

NATIONAL BUREAU OF STANDARDS REPORT

9594

Progress Report

on

X-RAY FLUORESCENCE ANALYSIS OF SILVER DENTAL
ALLOYS WITH CORRECTION FOR A LINE INTERFERENCE

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U.S. DEPARTMENT OF COMMERCE
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By

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X-Ray Fluorescence Analysis of Silver Dental Alloys With Correction For a Line Interference

S. D. Rasberry, H. J. Caul and A. Yezer

An x-ray fluorescence spectrometric method has been developed for the rapid analysis of granular silver dental amalgam alloys having the nominal composition, in percent, of silver 69, tin 26, copper 4, and zinc 1. Several methods of specimen preparation were investigated; a method employing briquettes pressed at 1400 kg/cm² without binder was the most satisfactory. Analytical curves relating intensities of K_{α} lines to concentration of silver, copper and zinc were linear but no calibration curve could be obtained for the tin K_{α} line due to line interference from the silver K_{β} emission. To correct for this interference the ratio of intensities $(\text{Sn } K_{\alpha} + \text{Ag } K_{\beta}) / \text{Ag } K_{\alpha}$ was plotted versus the ratio of concentrations Sn/Ag, producing a linear analytical curve. Observed typical coefficients of variation for the method were Ag 0.4 percent, Sn 0.8 percent, Cu 3 percent, and Zn 0.6 percent.

1. INTRODUCTION

Silver base alloys conventionally used in dentistry have the nominal composition in percent, of silver 69, tin 26, copper 4, and zinc 1.¹ Quantitative determination of these four elements by traditional methods of solution chemistry is a time-consuming task. One man-week is required to analyze four samples in duplicate using conventional gravimetric and electrolytic separation techniques.^{2,3}

A desire to reduce the time required for analysis while

retaining the precision and accuracy of conventional methods prompted an investigation of performing the analyses by x-ray spectrometric methods.^{4,5,6} With the availability of a multichannel x-ray spectrometer and a digital computer, both the measuring time and the computation time can be minimized. In this case specimen preparation time becomes a significant factor. Five techniques of specimen preparation were experimentally tested: unchanged specimens (loose turnings), sulfuric-nitric acid solutions, castings, pellets hydraulically compressed with a binder, and pellets pressed with no binder. The latter technique yielded the most precise, accurate, and rapid single method for determination of all four elements.

2. EXPERIMENTAL PROCEDURE

Silver base dental alloys are supplied by dental manufacturers as turnings from castings. These turnings are rough chips which vary from 10 to 100 μ in width and 20 to 800 μ in length, depending on manufacturer. Length and width for an average particle from three typical alloys used in this investigation are given in Table 1.

A group of 30 alloy turnings which had previously been analyzed by solution chemistry methods was available as a basis for comparisons of x-ray techniques. Nine alloys were selected from this group for detailed study. Alloys were chosen so that the entire expected concentration ranges of the four elements present were spanned.

Five preparation techniques were investigated for presenting a representative and homogeneous specimen surface to the primary x-ray beam. Only one of the five techniques was found to be satisfactory with regard to specimen stability and achieving accuracy of ± 0.5 weight percent. The result of these investigations are summarized in Table 2.

In the best method pellets were prepared without binder by weighing 4.0 g of the alloy turnings and loading this charge into a 1.27 cm diameter steel mold, which consists of a cylinder, piston, and cap. The pellets are 1.27 cm in diameter, and 0.48 cm high; each was compressed for 1/2 a minute under 1400 kg/cm^2 . The cap was surface polished before making any pellets because the pellet surface is an impression of the cap. It is desirable that the initial pellet surface be as smooth as possible, because no further smoothing of this surface can be accomplished without breaking the pellet. These pellets were found to be acceptable with respect to mechanical stability and analytical precision and accuracy.

A multichannel x-ray fluorescence spectrometer⁷ was used to measure the relative x-ray intensities of the AgK_α , SnK_α , CuK_α , and ZnK_α lines for each of the nine alloy compositions. The x-ray tube had a platinum target and was operated at 30 kV and 35 mA. The signal currents from x-ray detectors for each of the four elements were stored on integrating capacitors; the integrating period being approximately 60 sec. Actual measurement termination was effected by an external standard channel which consisted of a copper button in a portion of the x-ray beam, a nondispersive detector, and an integrating capacitor circuit which was adjusted to give measurement termination at a present capacitor charge. In order to calibrate the spectrometer, pellets were made for each of the nine selected alloys. The relative x-ray intensity for each element in each specimen was measured simultaneously and the measurements were made five times in a sequence designed to minimize effects of instrumental drift.

