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THE DETERMINATION OF TUNGSTEN IN ORE
TAILINGS BY X-RAY SPECTROGRAPHY
USING THE STANDARD ADDITION TECHNIQUE

by

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ABSTRACT

The determination of tungsten in tailings by standard addition using K and L X-radiation is compared. The effect of Compton scatter on the L results when a tungsten tube is used is discussed.

The standard addition technique is fully described and the significance of various factors noted.

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INTRODUCTION

A request from the Mineral Processing Division for the determination of tungsten in tailings focussed attention on some of the unique problems presented by its determination in ores by X-ray spectrography using a tungsten X-ray tube. The determination of rhenium and tantalum is affected by the same factors to a lesser degree.

The determination of small concentrations of elements in ores has always been made by the standard addition technique in this laboratory. Although it has been extensively used, this procedure has never been fully reported. Therefore it was decided to include a discussion of the technique in this report on the determination of tungsten.

FACTORS AFFECTING ORE ANALYSIS

Every element present in a sample affects the radiation of every other element present to some degree. In some cases there is direct interference with the radiation to be counted by radiation from neighbouring elements. Interference may arise from radiation of heavier elements which has similar energy or angular dispersion though it is of a different series or order. Aside from such direct interference, elements with absorption edges lying just to the low-energy side of characteristic radiation absorb it and any change in their concentration in samples has a marked effect on the determination of such characteristic radiation. In addition, there is a matrix effect which may be related to the mean atomic weight of the elements composing the samples.

In ore analysis the effect of an absorption edge may be vitiated only when the concentration of the element possessing the edge is known and proper standards are available. The general matrix effect is minimized by dilution of the sample. A dilution of as much as fifty of diluent to one of sample is often used. This results in an almost constant matrix being presented to the X-ray beam by the samples. Dilution is frequently achieved by fusion of the sample with a similarly large quantity of flux because fusion compensates for particle size effects as well.

Dilution is not a possible solution to interelemental effects when the concentration of an element in a sample is low. Using silica as a diluent with 98% silica to 2% sample, it has been found that amounts of an element less than 2% in the sample do not give, after dilution, a signal strong enough to be statistically significant. For such samples, standard addition is used in this laboratory.

STANDARD ADDITION

When standard addition is used, two additions of the element to be determined are made to portions of the sample. The sample is counted with and without the additions and the amount of the element present is determined from the increase in the counting rate due to the additions.

Method

It has been customary to weigh three five-gram portions of the sample. Additions of approximately 0.5 and 1% of the element as the oxide, sulphide or carbonate, preferably in the combination in which it occurs in the sample, are made to two of the portions. All three aliquots are mixed for twenty minutes in a Fisher automatic mortar. Peak and background counts are then taken and the net counting rate for the element is determined for each aliquot. The counts are plotted against the percentage added and a line is drawn through the points. A line parallel to this is drawn from the origin. The percentage corresponding to the point

where a vertical drawn from the point for the sample without addition cuts the parallel line is the amount in the sample. As an example, the determination of tantalum using its $L\beta_1$ line is shown in Figure 1. In some cases three additions may be necessary if the counts from the first two and the original sample do not give a straight line.

The amount present in the sample may be calculated, but it is well to plot the points to be sure they lie in a straight line. The calculation of the amount of rubidium in a sample was made as follows:

X alone	659 net cps		
X + 0.278% Rb	1667 net cps	0.278% = 1008 cps,	0.1% = 359
X + 0.557% Rb	2614 net cps	0.577% = 1955 cps,	0.1% = 333
		0.279% = 943 cps,	0.1% = 338
			mean : $\overline{343}$ cps
	% in sample	$(659/343)0.1 = 0.19$	

It is not necessary to use the difference between the two aliquots with the additions. Its inclusion in the calculations above had no effect on the result. However, it serves as a check on linearity if the points are not plotted.

Considerations

If a high potential is applied to the X-ray tube or if the sample is composed of elements of low atomic number, the sample may not be infinitely thick with respect to the X-ray beam. It is for this reason that the portion to which no addition is made is weighed. If it is not, it may differ significantly in weight from the other two portions and the proportion of the beam it reflects will not be the same as that reflected by the others.

