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Progress Report on Analysis of Gold and Platinum Group Alloys by X-Ray Emission

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ANALYSIS OF GOLD AND PLATINUM GROUP ALLOYS BY X-RAY EMISSION

Abstract

X-ray emission analysis was found to be a precise and fast procedure for analyzing noble metal alloys. Specimens of gold alloys were cast into disks and mounted in methyl methacrylate resin. Adequate surface preparation was obtained by finishing with 600 wet silicon carbide grit. The analytical curves for the elements Cu, Pd, Pt, and Zn were found to be linear with a deviation of less than 0.2% of the sample. However, a non-linear relationship existed for the gold and silver content. These discrepancies were found to be an interelement effect due to absorption and enhancement and were corrected by means of a mathematical treatment suggested by Lucas-Tooth and Price to an accuracy of 0.2%. The analysis by x-ray emission was accomplished in approximately one-tenth of the time necessary for conventional wet chemical methods.

1. Introduction

A paper by Mulligan, et al [6] indicated that the analysis of noble metal dental alloys by x-ray emission is feasible. The analytical curves were developed from data on four alloys of known composition. Linear relationships were observed for x-ray intensities versus concentration, although the silver plot showed some deviation. In our application of the method these same alloys, three dental gold casting alloys, and several gold binaries were analyzed. Discrepancies from chemical analysis were found for both silver and gold. A detailed study showed that specimen preparation and surface treatment were not responsible for this problem. The discrepancies were shown to be caused by interelement effects which were corrected by the Lucas-Tooth and Price equation [5] with excellent results.

2. Experimental

2.1 Apparatus. A Norelco inverted-sample, three-position spectrograph with molybdenum target x-ray tube, lithium fluoride crystal, and scintillation counter detector was employed. The optimum conditions for the x-ray emission intensity measurements were determined experimentally and are given in Table 1.

2.2 Materials. The chemical compositions of five gold alloy standards were determined by wet chemical analysis [1] and the results are shown in Table 2. The batch compositions, determined from careful weight measurement before alloying by The J. M. Ney Company, for three commercial alloys are listed in Table 3. Four binary alloys of 97, 94, 91, and 88% gold were formulated for each system of Au-Ag, Au-Cu, Au-Pd, and Au-Pt. In addition, a fifth binary alloy of 75% gold and 25% silver was included.

2.3 Procedure. Each alloy was cast into a flat disk approximately 0.8 mm thick and having a diameter of 32 mm. The "lost-wax casting technic" [9,11] was utilized with a gypsum bound investment. An electric inductance furnace connected to a centrifugal casting machine, with a pyrometer attached to measure the temperature to within ±15°C, was employed to melt and cast the alloys in molds preheated to 650°C. The specimens were quenched in a water bath immediately after casting, removed from the investment mold, and mounted in methyl methacrylate resin to facilitate surface preparation and x-ray analysis.

Six specimens of standard No. 5 (Table 2) were analyzed first by x-ray emission methods in the as-cast condition with no surface preparation. Four of the specimens were surfaced with progressively finer abrasives through 600 grit using wet silicon carbide paper and then were reanalyzed. Next, these four alloys were homogenized in an argon atmosphere at approximately 950°C for 6 hours and analyzed. Finally, the four specimens were polished through $\frac{1}{4}\mu$ diamond polish and their compositions were redetermined. X-ray intensity measurements were made five times for each specimen in the spectrometer in a sequence designed to minimize effects of instrumental drift [7]. The mean values of the five determinations for each surface preparation were compared using a two-sided T-test [2]

Since surfacing through 600 grit was adequate for the analysis, one specimen of each standard, commercial, and binary alloy was prepared through 600 grit. Five determinations of intensity (counts per second) for each element present were made and the data were compared.