3. CORRECTION TECHNIQUE FOR X-RAY LINE INTERFERENCE

During a one-year period, the spectrometer was calibrated several times for the analysis of silver base dental

alloys. In each case, linear analytical curves were obtained for silver, copper, and zinc. The average standard deviation, in percent concentration, for the standards comprising these analytical curves was silver 0.23, copper 0.08, and zinc 0.01.

In the case of tin, it is evident from the examination of Figure 1, that a useful calibration is not directly obtained from relative intensity integrated in the tin channel as a function of tin concentration. The tin spectrometer is fixed at a wavelength of 0.492 \AA (SnK_{α}); however, in addition to the tin line there are two silver lines, 0.497 \AA ($\text{AgK}_{\beta 1}$), and 0.487 \AA ($\text{AgK}_{\beta 2}$) which are near this wavelength. The two silver lines at 0.49 \AA are not resolved from each other or from the tin line. This condition of line overlap is illustrated in Figure 2. The effect of the interference is qualitatively demonstrated in Figure 1, where higher silver content produced higher relative intensities at nearly constant values of tin concentration.

A correction technique for x-ray line interferences of the sort to be described is particularly important in the case of rapid analysis using fixed-channel multi-channel spectrometers. In this type instrument it is usual to have, for each element of interest, one monochromator locked to one wavelength. In this case a wavelength, which is the only possible analytical line for an element, may be subjected to interference by a line of another element in the specimen.

We have developed a method for resolving line interferences that is valid when the interfering element can be independently quantitatively determined and when the K_{α}/K_{β} intensity ratio for the interfering element is constant for all specimens. Apart from effects of absorption and

fluorescence, intensity ratios are proportional to ratios of the concentrations of the element sought and the interfering element (Eq. 1), regardless of the presence of other elements in the specimens. For a given condition of excitation, the intensity ratio for the K_{α} and K_{β} lines of the same element is usually well approximated as a constant (Eq. 2). We derive (Eq. 3) a proportionality relating the intensities of unresolved and resolved x-ray lines:

$$\frac{I_{SnK_{\alpha}}}{I_{AgK_{\alpha}}} = k \frac{\%Sn}{\%Ag} \quad (1)$$

$$\frac{I_{AgK_{\beta}}}{I_{AgK_{\alpha}}} = k \quad (2)$$

by adding (2) to both sides of (1), we have:

$$\frac{(I_{SnK_{\alpha}} + I_{AgK_{\beta}})_{\text{unresolved}}}{(I_{AgK_{\alpha}})_{\text{resolved}}} = k_1 \frac{\%Sn}{\%Ag} + k_2 \quad (3)$$

The result of graphically applying Eq. 3 to the data of Figure 1 is shown by the analytical curve in Figure 3. This linear curve permits the determination of the Sn/Ag concentration ratio, and after silver has been determined on the basis of the K_{α} line, the concentration of tin may be computed. No extra standards are required for the application of this method. Although Eq. 3 has been derived specifically for the case of tin-silver interference, the derivation is based on general principles indicating that the procedure can be applied to other cases of line interference.

The right-hand side of Eq. 1 is not necessarily restricted to be a linear term so it is possible that the technique might be applicable in cases where x-ray intensity

is a nonlinear function of concentration. We have not tested such a case in this work.

This technique corrects only for line overlap and it must be applied with caution, as indicated by the following observations. SnK_β radiation is critically absorbed by silver and would therefore normally be expected to enhance the production of silver radiation, affecting the accuracy of analysis not only of silver, but, when the correction described here is applied, also of tin. Similarly, copper radiation is enhanced by the presence of zinc due to absorption of the ZnK_β line. The reason for errors due to enhancement not being observed in this study is that the concentration ranges covered for tin and zinc are very narrow.

The conditions for errors due to absorption effects are not strongly present in this system; however, in the general case, especially with more varied compositions, the possibilities of errors due both to absorption and enhancement must be considered.

One advantage of the technique presented is that it removes the necessity of producing a standard which has no tin present, but which does have the same preparation as the other standards and unknowns. Further, it prevents the determination of the correction constant K_2 from being based entirely on measurements on one specimen. Finally, the method is graphical and simple to use.

