a mean value of 893 cps and a standard deviation of ± 10 , while that at 21.80 $^\circ$ had corresponding values of 1055 and ± 21 . The sum of the two deviations multiplied by the slope of the regression line is equivalent to $\pm 0.003\%$. Duplicated net counts for many samples have agreed within 10 cps. Using this figure as a measure of reproducibility, the error is $\pm 0.001\%$.

In all the zirconium equations the intercept has been negative because the sample holders contain a small amount of the element. In the last equation the holders contributed 90 cps. This amount must be added to the figures substituted in the equation to determine the above errors or the intercept must be omitted.

The limit of detection of zirconium, using twice the mean standard deviation as a measure of this limit, is 0.003%. If, instead, 10 cps (which can be counted significantly above background) is used, the detection limit is 0.001% or 10 ppm.

Samples Containing Uranium

Secondary zirconium standards were used to analyze samples containing uranium in addition to zirconium. In Figure 2 a scan of such a sample at 70 kV, using a lithium fluoride crystal, shows the proximity of UL to ZrK radiation.

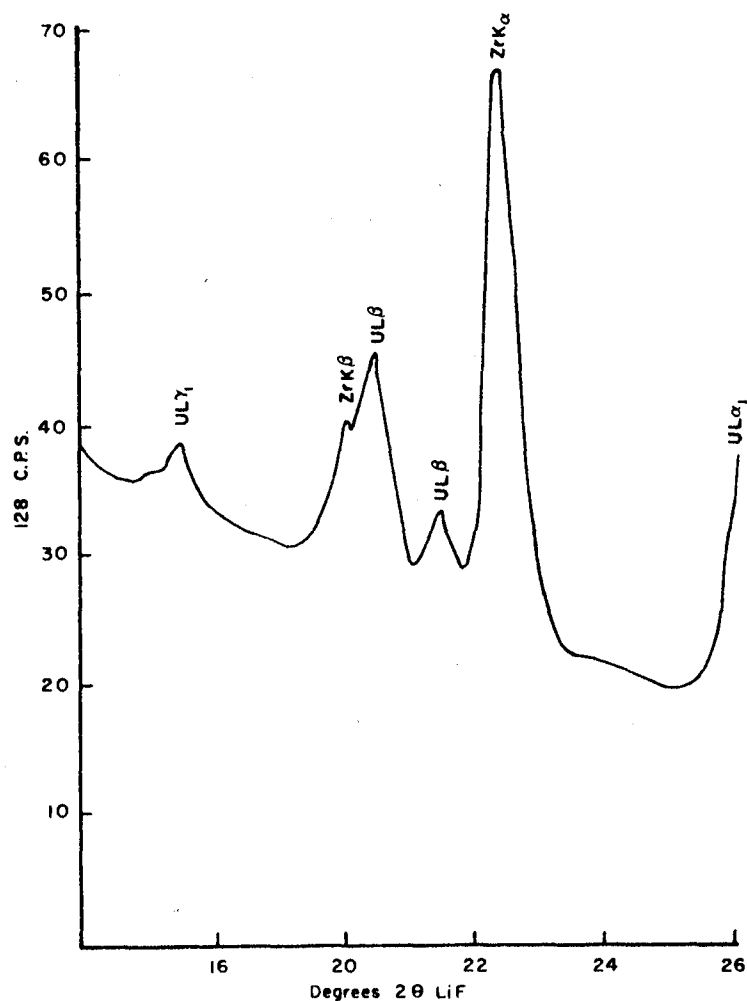


Figure 2. Scan of mild steel containing uranium and zirconium, at 70 kV.

The possible use of a quartz crystal ($2d = 2.74$) to separate $UL\beta_2$ from $ZrK\alpha$ was investigated. At 90 kV, sufficient sensitivity was obtained to establish a line with the equation $Y = 0.000586X - 0.0048$. The equation for the line using lithium fluoride under the same operating conditions was $Y = 0.0000606X - 0.0083$. In both cases, background counts were taken $\pm 0.70^\circ$ from the peak. The use of a quartz crystal is not recommended, because of the reduced sensitivity and the longer counting times required.

The difference in the slopes of the two lines derived from net counts is a measure of the difference in crystal reflectivity. A comparison of the peak counts obtained with the two crystals for three of the standards is given in Table 3 and shows that the ratio of the counts unexpectedly varied with the counting rate.

TABLE 3

ZrK α Counts from Two Crystals

% Zr	Counts per Second		Ratio
	LiF	Quartz	
0.015	1452	260	5.58
0.033	1660	280	5.93
0.071	2191	305	7.18

Use of High Accelerating Potentials

To determine an element by X-ray spectrography, the accelerating potential must exceed the critical. A kV two or three times the critical value is desirable for good sensitivity. To determine small concentrations, higher potentials are useful if they do not affect the peak-to-background ratio adversely.