3. Results and Discussion

A two-sided T-test indicated that a significant difference existed between the results obtained for four specimens of standard No. 5 in the non-surfaced condition when compared with the same specimens surfaced through 600 grit, homogenized, or polished through $\frac{1}{4}\mu$ diamond polish. There was a significant difference in gold concentration at the 99% confidence level and in copper concentration at the 95% confidence level for all four samples tested. In the as-cast condition the x-ray emission intensity counts for both gold and copper were low when compared with intensity counts in the other surfaced conditions. Better agreement was obtained when the specimens were surfaced through 600 grit as illustrated in Table 4.

There was no significant difference between the specimens surfaced through 600 grit, those homogenized, and those polished through $\frac{1}{4}\mu$ diamond polish. There was little or no coring, i. e. segregation, due to the casting of the alloys, or coring had little effect on the analysis. It also was not necessary to polish the specimens to a mirror-like surface with the $\frac{1}{4}\mu$ diamond polish in order to section through the grain structure.

When the commerical alloys, standards, and binaries, surfaced through 600 grit, were analyzed for gold by this x-ray emission method, a non-linear relationship was found between intensity and composition. Figure 1 shows the results when the standard and commercial alloys are compared with the binaries of Au-Ag, Au-Pd, Au-Pt, and Au-Cu. A discrepancy in the concentration of as much as 8% was apparent between the line formed by the Au-Ag binaries and that formed by the standards (Figure 1). Discrepancies also existed with the other three binary systems.

A non-linear relationship also existed when the silver concentration was determined (Figure 2). In this case, a discrepancy of as much as 2% existed between the standards and the binaries of Au-Ag. However, when Cu, Pd, Pt, and Zn were determined, a linear relationship existed with a maximum discrepancy of 0.2% concentration.

Surface effects and coring were eliminated as a cause of the discrepancies in the gold and silver determinations. It was thought that a complex interelement effect of absorption and enhancement possibly could cause the discrepancies since similar discrepancies in x-ray emission analysis exist with stainless steels [2], copper and nickel determinations in ores [4], high temperature alloys [3], and lead alloys [10]. These interelement effects may be corrected by a mathematical treatment developed by Lucas-Tooth and Price [5].

The Lucas-Tooth and Price equation [5,10] for a particular element in an alloy is:

$$P_{nm} = a_n + I_{nm} (K_o + \Sigma_x K_{nm} I_{xm})$$

where P_{nm} is the percentage and I_{nm} is the x-ray intensity of the nth element in the mth sample of a group of alloys. The a's and K's are constants derived empirically from x-ray analysis of standard alloys. The total number of standard alloys must exceed by two the number of elements present, and must have a range of composition which includes that of the unknowns to be analyzed [2, 3, 4, 10].

Values for the a's and K's for the gold alloys were determined by use of a computer to obtain a least squares fit of the equation to the x-ray emission data. With these constants, concentration values, corrected for both adsorption and enhancement, were then calculated.

The corrected x-ray emission analysis values for the gold content of the commercial alloys, standards, and binaries are plotted in Figure 3. This figure demonstrates that the mathematical treatment corrects the discrepancies for gold adequately. The silver data also were corrected and the same linear relationship was obtained. The maximum error and the average error for the gold and silver determinations after the results were corrected are listed in Table 5.

This x-ray emission procedure may be performed in approximately one-tenth the time [6] necessary for conventional wet chemical methods [1]. A single sample may be prepared and analyzed in a total of 4 hours, about half of the time being necessary for sample preparation and the other half for the actual analysis.

By applying the Lucas-Tooth and Price equation, it was possible to correct the gold and silver analysis to an accuracy of about 0.2%. The accuracy of the analysis for the other four elements, Cu, Pd, Pt, and Zn, was also about 0.2%, but a correction did not have to be applied to the data. The corrected x-ray emission analyses are

compared with the chemical analyses in Tables 2 and 3. Thus, the method of x-ray emission analysis of noble metal alloys may be performed to an adequate degree of accuracy.