MacNevin and Hakkila⁸ also described a method for correcting the intensities of unresolved x-ray lines. However, their method requires preparation and measurements of additional calibration standards for the interfering element which are free from the presence of the element sought.

Birks and Brooks⁹ described a method for treating the

case of the unresolved hafnium L_{β} and second-order zirconium K_{β} lines. The analytical curve was not linear in their technique, which, in general, is limited to the treatment of binaries or systems where only the two interfering elements vary in concentration.

4. RESULTS

The precision of analysis, calculated as the percent coefficient of variation for an individual determination in a group of 5, is given in Table 3. Table 4 compares the composition of the calibration standards as given by chemical analysis with that found by this x-ray method. This measure of accuracy indicates that there are no significant contributions due to systematic errors.

As a test of reproducibility in making the specimen pellets, 14 pellets were made and tested for each of four of the specimens. In this test the relative x-ray intensities were measured five times for each element for each of the 14 pellet replications. The mean of the five intensities from the individual replications were compared with the statistics for the 70 intensities obtained by pooling the data from the 14 replications. This comparison was extended to each element in each of the four specimens with the finding that the means from the replications were within the range of plus or minus one standard deviation of the means of pooled averages. Reproducibility in making specimen pellets is thus demonstrated.

5. CONCLUSIONS

The study of precision and accuracy of this method indicates that it is sufficiently accurate to serve as a primary analytical technique for silver dental alloys. An x-ray line interference on the tin K line was encountered and successfully resolved. This method has advantages of

simplicity of sample preparation and speed of measurement compared to wet chemical analysis, and to further reduce the time required for analysis, the data reduction has been programmed for automatic data processing.¹⁰

Approximately one man-day is required for the analysis of 20 unknown specimens; the time being divided 4 hours to specimen preparation, 3 hours to x-ray intensity measurements, and 1 hour to computation.

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TABLE 1
Average Particle Size for Three Typical Alloys

<u>Alloy No.</u>	<u>Length, μ</u>	<u>Width, μ</u>
1	200	30
2	350	50
5	700	40

TABLE 2
Summary of Specimen Preparation Techniques

<u>Technique</u>	<u>Result</u>
Loose turnings	Precision of Ag and Sn analyses not acceptable. Coefficients of variation greater than 1%.
Sulfuric-nitric solutions	High acid concentration not practical, Sn precipitated out under irradiation.
Castings (5)	50 to 70% of Zn (b.p. 907°C) vaporized during melting of alloy (815°C to 925°C).
3.5 cm diam pellets + boric acid binder + MnO ₂ binder	Precision of Ag and Sn analyses not acceptable. Coefficients of variation greater than 1%. Pellets fragile.
1.27 cm diam pellet	Acceptable method. Average coefficients of variation, Ag 0.5%, Sn 0.8%.

TABLE 3
Reproducibility of Single Determinations

Ag Concentration	CV ¹	Sn Concentration	CV	Cu Concentration	CV	Zn Concentration	CV
%	%	%	%	%	%	%	%
66.8	0.46	25.4	1.95	0.0 ²	2.0	0.0 ²	4.1
67.0	.47	25.6	0.63	1.0	5.3	.1	3.6
68.3	.22	25.7	.90	2.3	3.0	.6	0.29
69.5	.20	26.2	.67	2.6	3.8	.8	.58
70.1	.31	26.2	.47	3.4	2.5	.9	.51
70.2	.45	26.3	.80	3.6	1.7	.9	.37
70.3	.26	26.6	.51	3.9	1.4	.9	.43
72.0	.17	27.2	.79	4.9	1.3	1.0	.41
74.5	.21	27.6	.37	6.0	1.4	1.8	.19

¹CV = Observed percent coefficient of variation for an individual determination in a group of five:

$$CV = \frac{100}{\bar{c}} \sqrt{\frac{\sum_{i=1}^n (c_i - \bar{c})^2}{n-1}}$$

To obtain the CV for the mean the given factor would be divided by $\sqrt{5}$.

²Coefficient of variation for zero concentration is the value for the background radiation.