As already noted in Figure 1, the X-ray continuum, as it approaches its maximum, forms the background for first-order ZrK α radiation. The height and position of the maximum are affected by the applied potential (2). The effect of potential change on the ZrK α peak-to-background ratio has

been determined using two secondary standards. The background was measured at two of the points used for NBS standards, not at points $\pm 0.70^\circ$ 2θ of the peak. The results, given in Table 4, show that the ratio improved with increasing kV and thus justifies the use of high potentials when possible.

TABLE 4

Effect of kV on ZrK α Peak-to-Background Ratios

kV	Ratio	
	0.082% Zr	0.320% Zr
40	1.60	3.24
50	1.65	3.61
60	1.75	3.88
70	1.84	4.08
80	1.86	4.22
90	1.96	4.28

THE DETERMINATION OF NIOBIUM

Interpolated Background

For the determination of niobium in mild steels, the first approach used was the same as that for zirconium and had similar results. As long as conditions for a group of standards and samples were constant, variation from group to group in applied potential, in counter and baseline voltages, and in the 2θ angles for estimating the background, had no significant effect. A typical equation was $Y = 0.000103X - 0.0048$, obtained from counts on the NBS standards at 90 kV and 20 mA, using a background interpolated from measurements at 19.50 , 23.50 and $24.00^\circ 2\theta$ LiF. The correlation coefficient was $+ 0.9996$ and the standard error ± 0.002 .

Scan Count

A second approach to the determination of niobium involved an attempt to compensate for variation in the continuum slope by counting as the goniometer scanned the sample from a point below the niobium peak on the 2θ scale where the radiation emerged from the background to a point an equal distance above the peak. This procedure measured the total area under the peak and reduced the sensitivity because the intensity was measured over the full spread of the radiation, not just at its maximum. The background was taken as the mean of the counts at the two limiting points.

The Norelco counting panel can be used to count for a number of pre-set times. The maximum is 64 seconds, making it possible to scan $0.53^\circ 2\theta$ each side of the peak, with the goniometer moving through 1° per minute. This total 2θ angle of 1.06° marked the spread of the niobium radiation at 90 kV and 20 mA. A line established by this scan-count procedure had the equation $Y = 0.0002978X - 0.0026$, a correlation coefficient of $+ 0.9996$ and a standard error of ± 0.0015 .

Comparison with the niobium line above shows that the sensitivity was reduced by a factor of three using the scan count, but the error was of the same magnitude.

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 level. Because of the continuum slope, this is impossible in the case of niobium in steels. The

backgrounds measured for the scan counts were remarkably constant from sample to sample. Therefore, it was decided to measure the background where the niobium peak emerged from it. With secondary standards containing no interfering molybdenum or zirconium, counts at a potential of 80 kV were taken $\pm 0.75^\circ 2\theta$ from the peak to accommodate larger concentrations of niobium than had been measured by the scan-count procedure. The resultant line had the equation $Y = 0.00007466X - 0.00026$, a correlation of $+ 0.9992$ and an error of ± 0.0005 . The small value of the intercept indicated that the estimation of the background from counts taken near the limits of the peak spread was extremely good.

The reproducibility of niobium counts under these conditions may be judged by that of the background, as in the case of zirconium. Eleven samples counted in rotation in duplicate had, at the lower 2θ background, a mean counting rate of 1158 cps with a standard deviation of ± 11 . The mean of the higher 2θ background was 1029 cps and its standard deviation was ± 5 . From the equation, 16 cps are equal to 10 ppm. A detection limit of 10 cps above background equals 5 ppm.

THE DETERMINATION OF HAFNIUM

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 spectra varies from 9.5 to 11.3 kV, depending on the L sub-shell of electrons involved (3).

The L spectra suffer interference from tungsten L spectra which are generated from the target of the X-ray tube. This is evident in Figure 3, a scan of one of the synthetic standards. Substitution of the X-ray tube by one with a molybdenum target would not completely remove target interference, because second-order molybdenum K radiation would interfere as indicated in Figure 3. Moreover, molybdenum is not as efficient in exciting hafnium radiation as is tungsten (1).

HfLa_1 is the most intense peak. It occurs on the tail of WLa_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 equation.

The hafnium K spectrum suffers no similar tungsten interference. Tungsten K lines do not appear above the tube continuum, even at 100 kV excitation, though they are fluoresced from a sample once the critical potential is exceeded. Electrons do not as easily penetrate the outer electron shells as do neutral X-rays. However, first-order hafnium K lines occur near the continuum maximum. The resultant high background masks the few counts from low concentrations of hafnium, even in a count scan. This is shown in Figure 4(a), which is a count scan of a steel containing 0.20% Hf. First-order K radiation can be used only for much higher concentrations of hafnium.