If sufficient sample is available, it is often desirable to use ten-gram aliquots. In the case of a dense sample, five grams may not cover the bottom of the sample holder adequately.

If trace amounts of an element are to be determined, smaller additions, i. e., 0.1 and 0.2%, are preferable. This keeps the significance of the sample counts on a par with that of the additions.

Standard addition cannot be used for large concentrations of an element in a sample, nor is it wise to make the additions any larger than necessary because of the effect of such additions on the matrix. In a few cases, even with additions not exceeding 1%, the factor has been found to change with the amount added. The four points (sample plus three additions because a difference in the factor with only two additions may be due to weighing or mixing errors) plot to give a curved line. In such a case the proper factor for the zero addition level may be found by extrapolation as shown in Figure 2.

Standard addition works well for the determination of small amounts of an element in a sample only when great care is taken to obtain the true background under the peak used. In methods where standards are used, the background determination is not critical because a constant error in its determination will be reflected by the intercept of the standard line and compensated for by it. In standard addition any error in the background determination has a significant effect on the result because it is included in the net sample counts only. The background is difficult to determine in the presence of neighbouring elements or when the characteristic radiation occurs near the continuum maximum or the slope leading to it. In the first instance it may be impossible to obtain the true first order background and second order radiation may have to be used in spite of its significantly lower intensity. In the second case, the background may be determined by interpolation from three or four points.

FACTORS IN THE DETERMINATION OF TUNGSTEN

Sample Composition

With the 100kV spectrograph it is possible to use either K or L lines of tungsten for its determination. One or more of the L lines suffer direct interference from the K lines of common elements such as copper, zinc, nickel and arsenic, as well as molybdenum, niobium, tin and antimony,

and from L lines of tantalum, hafnium, lead and uranium. Only lines from neighbouring elements interfere with the K lines of the element. Sample composition can thus be a factor in line choice.

Spectrographic Components

There are a number of lines commonly found in the X-ray spectrum recorded from a sample that do not arise in the sample. These are the lines of nickel from the collimator, of zinc, copper, lead and iron from the components of the optical path of the spectrograph and of various elements composing different sample holders. For all of these, it is possible to make satisfactory corrections and thus determine these and the elements with which they interfere in spite of direct interference. A number of samples free of the particular element are placed in the spectrograph and the ratio of the peak counts to those of a nearby background is determined. This ratio, which measures the non-sample intensity, will remain constant for given excitation conditions unless the samples contain a varying component whose radiation has energy just greater than that of the absorption edge of this element. During analysis, by taking counts at the chosen background, the counts due to the spectrographic component can be calculated from the pre-determined ratio and subtracted from the total counts to give those due to the element in the sample.

Though spectrographic components are not a major factor in choosing a line for analysis, if a sensitive line can be found that does not require correction for such interference, it simplifies the counting procedure and removes a possible source of error. The position of such lines relevant to tungsten L lines are shown in Figure 3.

X-ray Tube

Other radiation found in recorded spectra arises in the X-ray tube. When the potential applied to a tube exceeds the energy of the absorption edge of the target element, the spectrum emitted by the tube usually contains the characteristic lines of the target material superimposed upon the

continuum. Thus, if an X-ray tube of target Z is used for the determination of Z, the observed intensity is due to that from the sample plus that from the target. Unfortunately, because of Compton scatter, which affects only the tube spectrum, the intensity of the tube lines is not constant unless the mean atomic weight of the samples is constant. Their contribution to the observed intensity cannot be determined by a ratio technique for ore fractions because of the variable sample composition.

For most analyses the tube contribution is not a factor to be considered because it is not common practice to excite an element using a tube having a target of that element. Neighbouring elements are affected by the target lines as are elements where lines of the preferred series have the same energy as the lines emitted by the target. The latter is the case for zinc where the K lines fall close to tungsten L lines, as Figure 3 illustrates. However, the tungsten tube is the most efficient exciter for elements heavier than titanium, including itself, so self-excitation had to be considered in this case.