TABLE 4

Composition of Standards Given by Chemical Analysis
and Found by X-ray Analysis (in Weight Percent)

Element and Method								
Alloy	Ag		Sn		Cu		Zn	
	Chem. x-ray		Chem. x-ray		Chem. x-ray		Chem. x-ray	
1	66.8	66.7	26.2	25.9	6.0	6.1	1.0	0.99
2	70.1	70.1	26.6	26.7	2.6	2.7	0.6	0.60
3	70.3	70.2	25.6	25.4	2.3	2.3	1.8	1.76
4	68.3	68.5	27.6	27.9	3.4	3.4	0.8	0.78
5	70.2	70.1	26.3	26.2	3.6	3.5	0.0	0.0
6	69.5	69.4	25.7	25.4	3.9	3.9	0.9	0.90
7	72.0	72.0	26.2	26.4	1.0	1.0	0.9	0.90
8	67.0	67.1	27.2	27.1	4.9	4.9	0.9	0.94
9	74.5	74.3	25.4	25.7	0.0	0.0	0.1	0.14

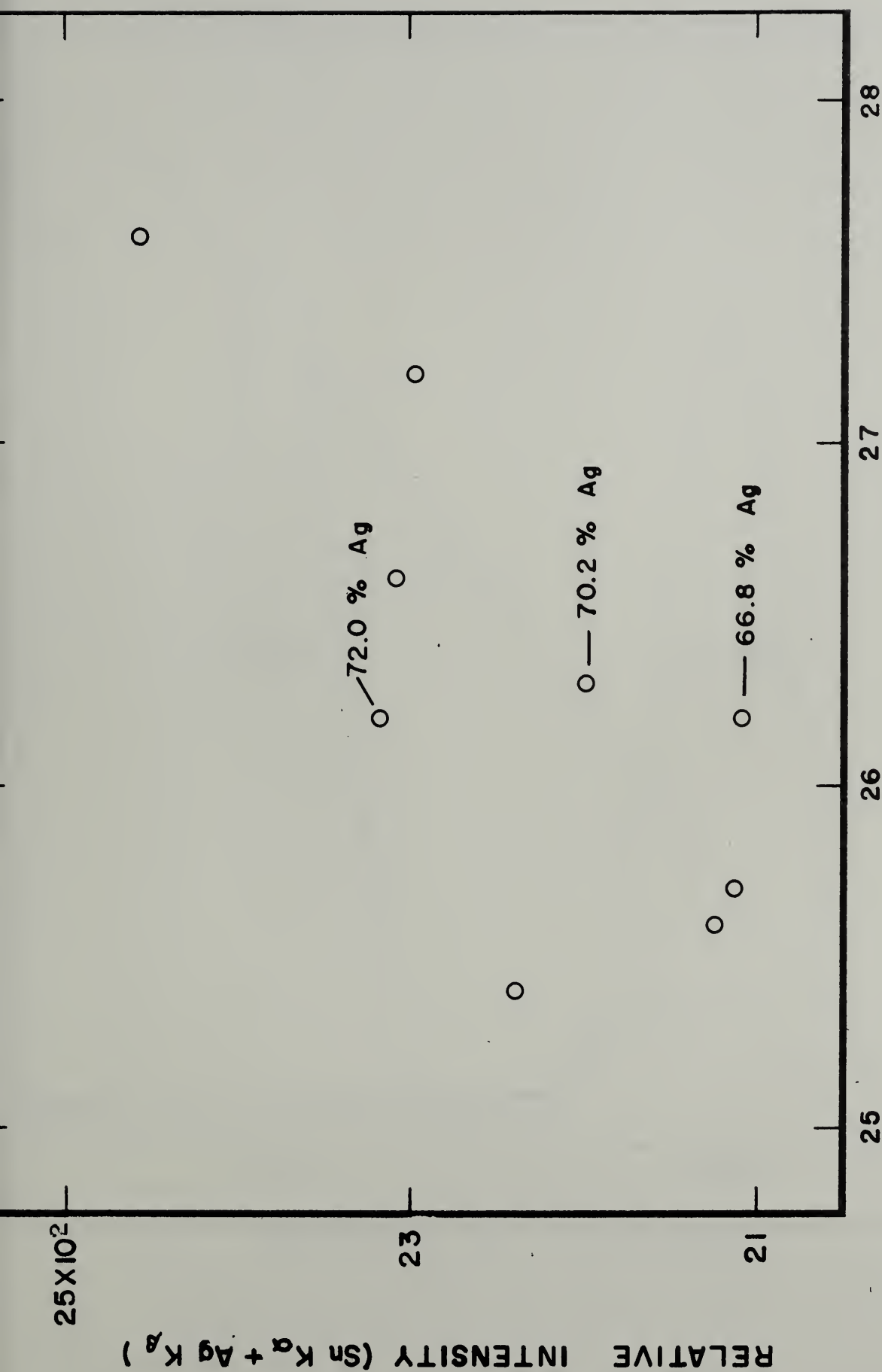


Fig. 1. Relative x-ray intensity recorded at 0.492 Å versus the concentration of tin. At constant tin concentration an increase in silver concentration causes an increase in intensity.