Figure 4(b) presents a chart scan for second-order K radiation from the same sample. In the curve using a 6 V threshold, the $\text{K}\alpha$ peak is evident while the $\text{K}\beta$ is barely indicated. To determine how much a higher

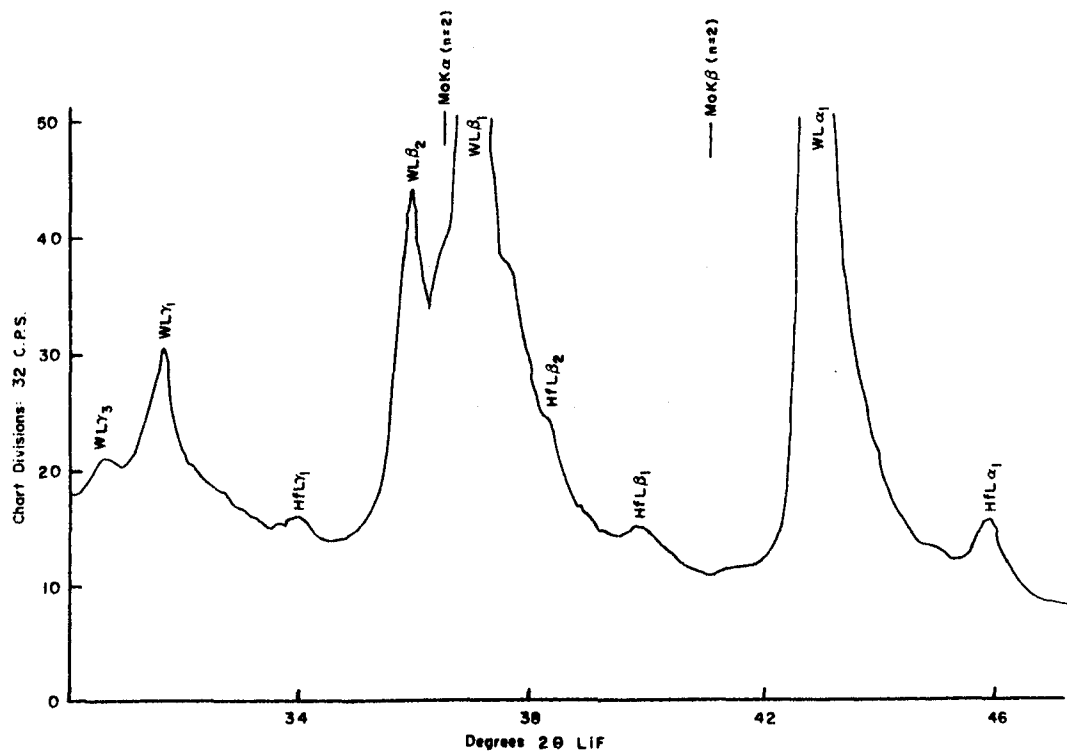


Figure 3. Scan of synthetic standard 0.276% Hf.