4. Conclusions

1. Specimen preparation and surface treatment were established through a detailed study.

2. Deviations from a linear analytical curve for gold and silver were found. These discrepancies were caused by absorption and enhancement effects and were corrected by the Lucas-Tooth and Price equation with excellent results.

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Table 1

Operating Parameters for Noble Metal Alloy Analysis

Element	X-ray Line	X-ray Tube Operating Parameters kv	ma	Counts per Determination
Au	$L\beta_1$-1.083Å	30	22	256,000
Ag	$K\alpha$-0.559	30	45	32,000
Cu	$K\alpha$-1.540	30	45	128,000
Pd	$K\alpha$-0.585	40	45	64,000
Pt	$L\alpha_1$-1.313	40	45	128,000
Zn	$K\alpha$-1.435	40	45	64,000

Table 2

Compositions of Standard Alloys

Element		Standard 1 %	2 %	3 %	4 %	5 %
Au	(chemical)	68.3	72.0	78.1	79.1	91.6
	(x-ray)	68.3	72.1	77.8	79.0	92.0
Ag	(chemical)	11.6	10.9	8.1	13.9	5.9
	(x-ray)	11.6	10.8	8.2	13.9	5.8
Cu	(chemical)	11.9	10.0	7.9	6.0	2.4
	(x-ray)	11.9	10.0	7.9	6.0	2.3
Pd	(chemical)	0.0	2.0	2.8	1.0	0.0
	(x-ray)	0.0	1.9	2.8	1.0	-0.1
Pt	(chemical)	6.3	3.8	2.2	0.0	0.0
	(x-ray)	6.2	4.1	2.0	0.1	-0.2
Zn	(chemical)	1.9	1.4	0.9	0.0	0.0
	(x-ray)	1.9	1.3	0.9	0.0	0.0
Totals	(chemical)	100.0	100.1	100.0	100.0	99.9
	(x-ray)	99.9	100.2	99.6	100.0	99.8

Table 3

Composition of Commercial Alloys

Element		Alloy A %	B %	C %
Au	(chemical)	92.5	80.7	75.0
	(x-ray)	92.5	80.9	75.0
Ag	(chemical)	4.5	11.8	14.5
	(x-ray)	4.4	11.8	14.5
Cu	(chemical)	2.5	3.2	6.8
	(x-ray)	2.7	3.2	6.8
Pd	(chemical)	0.5	4.0	3.0
	(x-ray)	0.5	3.8	3.0
Pt	(chemical)	0.0	0.0	0.0
	(x-ray)	0.0	0.0	0.0
Zn	(chemical)	0.0	0.3	0.7
	(x-ray)	0.0	0.3	0.7
Totals	(chemical)	100.0	100.0	100.0
	(x-ray)	100.1	100.0	100.0

Table 4

Surface Effects on X-Ray Emission Analysis

	Au %	Ag %	Cu %
As-cast	88.0	5.8	1.5
Surfaced through 600 grit (not homogenized)	91.6	5.9	2.4
Surfaced through 600 grit + homogenized	91.6	5.9	2.4
Surfaced through $\frac{1}{4}\mu$ polish (not homogenized)	91.6	5.9	2.4
Surfaced through $\frac{1}{4}\mu$ polish + homogenized	91.7	5.9	2.4
Chemical composition	91.6	5.9	2.4

Table 5

Errors

	Average %	Maximum %
Gold (Au-Ag)	0.1	0.4
Gold (Au-Pd)	0.1	0.3
Gold (Au-Pt)	0.1	0.3
Gold (Au-Cu)	0.1	0.3
Silver (Au-Ag)	0.0	0.1

