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# Computational Method for Chemical Composition by X-Ray Fluorescence Analysis

## The Pure Standard Program Employed on Copper-Silver Binary Alloys

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## ABSTRACT

A program has been developed to analyze the interelement effects in x-ray fluorescence data for alloys and homogeneous mixtures. Chemical analysis is thereby possible using either a standard of known composition or a set of pure-element standards. The program was tested on copper-silver binary alloys. The agreement was excellent for the silver calculation but unacceptable for copper. However, the copper calibration agreed with an independent computer calculation from a different source. These results indicate that the data may be improved in subsequent work.

## PROBLEM STATUS

This is an interim report; work on the problem is continuing.

## AUTHORIZATION

NRL Problem MO1-20  
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# COMPUTATIONAL METHOD FOR CHEMICAL COMPOSITION BY X-RAY FLUORESCENCE ANALYSIS

## THE PURE STANDARD PROGRAM EMPLOYED ON COPPER-SILVER BINARY ALLOYS

### BACKGROUND

One of the main problems in x-ray fluorescence analysis has been the quantitative calibration of compositional x-ray data. There are two primary sources of difficulty: First, interelement effects in alloys and mixtures cause fluorescent x-ray output to be nonlinear with composition and, second, instrumental effects change intensities of characteristic elemental lines unequally. These difficulties can be circumvented by using standard samples. Standards virtually eliminate instrument effects since a given characteristic line in the unknown and in the standard will be altered by the same factor. The interelement errors can be minimized by having several standards that span the concentration range of the unknowns. The standards provide a smooth curve which gives a profile of the nonlinear effect previously mentioned.

However, standards often create as many difficulties as they solve. Ideally, they should be identical in physical properties to the unknown samples as well as to each other. They have to be analyzed by some other method, which in practice usually means chemical analysis of companion pieces. Synthetic standards are frequently harder to produce than the original samples. The spectroscopist is thereby required to be metallurgist, engineer, or chemist. The analyst's goal is to reduce the need for standards as much as possible.

Formulas have been derived which predict the interelement effects for alloys. By utilizing a digital computer, it becomes practical to calculate these effects and correct for them. Only one standard is then required to adjust for instrumental effects.

Criss developed a program to perform the calculations for interelement effects (1). The program was tested on four elements in simple steels with conditional accuracy. Although the program was flexible, it was primarily suited to programmers, so an attempt was made to streamline the program for use by nonprogrammers. Unfortunately, the program lost most of its flexibility while gaining little utility; therefore, new programs were written from the original formulas to simplify the data and make them consistent with programs to follow. The program reported here executes the same basic function as Criss's original program. However, the ultimate goal is to produce programs which will handle raw data without using standard measurements.

### THEORY

The calculation of the primary fluorescent x-ray intensity expected from a mixture of elements was first derived by Sherman (2). Shiraiwa and Fujino have the derivation of primary, secondary, and tertiary fluorescent x radiation and show results of calculations using these formulas (3). Their development is clear, and only the primary and secondary expressions will be reproduced here.

We assume a homogeneous sample with a flat surface and infinite thickness. Since the penetration of x rays in most materials is macroscopically small, these assumptions are not overly restrictive. The sample is irradiated by incident x radiation ( $I_0$ ), producing the primary fluorescent radiation  $I_1(i, p)$  of element  $i$  and characteristic line  $p$ :

$$I_1(i, p) = \frac{1}{\sin \Psi} \int_{\lambda_m}^{\lambda_i} \frac{\mu_i(\lambda) W_i K_i \omega_i R_p^i I_0(\lambda)}{\frac{\mu(\lambda)}{\sin \Phi} + \frac{\mu(i, p)}{\sin \Psi}} d\lambda,$$

where  $\Phi$  is the angle of incident radiation to the sample,  $\Psi$  is the takeoff angle of the radiation,  $\mu_i$  is the mass absorption coefficient for element  $i$ ,  $\mu$  is the mass absorption coefficient for the mixture,  $K_i \omega_i R_p^i$  are fluorescent yield terms,  $W_i$  is the weight percentage of element  $i$  in the sample,  $\lambda_m$  is the minimum wavelength in  $I_0$ , and  $\lambda$  is the wavelength of the absorption edge for element  $i$ . The secondary intensity  $I_2(i, p)$  is excited by the primary fluorescent radiation emanating from within the sample itself.