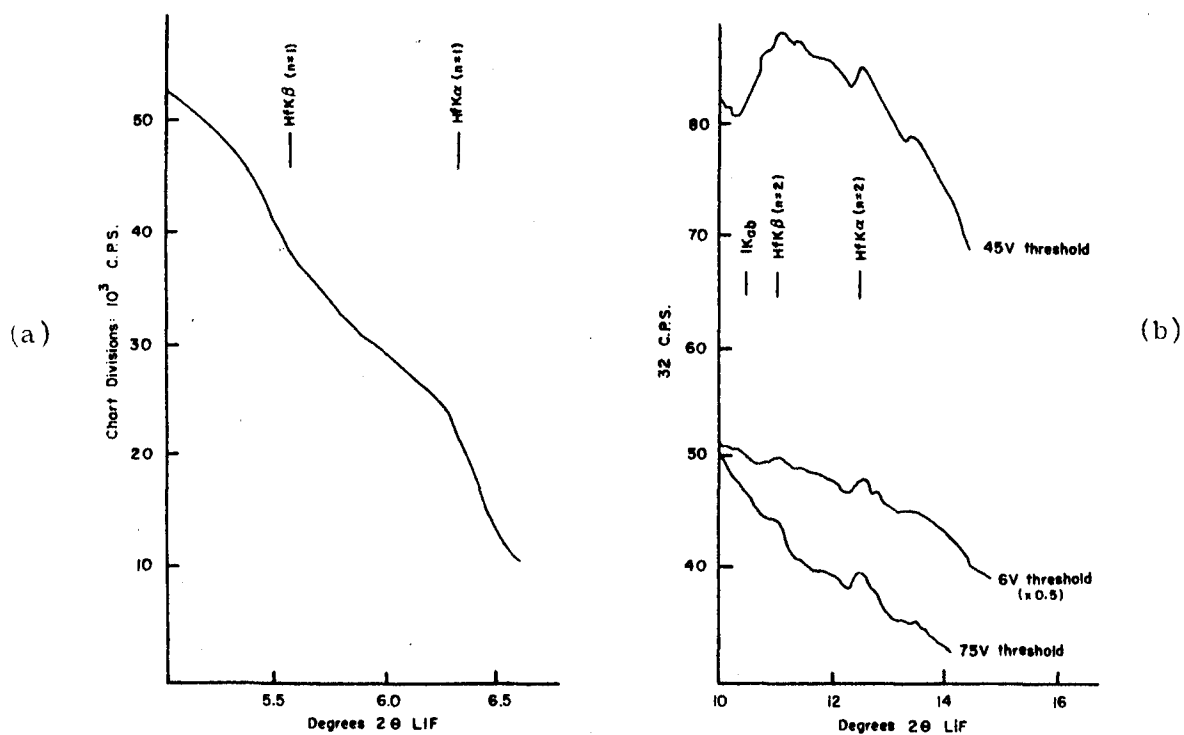


Figure 4. Scans of a steel disc containing 0.20% Hf.

threshold would improve the peak-to-background ratio, pulse amplitude distribution curves were run on hafnium metal. The scintillation counter plateau of HfK α radiation extended from 700 to 900 V. Curves were run at the second-order peak with 700, 800 and 900 V applied to the counter, using a 0.5 V channel and an amplifier gain of 10; those for the latter two are shown in Figure 5. At 900 V the pulse amplitude was 107 V and the width at half-height, 22 V. For the 800 V curve, these values were 45 and 13 V. Both curves had an escape peak. That for the higher potential occurred at 53 V, that for the lower at 21 V. Both contained approximately 17% of the energy. The 700 V curve is not shown in Figure 5. The main peak at 16 V was not completely separated from the escape peak at 8 V.

Included in Figure 5, for interest, is the distribution of the same peak from 0.2% Hf in steel. In this instance the background, which is of different energy than the hafnium radiation, contributed a much greater share of the energy analyzed. The skewness of the main peak is evident. The escape peak contained 55% of the energy.

Figure 4 (b) also presents scans, made with 900 V applied to the counter, using a 45 V threshold which includes most of the escape peak and a 75 V one which excludes all radiation having less energy than HfK α . While the hafnium peaks are not affected, the effect of the threshold on the continuum height is readily seen. The threshold effect was corroborated by duplicate background counts taken at 13.25° 2 θ LiF on six steel discs containing hafnium. For the 6 V threshold, the mean was 3081 cps, with a standard deviation of ± 22 . For a 39 V one, used to ensure total inclusion of the escape peak, the mean counting rate was 2931 and the deviation ± 19 . For a 75 V

threshold, comparable figures were 1288 cps and ± 11 .