Though a number of tubes are available with targets other than tungsten, the only other available in this laboratory has a molybdenum target. Second order K lines of this element interfere with all but L_{γ} of the principal tungsten lines (see Figure 3) and this line has the least intensity of those of practical use. Of the X-ray tubes commercially available, only those with a chromium target leave the L lines of tungsten entirely free and they are poor exciters of the tungsten spectrum. Platinum tubes leave the L_{α} lines free, as Figure 3 shows.

The choice for analysis of the ore tailings was between poor excitation of a weak line using a molybdenum tube and good excitation using a tungsten one, which interferes with its own L spectrum and whose K spectrum has background determination difficulties. The L spectrum suffers from Compton scatter, but the K does not. No observable K lines are generated by the tungsten tube.

THE DETERMINATION OF TUNGSTEN

While the determination of tungsten was being investigated, it was decided to compare results obtained using both the K and L radiation. Results using the L lines were not expected to be satisfactory, but only a few laboratories are able to use the K lines and the discrepancy between them has not been reported as far as we are aware.

The use of LiF (220) as the analysing crystal seemed advantageous because its greater dispersion reflects the K lines to higher angles than LiF (200) does and separates the L lines from interfering radiation to a greater degree.

The Use of K Lines

The scan of the head sample over the K range is shown in Figure 4a. The unmarked peak is part of the continuum. To remove the undifferentiated radiation from the continuum at low angles and thus reduce the continuum maximum which makes a good signal-to-noise ratio difficult to achieve at low angles, a lead mask was introduced at the exit end of the receiving collimator (1). Without this mask the continuum would continue at angles of less than 9° as shown by the dashed line. The effect of the mask on the continuum results in an anomalous peak which is sufficiently removed from the tungsten peak not to interfere with its determination.

Even with the lead mask in place, the continuum is pronounced enough that it is difficult to measure the true background under the $L\alpha$ peak. An attempt was made to establish a ratio for the continuum at 8.16° , the alpha peak angle, to that at 6.20° . Eleven different elements and compounds free of tungsten were counted at these angles and their ratios determined. These varied from 1.52 to 1.92 and obviously could not be used to determine the background under the peak. The continuum is due to the radiation scattered by the sample and the range in the ratio indicates how the maximum varies with the mean atomic weight of the sample. This is Rayleigh scatter and not the same as Compton scatter that affects the L line ratio above.

The background was determined as shown by the dotted line in the figure. Counts were taken at 7.50, 7.60 and 7.70° below the peak and at 8.80, 8.90 and 9.00° above it. The counts per second were plotted and, from the line drawn through them, the counting rate for the background at 8.16° was determined. In most cases five of the points gave a straight line, occasionally six did; but 9.00° was close enough to the anomalous peak to be affected by it in most samples.

Samples with three additions of WO_3 were thus counted at seven points and the net counts for them determined using the interpolated background. The additions had no effect on the background. A typical calculation of the final result from the net counts follows:

sample	643 cps		
+0.407%	948 cps, addition = 305 cps	∴ 1% equivalent = 749 cps	
+0.195%	790 cps	147 cps	753 cps
+0.634%	1126 cps	483 cps	762 cps
			mean: <u>755</u>

$$\% \text{ in sample: } 643/755 = 0.85$$

The Use of L Lines

The scan of the head sample over the $L\gamma$ and $L\beta$ range is shown in Figure 4b. It was decided to count the samples with the same additions as used for the K lines at $L\gamma_1$ and $L\beta_2$ because good backgrounds could be counted for these lines. WLa suffered a similar drawback as that shown for $L\beta_1$ with respect to background.

For net counts it was necessary to try to determine the tube contribution to the peaks. As mentioned above, because of Compton scatter, this contribution was expected to vary. From various oxides free of tungsten, the mean ratio of $L\gamma_1$ to the 47° background was found to be 1.853 and of $L\beta_2$ to 50° to be 2.854. These ratios were used to determine the tube contribution to sample peaks from their background counts at these angles. Results were calculated in the usual manner from the net counts for the samples with and without additions.

Results

The results are shown in Table 1. The MPD results shown were considered unsatisfactory and are given for reference only. It is readily seen that the results from the K and L lines do not agree, nor do those from the two L lines. It was expected that the L lines would be unsatisfactory, but this was not sufficient reason for accepting the K lines, although there was no obvious reason why they should be unsatisfactory except for background error.