To save time, we substitute  $Q_{ip}(\lambda)$  for  $\mu_i(\lambda) W_i K_i \omega_i R_p^i$ :

$$I_2(i, p) = \frac{1}{2 \sin \Psi} \sum_{jq} \int_{\lambda_m}^{\lambda_j} \frac{Q_{jq}(\lambda) Q_{ip}(j, q) I_0(\lambda)}{\frac{\mu(\lambda)}{\sin \Phi} + \frac{\mu(i, p)}{\sin \Psi}} \{F\} d\lambda,$$

where

$$\{F\} = \frac{\sin \Psi}{\mu(i, p)} \ell_n \left[ 1 + \frac{\mu(i, p) / \sin \Psi}{\mu(j, q)} \right] + \frac{\sin \Phi}{\mu(\lambda)} \ell_n \left[ 1 + \frac{\mu(\lambda) / \sin \Phi}{\mu(j, q)} \right]$$

and where the subscripts  $j, q$  refer to the  $q$ th characteristic line of the intermediate element  $j$ . Any element  $j$  whose characteristic radiation  $j, q$  is higher in energy than the absorption edge of element  $i$  may excite secondary radiation from  $i$ .

The program deals not in absolute intensities, but in ratios of sample intensities to either a known standard or pure-element standards. Each has certain advantages: Pure elemental standards require no corroborative analysis of the standards themselves. Yet a known standard, if chosen carefully, can be closer in actual composition to the unknowns, thus providing greater accuracy. All of the results given in this report are obtained using pure elemental standards.

We are interested in determining the weight percentages  $W_i$  of each element in the sample. Note that the  $\mu$ 's under the integral depend on  $W_i$  by the addition formula  $\mu_{\text{alloy}} = \sum \mu_i W_i$  prohibiting one from calculating  $W_i$  explicitly. For this reason  $W_i$  must be assumed and the resulting intensity ratio compared to the measured intensity data. The percentage is then iterated until calculated and measured intensities agree to a predetermined tolerance value.

There are many slight differences between this program and others similar to it, such as input/output formats, methods for calculating coefficients, division of intervals, and order of calculation. However, there is one significant departure from previous work. The usual iteration procedure is to scale the measured intensities as a group to conform to a theoretically possible set of calculated intensities. This means that the calculations for each element converge simultaneously and the results obtained are the most consistent possible for all the data. A difficulty lies here if one of the data points is inaccurate, for it will affect all the results.

With this program, the measured values are not scaled. Rather, each element is iterated independently with the remaining intensities being scaled. A set of results is printed for each element being analyzed. The relative agreement from element to element should give a measure of the accuracy of the data, and any faulty reading should be revealed. Although the output is longer, it provides the analyst useful information which may justify the extra computer time and complication of results. For well-established routine analyses, this procedure would be inappropriate, but for nonstandard developmental problems, such as this laboratory handles, it seems to be useful.

## EXPERIMENTAL PROCEDURE

It was decided to test the calculations with several binary alloy series. Each series should span the major constituent range (10%-90%). Since most binary systems are not soluble over the whole range, there was some difficulty in finding good alloys. We chose the copper-silver system since it would be the easiest to melt and since copper and silver are soluble over the whole range.

The series of alloys was prepared from commercially pure copper and silver. Spectrographic examination of the starting metals showed no significant impurities in the copper and only a slight amount of lead in the silver.

With appropriate consideration for the conservation of silver, a sample size of approximately 50 grams was chosen to provide an adequate final geometry for the specimens after preparatory techniques and sampling for chemical analysis.

In order to achieve homogeneity on samples of this small size, the metals were melted in flat-bottomed quartz tubes under a carbon dioxide atmosphere. The heating process was observed through a protective shield and was continued approximately 1 minute beyond the melting time. The temperature at this point was approximately 100°C above the melting point for each particular alloy. The agitation was discontinued and the bottom of the quartz tube was quenched with water. Solidification was almost instantaneous. The sample was cooled to room temperature under an inert atmosphere, which resulted in clean, unoxidized surfaces with approximately parallel faces.

The samples were then rolled to a thickness of approximately 1/16 inch and flattened with abrasive papers. Pieces were cut off opposite ends for chemical analysis. The remaining samples filled the specimen holder window of rectangular area (1 in. by 1-1/2 in.) Readings from opposite sides of the sample show that homogeneity is a problem for the middle-range alloys of 40 to 60%. Of the six alloys made, four were in this range. Only two were finally used, and they still had some side-to-side difference.

The samples were measured on a Philips 50-kilovolt x-ray spectrometer employing a wide-range goniometer (LiF crystal, scintillation counter detector). The data were collected and handled manually as were corrections for dead time and background. Because of the size and concentration levels of the samples, especially the pure samples, the dead-time corrections were significant. The accuracy expected on an instrument of this type is 1% of the amount present for major constituents.