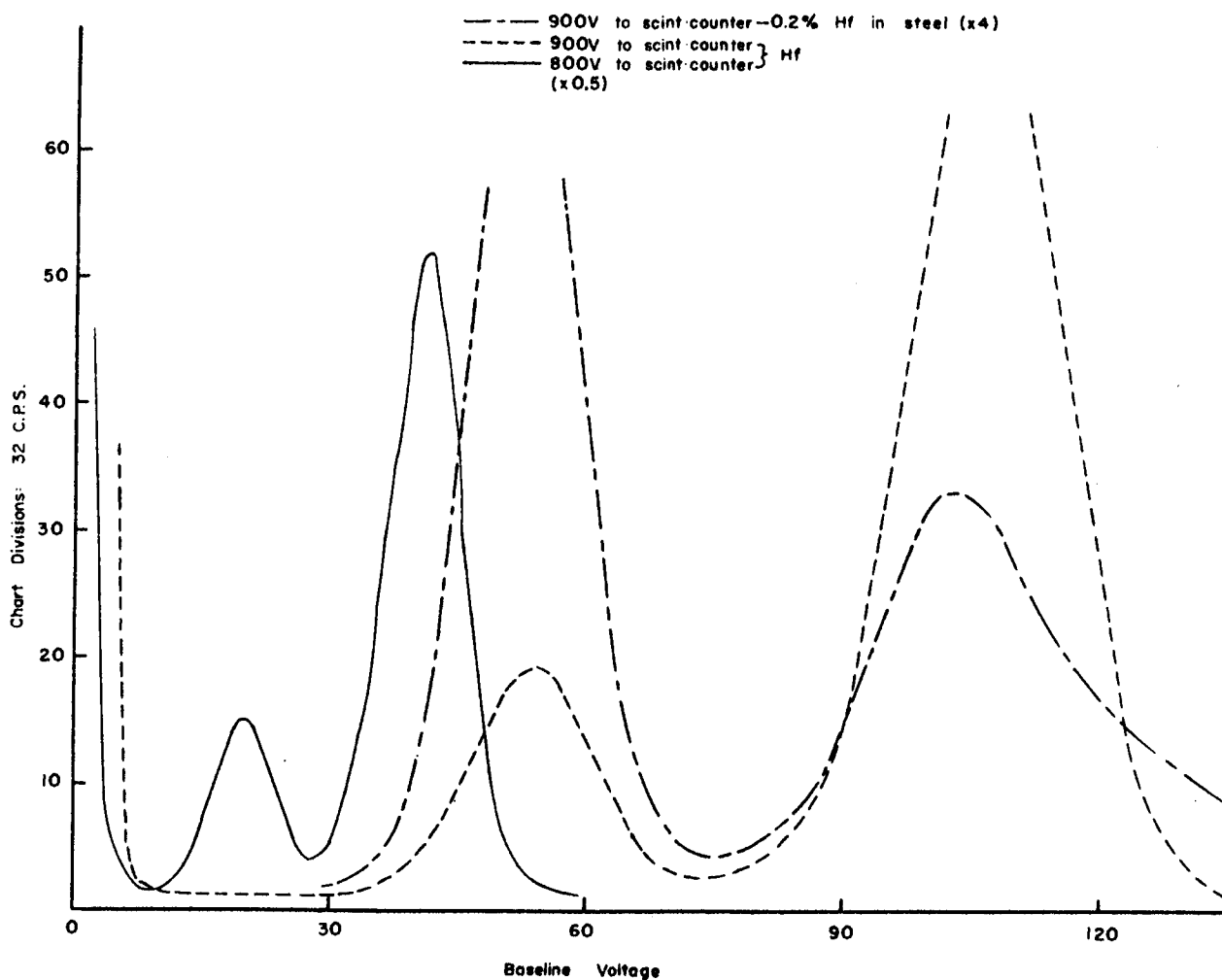


Figure 5. HfKa (n=2) pulse amplitude distribution curves.

Methods of Analysis

Synthetic standards and powders prepared from the samples were counted at HfLa₁, using 80 kV, 20 mA, a 6 V threshold, an amplifier gain of 10, and a 900 V potential to the scintillation counter. Counts were taken at 45.80° 2 θ LiF for the peak and at 47.50° for the background. The resulting regression line had the equation $Y = 0.001020X - 0.0527$. When

there was no hafnium in the sample, X was equal to 52 cps from the equation and this figure may be considered a measure of the tungsten interference.

Two blank samples had actual net counts of 52 and 57 cps, which were in reasonable agreement with the derived figure. The correlation in the regression was $+ 0.9973$ and the standard error ± 0.007 .

The steel discs were counted and a line set up to determine the error should these discs be used as secondary standards with values assigned from the corresponding powders. In this case the equation was $Y = 0.00060673X - 0.014$, the correlation $+ 0.9998$, and the error ± 0.002 . This equation gave 23 cps with zero hafnium for the tungsten interference, compared with actual counts of 22 and 26 on two blanks. The better error and correlation from the discs reflected in part the difficulty in packing powders uniformly.

The discs were also counted at $\text{HfK}\alpha_1$ ($n = 2$) to check the sensitivity of this peak. An accelerating voltage of 90 kV was used, with the other counting conditions unchanged. Peak counts were taken at 12.54° , and background counts at 12.30 and 13.25° 2θ . The counts at 12.30° were consistent, but for some samples they were higher than peak counts. Therefore, the ratios of the counts were used rather than the net counts. Counts were repeated with 39 and 75 V thresholds, using 13.25° as the background. The equation characteristics for $\text{HfK}\alpha_1$ ($n = 2$) lines are given in Table 5. The use of the 75 V threshold reduces the error and improves correlation.

TABLE 5

HfKa₁ (n = 2) Regressions

Threshold	b	a	n	Se	pk/bg*	cv of y
a) 13.25° background						
6 V	0.000760	+0.0233	+0.984	±0.013	1.070	11.06%
39 V	0.000789	+0.0367	+0.980	±0.014	1.070	11.91%
75 V	0.000877	+0.0022	+0.996	±0.006	1.175	5.11%
b) ratio to 13.25°						
6 V	2.3867	-2.3642	+0.989	±0.010		8.51%
39 V	2.3025	-2.2647	+0.980	±0.014		11.91%
75 V	1.1247	-1.1226	+0.996	±0.006		5.11%
c) ratio to 12.30°						
6 V	2.7412	-0.6714	+0.993	±0.007		5.96%

* 0.20% Hf.

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 these samples. Counts from the sample containing the most hafnium were taken as unity and those from the others related to it.

Results

The results for four samples are shown in Table 6. The percentages of hafnium determined on the drillings, using synthetic standards, agree well with neutron activation ratios. The net counts on the discs are included to illustrate the sensitivity of the K and L peaks. These counts cannot be related to the hafnium concentration or the neutron ratio directly,

because, as the values of "b" show, the slope of the regression lines is not 45°. In addition, allowance must be made for the intercept of the lines.