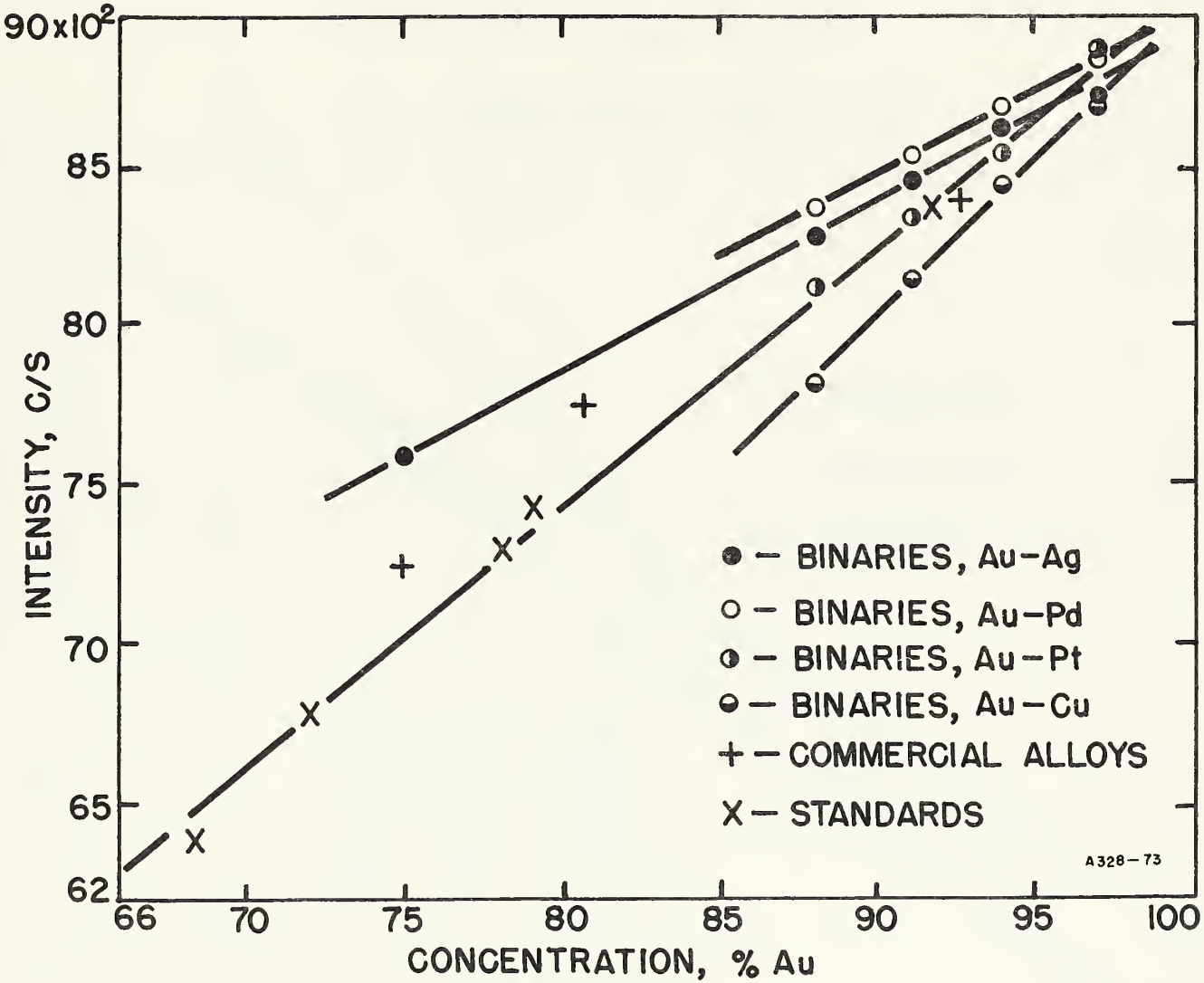

Figure 1. Uncorrected Gold Analysis Curves. Au-Ag, Au-Pd, Au-Pt, and Au-Cu binaries, commercial alloys, and standards.