In 1962 a large number of ore fractions had been analysed by wet chemical methods for tungsten. A number of these were still available. Four of these that were large enough to make additions possible and that also covered the range of the MPD samples were chosen. They had caked with standing in the sample envelopes and had to be ground and sieved. Results using the $K\alpha$ line for these are compared with the original results in Table 2. Except for one sample, agreement is satisfactory. With this evidence, in addition to the constant background obtained for the K counts on samples with and without additions, it was decided that the results from the K line were acceptable.

Matrix Effect

In both tables the final column lists the counting rate equivalent to 1% WO_3 in the samples. The variation in these figures is a good illustration of how large the matrix effects can be, even from the same orebody, and why it is not possible to compare peaks from different samples.

Sample Weight

Many of the samples received in this laboratory for analysis are small. A high potential must be applied to the X-ray tube to excite the K lines of heavy elements. The X-rays generated are penetrating and for powder samples it can be difficult to achieve infinite thickness, which is regarded as desirable, although a constant thickness has been found to be satisfactory. This problem does not arise with L lines.

No sample at hand was large enough to run weight tests, so a number were combined for this purpose. Different weights of the combination were placed in the sample holder and counted at the peak and four background angles. Forty-five grams was the maximum the holder would contain. Taking the counts from this weight as 100%, the percentages of the counts from the other weights are shown in Table 3. The consistency between peak and background counts demonstrates that any weight of sample that will give a constant thickness on covering the sample holder is satisfactory, although sensitivity is reduced.

In our analysis we are often limited to five grams because small samples are submitted for analysis. Table 3 shows that results using this weight were satisfactory for these ore samples. Of course, the minimum weight that may be used will vary with the density of the sample.

DISCUSSION

Tungsten L excitation by the molybdenum tube was not investigated because only the $L\gamma_1$ line is free of interference. This is not a sensitive line, as Table 1 shows. When poor excitation was considered as an additional factor, doubts arose as to the statistical significance of the low counting rates expected. When tubes with other targets are available to us, it would be profitable to investigate the use of L lines for ore analysis again.

Remarks concerning the use of L lines and the limitations due to Compton scatter apply to the standard addition technique only when an element is excited by a tube having a target of the same or a neighbouring element. For any analysis where a satisfactory range of standards is available or where the matrix is relatively constant, proper standards will compensate for Compton scatter of the tube lines.

CONCLUSIONS

The standard addition technique is satisfactory for the determination of small quantities of tungsten in ore fractions by X-ray spectrography using a tungsten X-ray tube if the K lines of the element are used.

REFERENCE

Reed, D. J. X-ray Spectrographic Analysis at Low Two-Theta Angles. *Canad. Spectro.*, 15, 49 (1970).

TABLE 1

Comparison of Tungsten Results

No.	MPD	WK α		WL γ_1		WL β_2		1% equiv.: cps		
		%	cps	%	cps	%	cps	K α	L γ	L β
5	1.97	1.34	990	1.28	104	1.09	137	740	103	126
37	0.58	0.64	530	0.43	45	0.45	66	830	104	146
41	0.34	0.45	335	0.11	16	0.50	54	795	144	108
46	0.25	0.85	643	0.45	55			768	112	
49	0.13	0.51	385	0.28	30	0.41	51	755	108	124
50	0.89	0.41	329	0.26	25	0.34	41	669	96	119
51	4.36	0.64	400	0.26	26	0.42	53	642	100	126

TABLE 2

Comparison of Chemical and X-Ray Results

No.	Chem	X-Ray		1% Equivalent in cps
	%	%	cps	
1514	0.35	0.35	438	1251
1990	0.89	0.31	316	1020
1538	1.48	1.60	1375	860
1517	2.89	2.75	2559	930

TABLE 3

Effect of Sample Weight

Weight	% of Counting Rate from 45 grams at Various Angles					
	7.50	7.70	8.16	8.70	8.80	Mean
5 g	75.5	74.9	73.7	74.1	73.7	74.4
10 g	84.2	83.6	82.5	83.8	82.8	83.4
15 g	89.4	89.5	88.7	89.4	89.5	89.3
20 g	91.9	92.9	91.9	92.1	91.5	92.1
25 g	95.9	96.1	95.7	96.0	95.6	95.9