TABLE 6
Hafnium in Mild Steels

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

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

Again, the reproducibility of hafnium counts may be evaluated by that of the background. Substituting the standard deviations of the backgrounds with different thresholds given above in their corresponding equations, the 75 V line gives 0.010% Hf, the 39 V line 0.015%, and the 6 V line 0.071% Hf. These values slightly exceed the standard errors reported in Table 5. This would indicate that the deviation in net counts is slightly less than that of the background.

The HfLa₁ background had a mean of 281 counts and a deviation of ± 17 which is equivalent to 0.011% when substituted in the L equation. These results indicate that there is little difference between K and L lines of hafnium so far as sensitivity and reproducibility are concerned.

THE USE OF SECONDARY STANDARDS

Secondary standards were established for the analysis of mild steels, primarily to increase the sensitivity of determinations by increasing the sample area exposed. Figure 6 illustrates the effects of the mask and applied potential on zirconium counts. Eight secondary standards were counted, in duplicate, at 60 kV with and without the platinum mask and at 80 kV without it. The greater sensitivity due to both increased potential and surface area is evident. To illustrate the effect as clearly as possible, concentration has been plotted along the X axis in contrast to the regression lines where it is the Y variable. The three lines have the same origin. The zirconium in the sample holders is responsible for the intercepts.

In Figure 7 the line from secondary niobium standards at 80 kV is compared with the line from NBS standards at 90 kV. The increase in sensitivity due to the larger area of the secondary standards is pronounced. The equation for the secondary standards is $Y = 0.00007527X - 0.0003$ and the error ± 0.0014 . As a check on instrument stability the line was re-established after six months, giving an equation $Y = 0.00007735X - 0.0006$ with an error ± 0.0012 . The stability was considered satisfactory.

Once secondary standards were available, all samples were analyzed by comparison with them because of their greater convenience and sensitivity. As new samples presented a wider range of concentration, selected ones were analyzed several times and used as additional secondary standards.

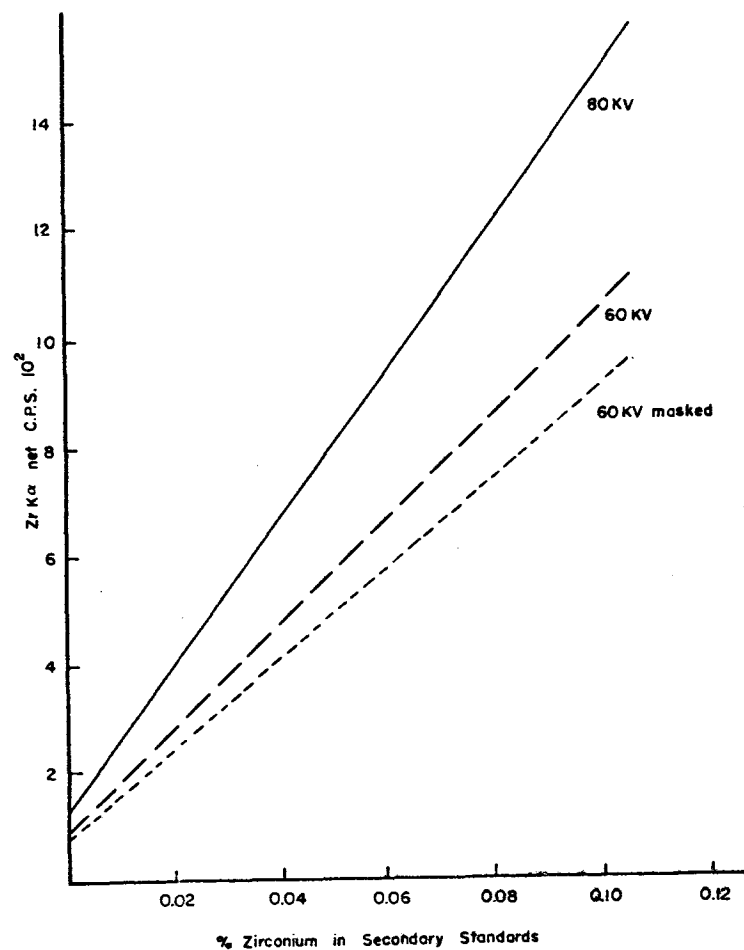


Figure 6. Effect of exposed sample area and kV on zirconium counts.