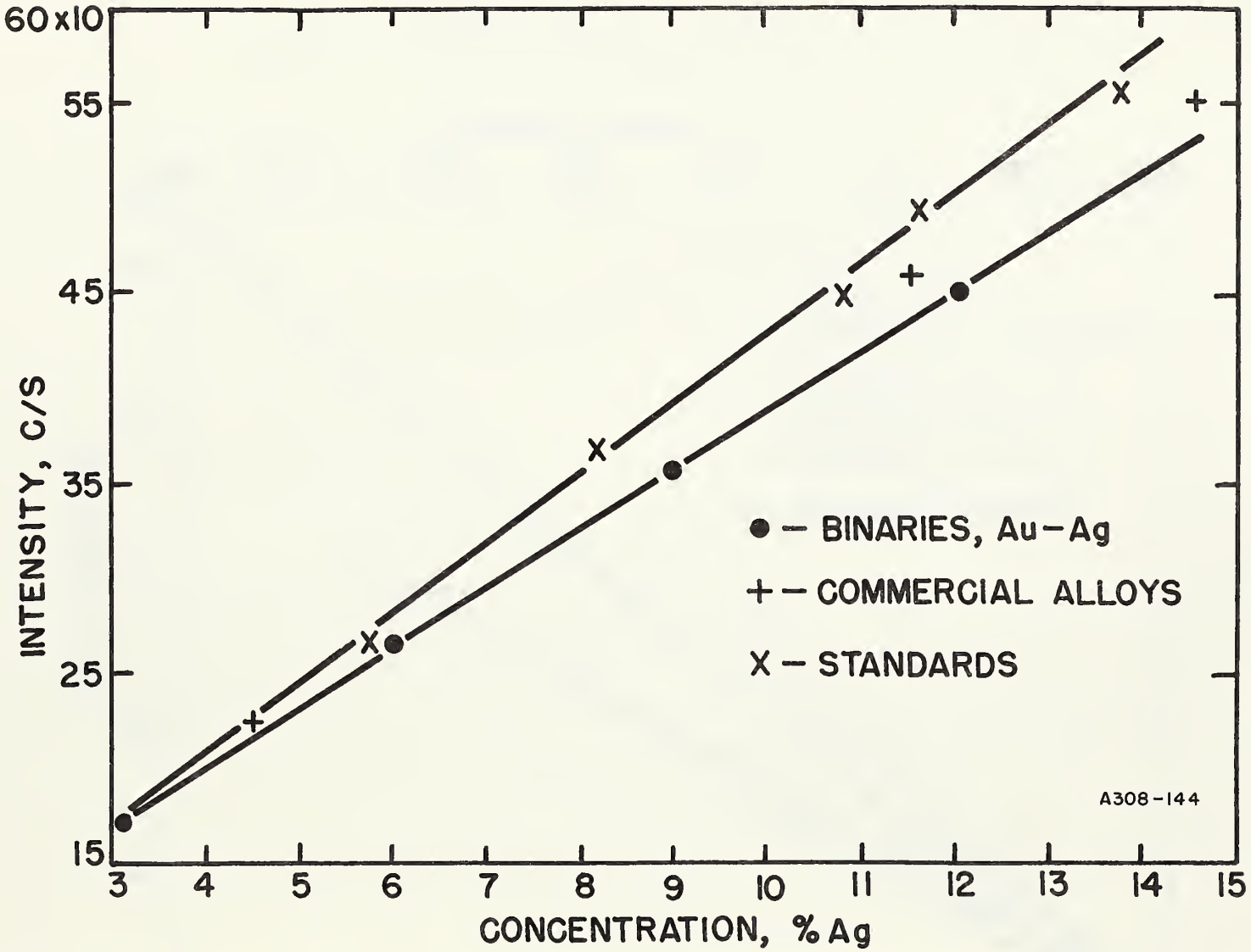

Figure 2. Uncorrected Silver Analysis Curves. Au-Ag binaries, commercial alloys, and standards.