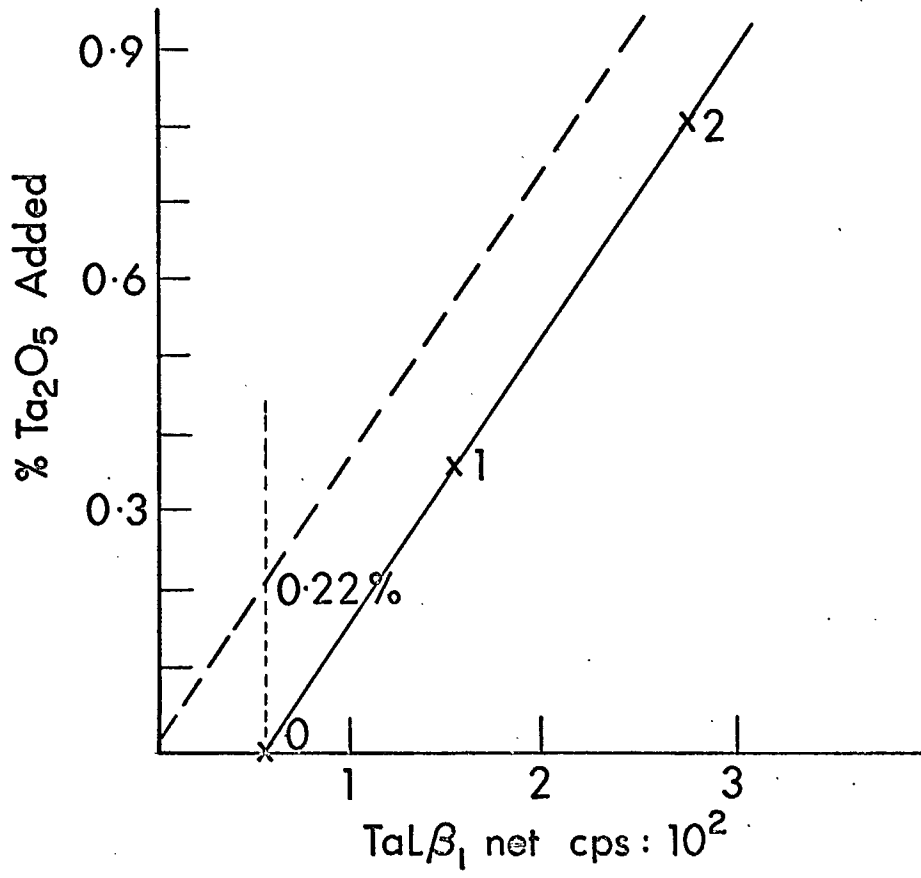


Figure 1. Graphic Determination of % Ta₂O₅ in a Sample by Standard Addition.