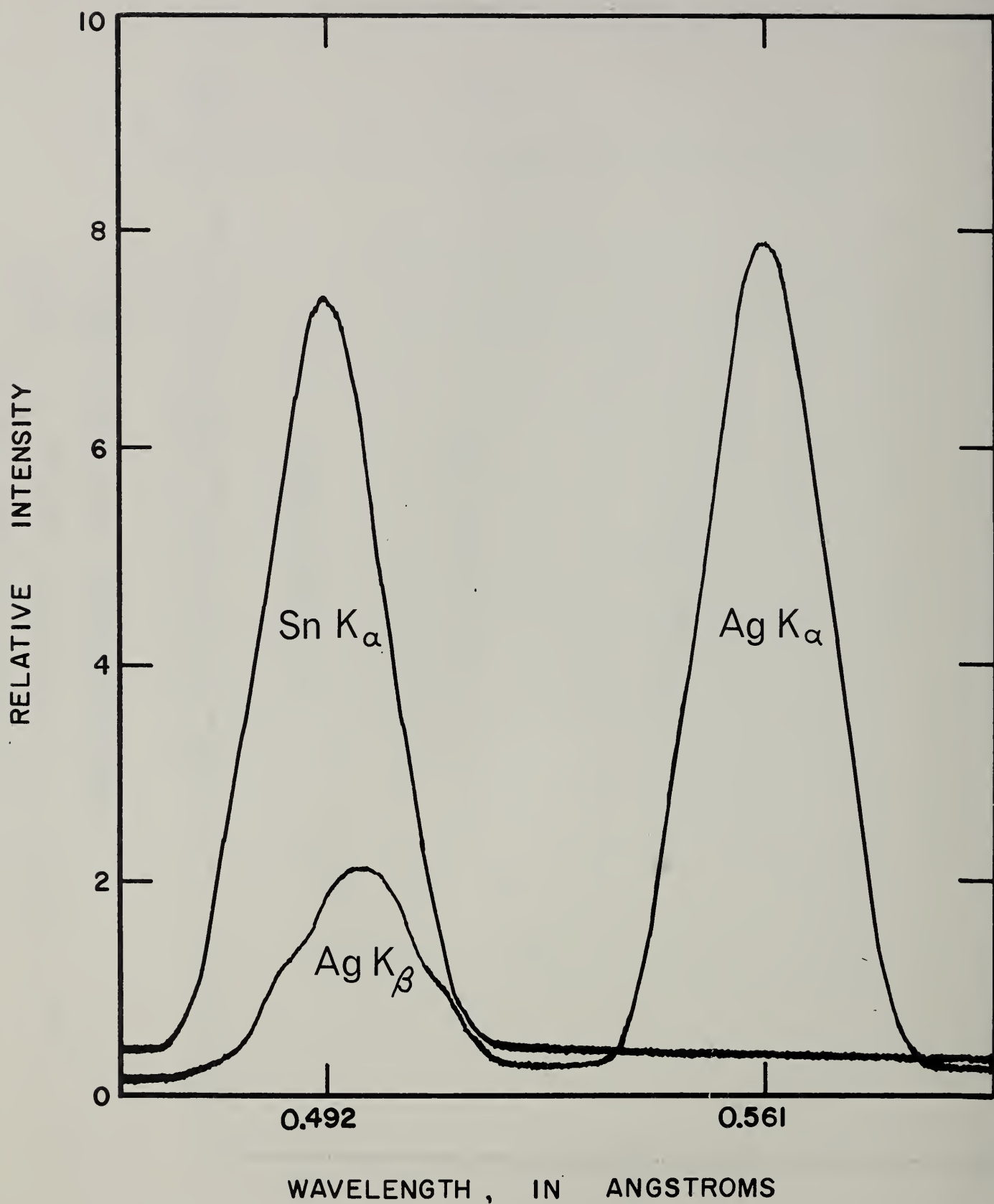
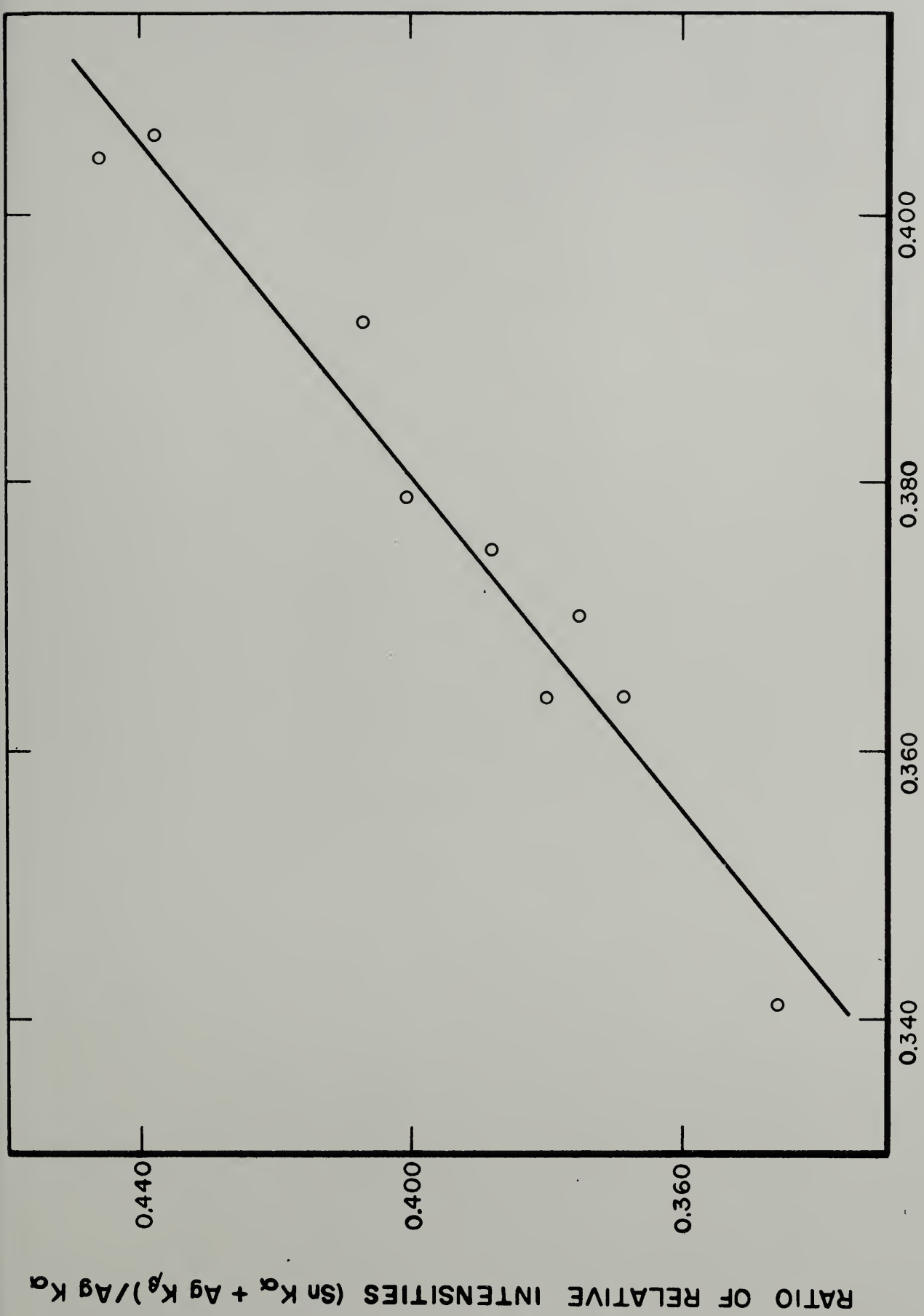


Fig. 2. Line profiles for pure silver and tin. Ag K_{α} is near 0.561 Å, Ag K_{β} and Sn K_{α} are near 0.492 Å, with the tin peak being the larger of the two.



RATIO OF CONCENTRATIONS TIN / SILVER, %

Fig. 3. Analytical curve for tin, silver.