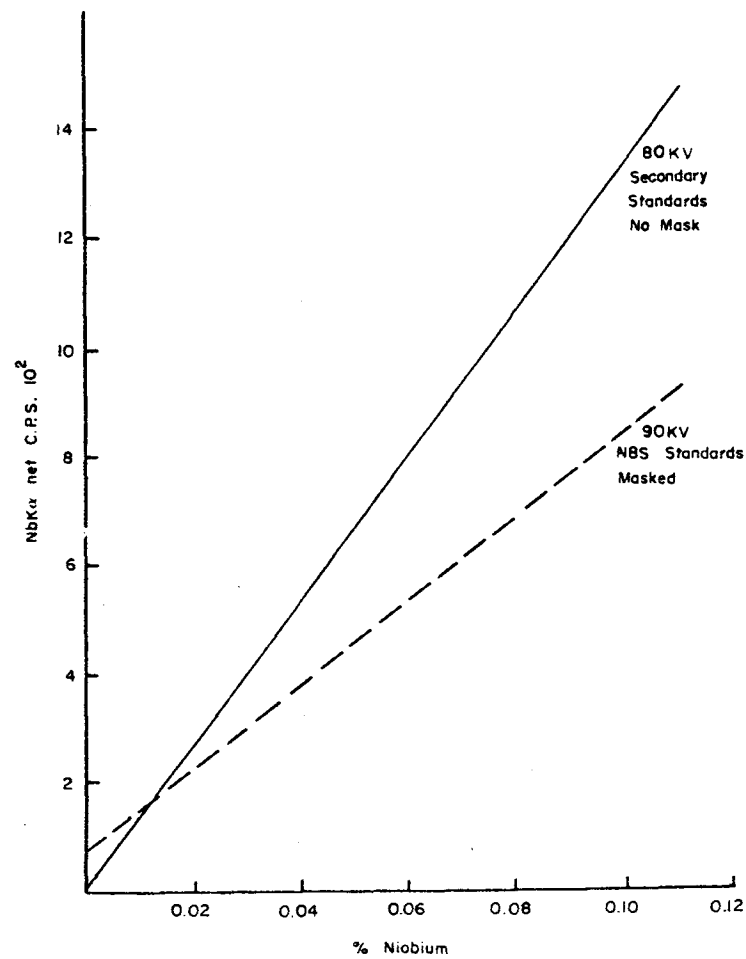


Figure 7. Effect of exposed sample area on niobium counts.

This had led to extrapolation beyond the original synthetic standard range, and concern has been felt that any error in the original secondary standards could have been compounded as the later standards were added.

When a group of steels was received for the determination of niobium in which the expected concentration was more than double that of the highest secondary standard, it was decided to use a mixture of NBS and secondary standards rather than prepare synthetic standards to cover the concentration range. This was simpler and would resolve any doubts about the secondary standards. Three NBS and four Mines Branch standards were selected. Because molybdenum and zirconium were present in the NBS ones, the background had to be determined by interpolation from counts at four points. This procedure resulted in greater error than when two counts equidistant from the peak were used. The net counts in duplicate are shown in Figure 8 with the resultant line.

As a further check on secondary standards, Mines Branch zirconium and NBS ones were compared. Again the background was interpolated. Four points were used for the Mines Branch standards, but only three for the NBS standards because of the presence of niobium. The results, presented in Figure 9, showed a greater scatter than the corresponding niobium counts. The NBS standards do not fall on the line because the niobium, which is present in amounts equivalent to or greater than the zirconium content (Table 1), has contributed to the zirconium counts. In this instance the secondary standards give a better line.

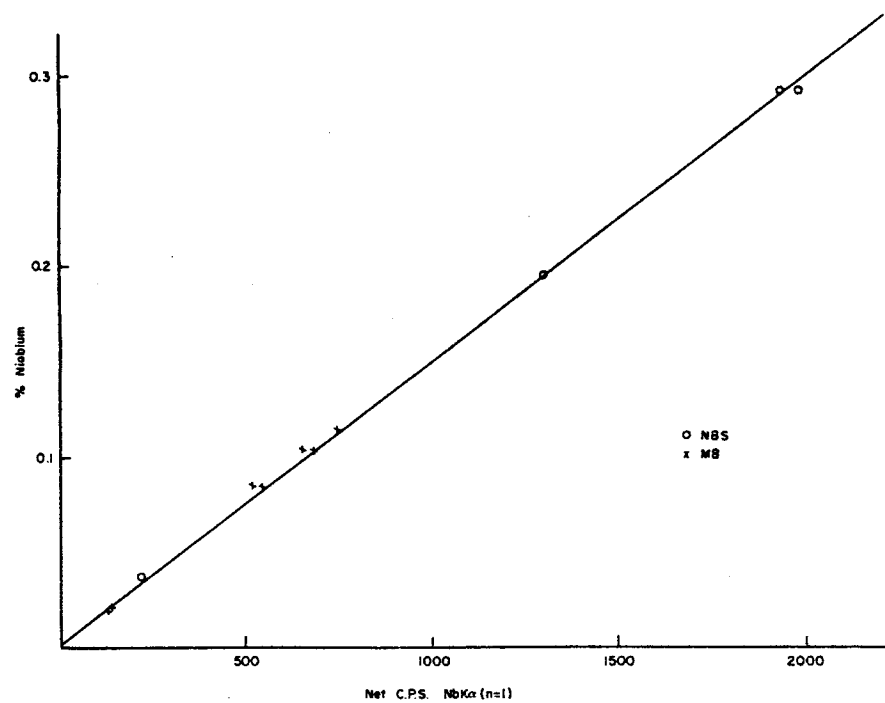


Figure 8. Comparison of NBS and secondary standards for niobium.