The program is written in Fortran for a CDC Model 3800 system, runs on the order of 1-minute computer time, and employs a minimum of external data. For each element the data required are: symbol, atomic number, line being measured ( $K_\alpha$  or  $K_\beta$ ), wavelengths of K lines, wavelength of absorption edge, incident and takeoff angles of the radiation, and x-ray intensity ratio. The other necessary parameters are calculated internally. The exciting spectra used are those published for similar x-ray tubes by Gilfrich and Birks (4). The mass absorption coefficients presently used are fitted to Heinrich's

published data (5). The jump factors are calculated from the absorption coefficients, and the fluorescent yields are calculated by an empirical formula (5). In energy regions where Heinrich has no absorption coefficient data, McMaster's tabulation of coefficients has been employed (6).

The x-ray data were taken at 45 and 50 kilovolts at 10-milliamp tube current. The digital readout provided both peak height and peak area data, but we found the area data more accurate, as expected. Two different exciting spectra are employed for 45 and 50 kilovolts, and the results agree substantially with each other. The results published are for 45-kilovolt area counts. Attenuating foils were used in front of the detector to bring the count rate down to 11,000 cps or less, which should eliminate the necessity for dead-time calculations. Tin foils were used for the silver measurements and aluminum foils for the copper measurements.

## RESULTS

Table I compares silver composition to calculated values as determined from the silver iteration. The agreement to 0.25% is actually better than should be expected from the x-ray error analysis. The copper answers were  $[100\% - W(\text{Ag})]$  in this case. The copper numbers also agree with chemical analysis for the silver iteration.

Table 2 shows the results of the copper percentages as determined by iteration of the copper calculation. This accuracy is clearly not acceptable. The error cannot be

Table I  
Silver Percentage Composition Data

Sample	Side	Made-Up(%)	Chemical	X Ray Calculated
C	Both	21.8	20.8	20.8
D	1			37.3
D	Av	38.9	38.9	38.8
D	2			40.3
E	1			55.1
E	Av	65.0	55.9	55.9
E	2			56.7
B	Both	82.3	83.1	83.3

Table 2  
Copper Percentage Composition Data

Sample	Side	Made-Up(%)	Chemical	X Ray Calculated
C	Both	78.1	79.1	81.0
D	1			65.7
D	Av	60.9	60.9	64.9
D	2			64.2
E	1			48.2
E	Av	35.0	43.9	46.9
E	2			45.7
B	Both	17.4	16.6	17.5

attributed to data collection errors, since the composition deviations are ten times greater than those of the data readings. Mass absorption coefficient data were varied within reasonable precision limits. Again the effect was too small to explain the discrepancy. Likewise dependence on fluorescent yields, absorption edges, and incidence angles proved fruitless. In an effort to check the calculations, calibration curves were obtained from Criss's Fluoran program. The results for the copper calibration are shown in Fig. 1. The data points are our calculations for the four samples. Fluoran employed the same exciting spectrum as well as Heinrich's absorption coefficients. It can be seen that the two calibrations are in close agreement over the whole range. Thus, the mechanics of the calculation must be assumed to be correct.

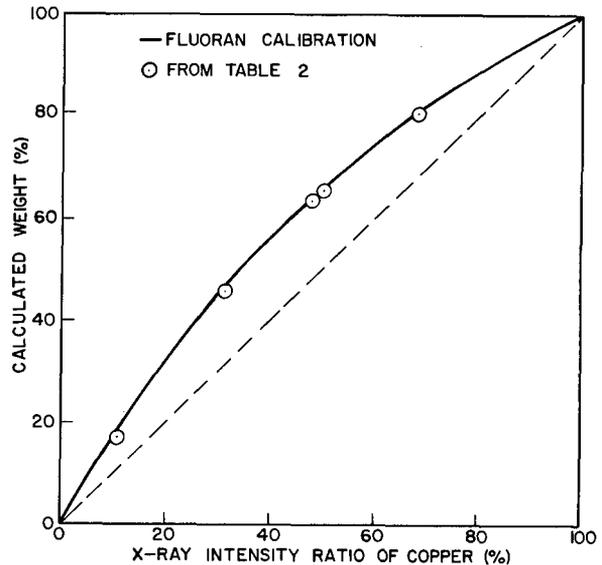


Fig. 1 - Comparison of copper calibrations

Work will continue in this area to determine the source of discrepancy in the copper analysis. Experimental procedures, such as dead-time corrections and current settings, will be reviewed. There may be a misrepresentation of the exciting spectrum which could affect the predictions. Also, a study will be made of the analogous palladium-nickel system to see if nickel shows the same copper difficulty.

Even so, the silver results are encouraging, and the agreement with earlier calculations is also gratifying. The program has already shown marginal success with simple steels and could help ease the routine sample burden on this laboratory. Its ease of operation commends it for use by nonmathematical personnel. With future development, it should prove to be a useful and especially fast tool in the research analytical laboratory.

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