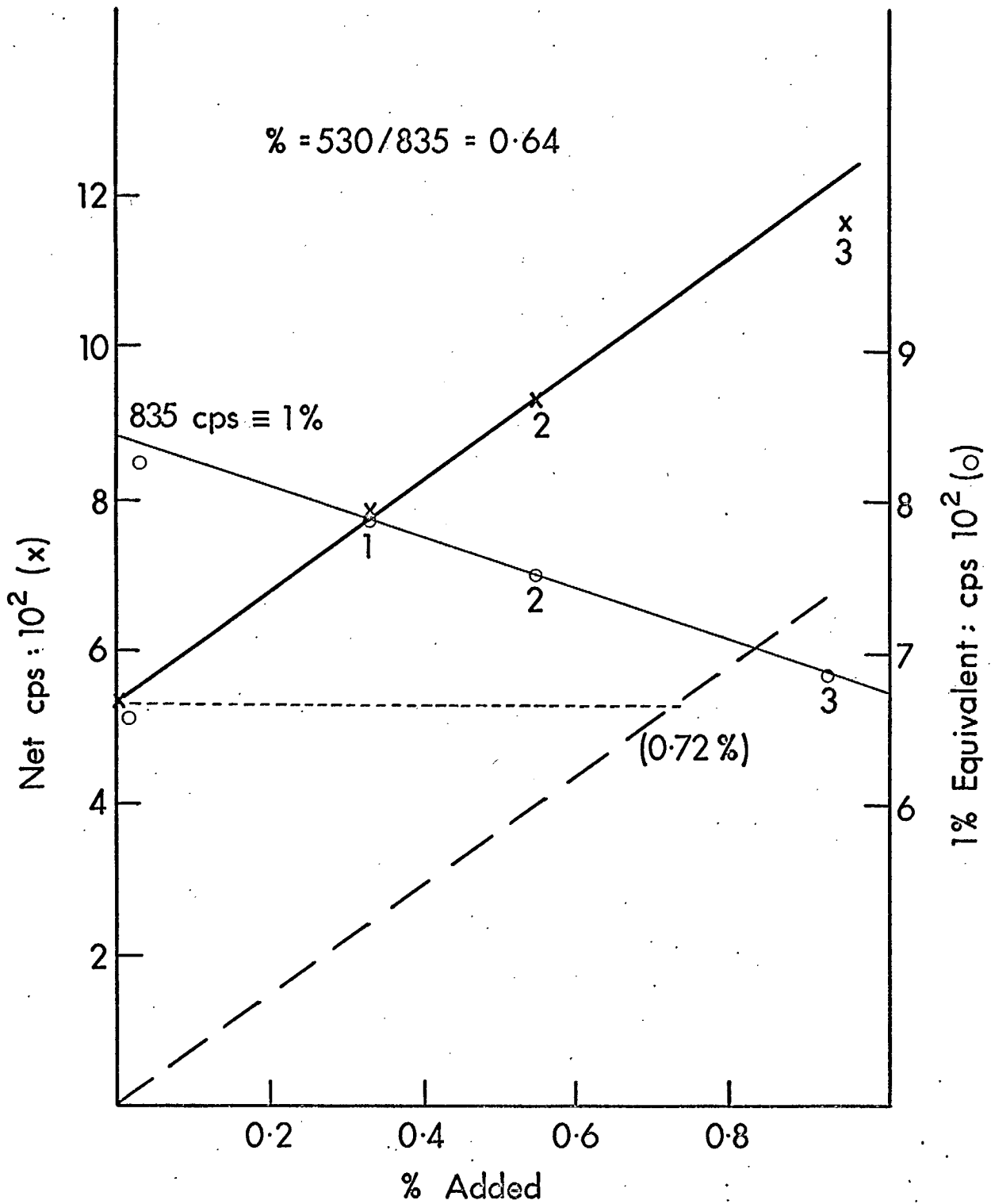


Figure 2. Graphic Determination of an Element in a Sample when the 1% Equivalent Varies.