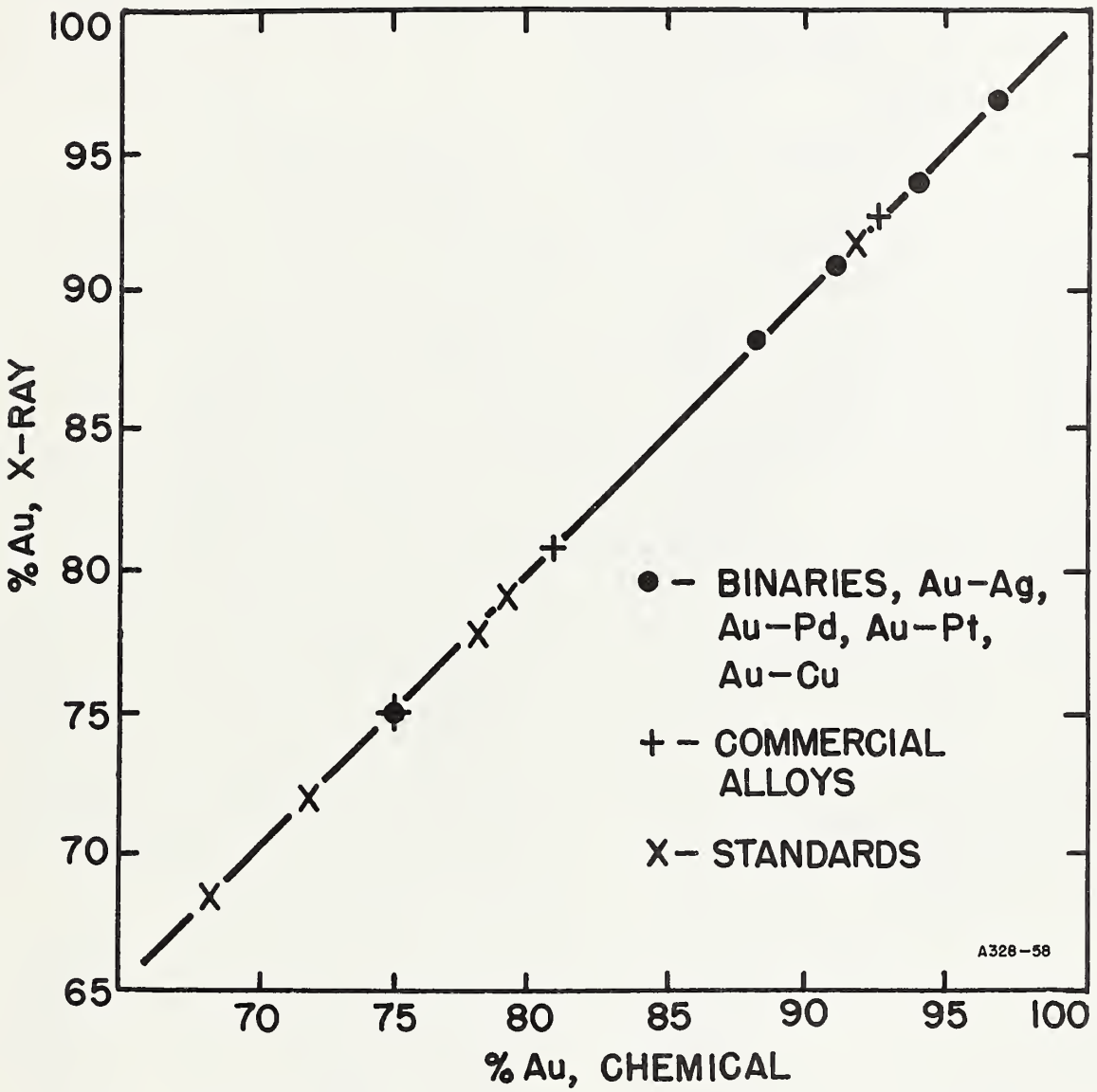

Figure 3. Corrected Gold Analysis Curves. Au-Ag, Au-Pd, Au-Pt, and Au-Cu binaries, commercial alloys, and standards.