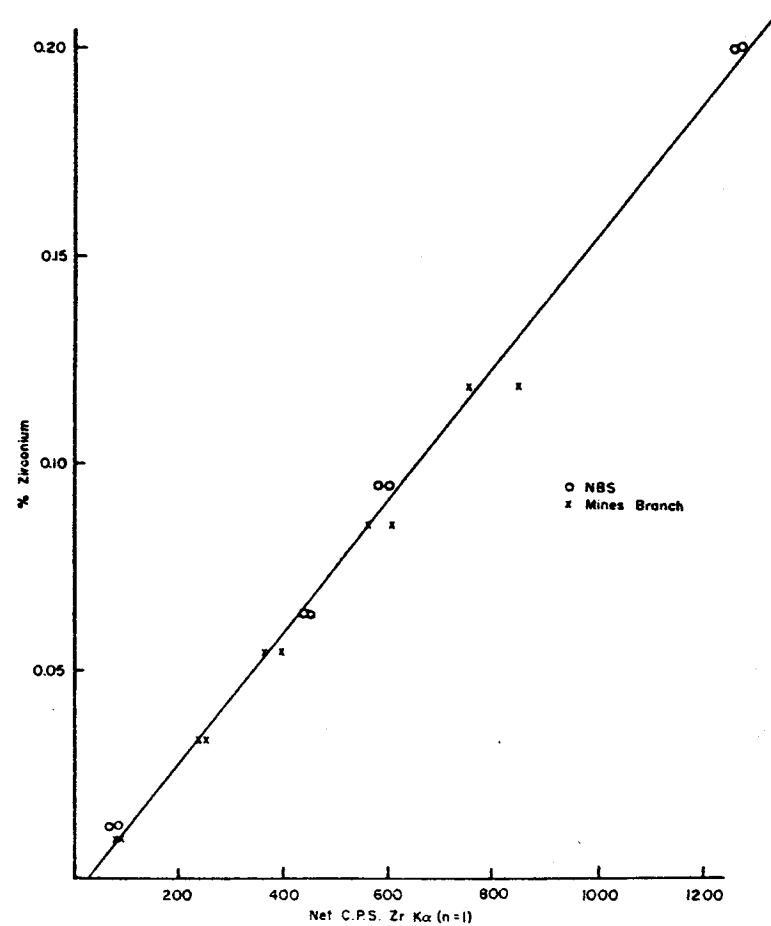


Figure 9. Comparison of NBS and secondary standards for zirconium.

From Figures 8 and 9 it is apparent that the use of Mines Branch secondary standards is satisfactory for the determination of zirconium and niobium in mild steels, and that the values assigned to them are within the limits of experimental accuracy of X-ray spectrography.

CONCLUSIONS

Niobium and zirconium may be determined in low-alloy steel by X-ray spectrography in amounts as low as 10 ppm, and hafnium down to 0.01%.

The use of synthetic standards is justified when appropriate standards are not available.

The establishment of secondary standards from synthetic standards or NBS ones increases the sensitivity by increasing the area exposed.

The use of high accelerating potentials - 80 or 90 kV - significantly increases the sensitivity.

Where a peak occurs on the continuum maximum, as with hafnium, the use of a high threshold increases sensitivity and decreases error.

There is little difference in sensitivity and reproducibility between the K and L radiations for the determination of hafnium.

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APPENDIX

Relevant Statistics

The following statistical formulas have been used:

- 1) Regression equation $Y = a + bX$, where Y = per cent of the element in question and X = net counts per second or modification thereof. The line is fitted by the method of least squares where

$$b = \frac{\sum xy - \frac{\sum x \sum y}{N}}{\sum (x - \bar{x})^2}$$

and $a = \bar{y} - b\bar{x}$. In these formulas, x and y represent individual values and N is the number of observations. Barred symbols are used to signify the mean.

$$2) \text{ Correlation coefficient: } r = \frac{\sum xy - \frac{\sum x \sum y}{N}}{\left(\sum (x - \bar{x})^2 \cdot \sum (y - \bar{y})^2 \right)^{\frac{1}{2}}}$$

$$3) \text{ Standard error: } Se = \left(\frac{\sum (y - \bar{y})^2 - b^2 \cdot \sum (x - \bar{x})^2}{N - 2} \right)^{\frac{1}{2}}$$

$$4) \text{ Standard deviation or root mean square: } \delta = \left(\frac{\sum (x - \bar{x})^2}{N - 1} \right)^{\frac{1}{2}}.$$

The denominator of $N - 1$ allocates one degree of freedom to the mean.

$$5) \text{ Coefficient of variance of } \bar{y}: cv = \frac{Se \times 100}{\bar{y}}$$

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