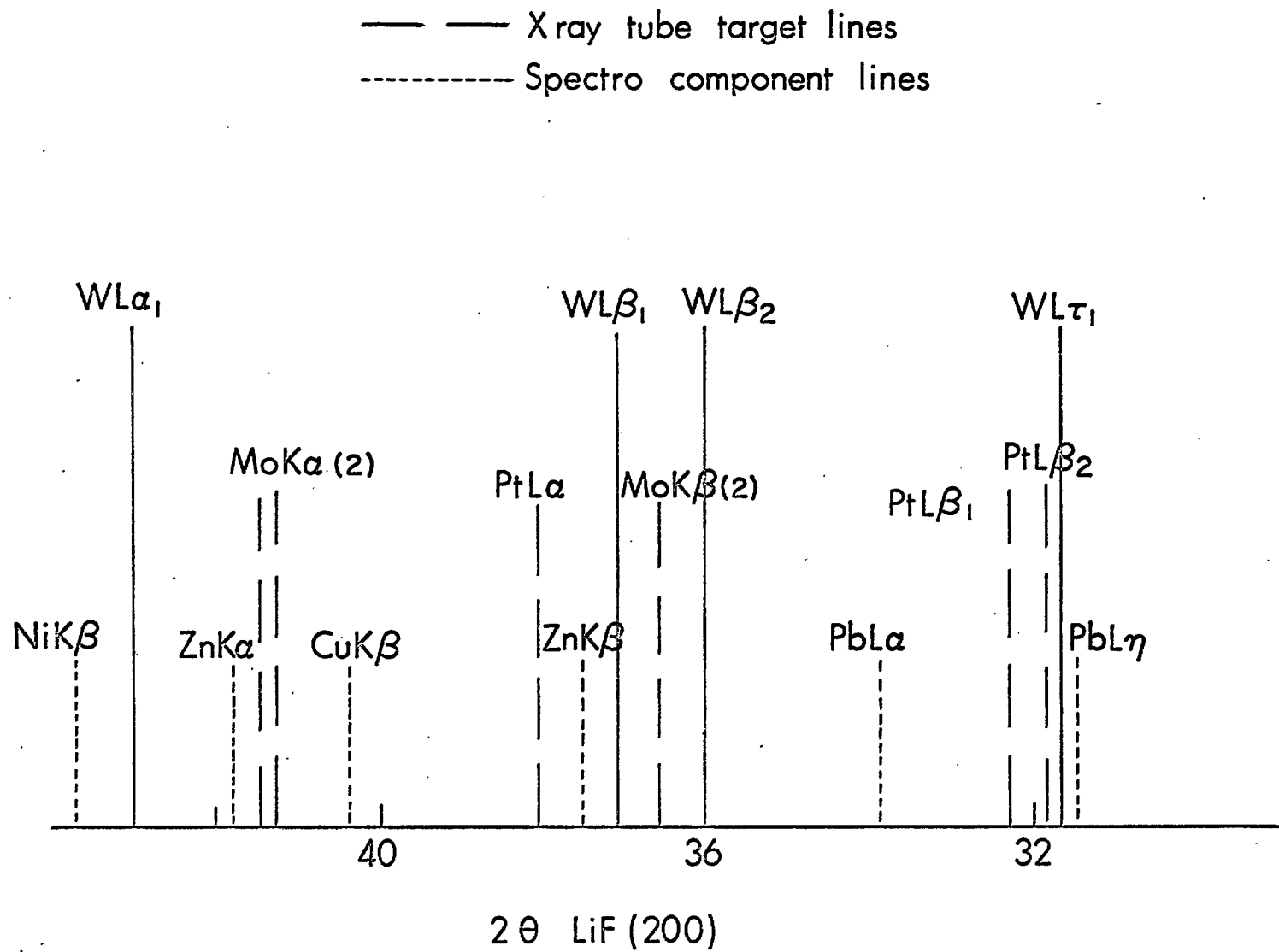


Figure 3. Instrumental Interference with Tungsten L Lines.

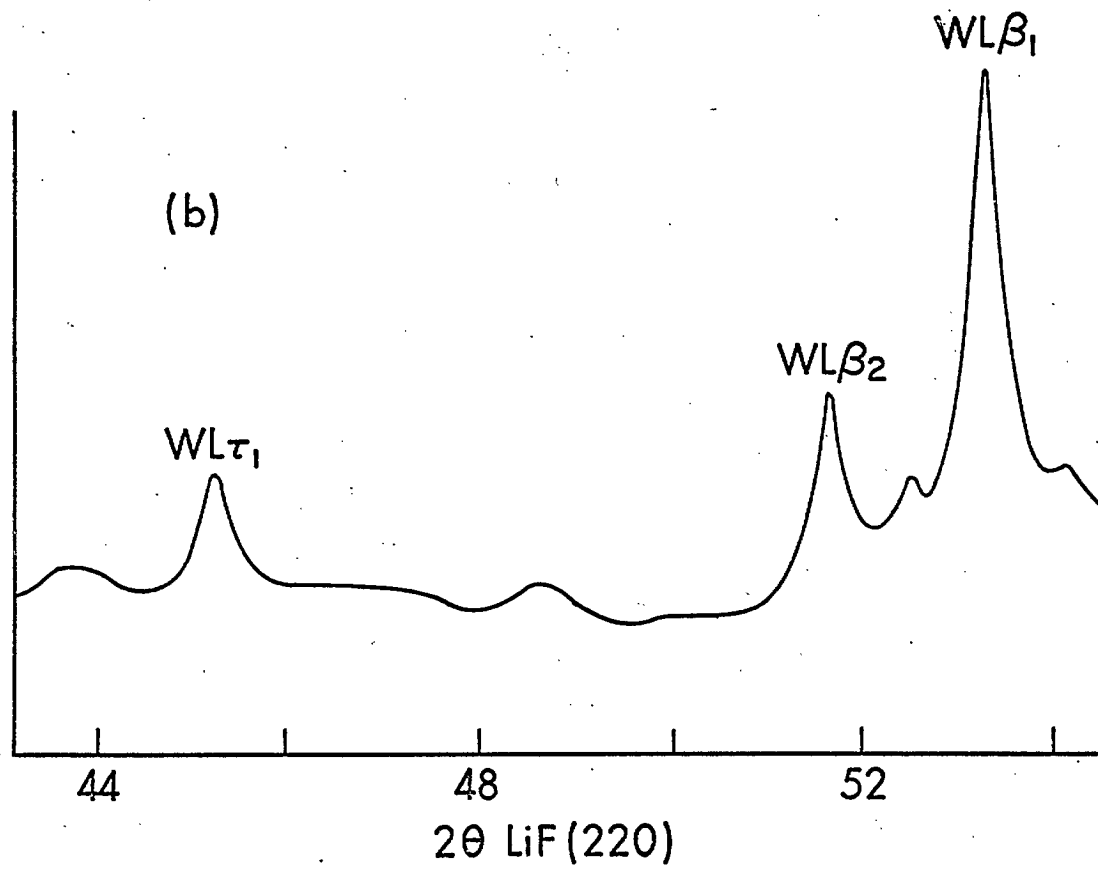
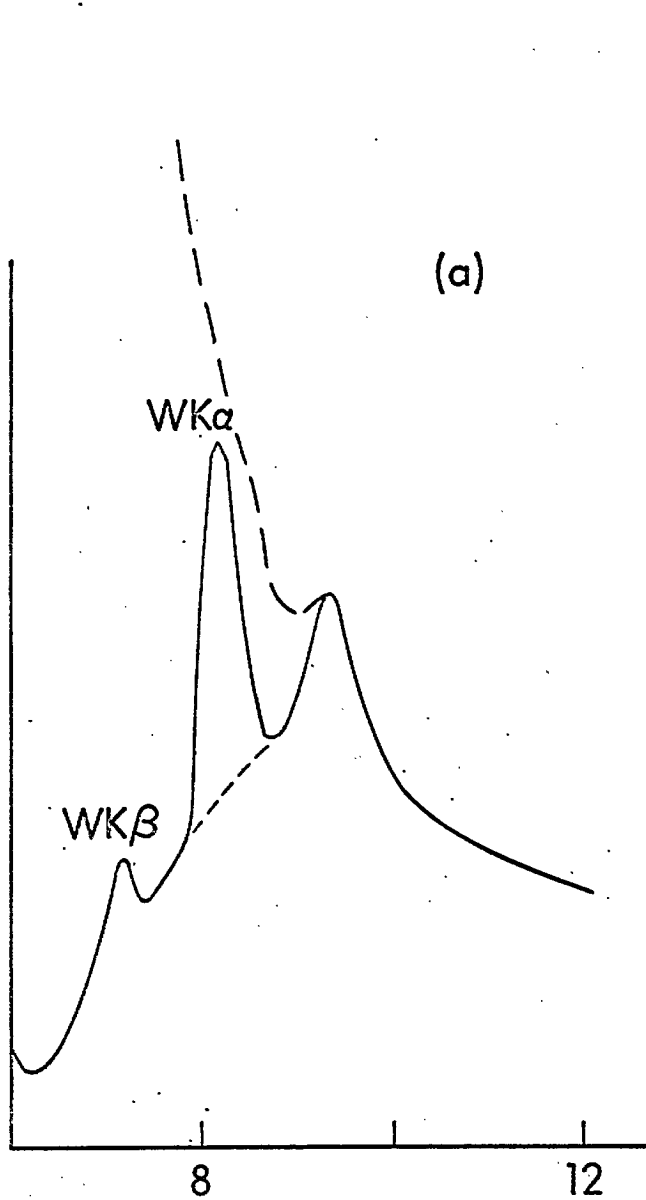


Figure 4a. Tungsten K Lines Using LiF (220).

Figure 4b. Some Tungsten L Lines Using LiF (200).