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REPORT ON DENTAL RESEARCH
AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

July 1 to December 31, 1962

The dental research program at the National Bureau of Standards is carried on in cooperation with the Council on Dental Research of the American Dental Association; the Army Dental Corps; the Dental Sciences Division of the School of Aerospace Medicine, USAF; and the Veterans Administration.

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

REPORT ON DENTAL RESEARCH
AT THE NATIONAL BUREAU OF STANDARDS

1. INTRODUCTION

Research on dental materials, dental equipment and natural tooth structure continued at the National Bureau of Standards during the half year ending December 31, 1962.

Summaries of results obtained on work in progress, a list of reports issued and a list of papers published during the period are given below. Copies of the reports are appended.

2. REPORTS ISSUED

NBS Report 7809	X-Ray Spectroscopic Analysis of Noble Metal Alloys.
NBS Report 7825	Studies of Dental Calculus: Organic Portion.
NBS Report 7838	Specification for Hydrocolloidal Impression Material-Alginate Type.
NBS Report 7854	Properties of Dental Amalgam and Gallium Alloys Produced by Using Spherical Alloy Powders.

3. PAPERS PUBLISHED

Synthesis of 2-propoxy-5-methylbenzoic acid. G. M. Brauer and L. Simon. J. Research NBS 66A:313, July-Aug. 1962.

Some tensile properties of amalgam. M. S. Rodriguez and G. Dickson. J. D. Res. 41:840, July-Aug. 1962.

Properties of dental amalgam made from spherical alloy particles. N. C. Demaree and D. F. Taylor. J. D. Res. 41:890, July-Aug. 1962.

Improved zinc oxide-eugenol type cements. G. M. Brauer, L. Simon and L. Sangermano. J. D. Res. 41:1096, Sept.-Oct., 1962.

Dimensional changes in dentures. J. B. Woelfel, G. C. Paffenbarger, and W. T. Sweeney. Dent. Practitioner and Dent. Record 13:64, Oct., 1962.

Dimensional changes in complete dentures on drying, wetting and heating in water. J. B. Woelfel, G. C. Paffenbarger and W. T. Sweeney. J.A.D.A. 65:495 Oct., 1962.

Dental filling material comprising vinyl silane treated fused silica and a binder consisting of the reaction products of bis phenol and glycidyl acrylate. R. L. Bowen. U.S. Patent No. 3,066,112, Nov. 27, 1962.

Fluorescence of teeth. A. F. Forziati and M. P. Kumpula. Frontiers of Dental Science. National Science Teachers Association. Dec., 1962, p. 106.

Horizons in dentistry. G. C. Paffenbarger. Frontiers of Dental Science. National Science Teachers Association. Dec., 1962, p. 122.

4. WORK IN PROGRESS

4.1 Human Tooth Enamel and Dentin

(a) Structure of Calcified Tissues.

The structure and chemical properties of octacalcium phosphate are such that it may play an important part in the growth of hard tissues and in determining their chemical properties. Emphasis has been placed, therefore, on uncovering the role of octacalcium phosphate in the chemistry of hard tissues.

Electron micrographs of enamel at various stages of development reveal that the crystallites form initially as extremely long ribbons that subsequently thicken and broaden by deposition of hydroxyapatite. It is concluded that a single unit-cell thickness of octacalcium phosphate is the most suitable prototype for the ribbons. This has important consequences relative to the mode of action of fluoride in the prevention of dental caries.

Detailed consideration has been given, also, to crystallographic properties of hydroxyapatite and octacalcium phosphate with the result that three mechanisms for twinning in octacalcium phosphate and one for hydroxyapatite, all parallel to their 100 faces, have been devised. It has been shown that even one layer, a few unit cells thick, of one salt in a crystal of the other may have a pronounced effect on the x-ray properties of the crystal; and additional insight has been gained into (1) the relative importance of thermodynamic and kinetic factors in the formation of seed crystals and the deposition of one salt or the other on the seed crystals, (2) the mechanism by which habit modifiers may cause hard tissues to vary so greatly in their crystallite size and shape, and (3) the possible role of octacalcium phosphate in the growth of hydroxyapatite and its connection with the occlusion of foreign ions in the hydroxyapatite lattice.

(b) Heat of Immersion of the Components of Teeth.

To increase the sensitivity of the calorimeter previously designed for determining heat of immersion was modified and all connections were shielded to minimize the noise. The energy equivalent of the calorimeter was determined within ± 2% by the addition of a measured quantity of electrical energy. Secondary calibration by measuring the heat of solution of potassium chloride gave results which were well within 1% of the literature value. The calorimeter is therefore capable of measuring heats of reactions of the order of 5 cal within 2% or better.

(c) Dental Calculus: Organic Portion.

Electrophoretic studies of the organic content of dental calculus and of mucin indicate that the mucoprotein present in both might be a glycolipoprotein instead of a simple glycoprotein. In addition, small amounts of citric acid were found in calculus by electrophoretic and spectrophotometric technics. A detailed report is appended.

(d) Fluorescence Studies.

Studies of the fluorescence of calcified tissues were continued with emphasis on starch gel electrophoretic technics of separation of peptides of bone and teeth. Minor adjustments were made in the portable fluorometer and limited animal studies were initiated at the Naval Dental School, National Naval Medical Center, Bethesda, Maryland.

4.2 METALS

(a) Amalgam.

In the rheological study of amalgam emphasis was placed on the development of an electronic computer program which will give a detailed interpretation of the phenomenological and mechanical characterisitcs of a material without the direct application of complicated rheological theory and involved mathematical procedures to each set of data. It is expected that eventually such a program will provide a simple means of obtaining the description of rheological behavior and mechanical constants from simple strain-time and stress-strain experiments. It has been observed that stress-time curves for some alloys that meet present standard specifications are very different. The objective is to specify more exactly properties that can later be correlated with clinical results and to determine which set of properties are the most useful in dental practice.

X-ray diffraction studies have been conducted on dental silver-tin alloys in an effort to correlate line-broadening effects with the presence of internal strains in un-annealed alloy filings. A number of commercial alloys have been examined in both the annealed and un-annealed conditions. Line-broadening was detected in X-ray patterns from the un-annealed powders. This seems to indicate the presence of internal strains since there was no detectable line broadening in these alloys after annealing at 100° C. Spherical silver-tin alloy powders were also examined in the annealed and un-annealed conditions. There was no pronounced line broadening and no detectable difference in their X-ray patterns before and after annealing. The spherical powders seem to be relatively free of internal strains. This may be a result of the unique atomization process used in their manufacture.

(c) Gallium.

A detailed report on the properties of dental amalgam and gallium alloys produced by the use of spherical particles is appended.

(c) Gold Alloys.

A report on the development of X-ray spectrographic methods for analysis of dental gold alloys is appended.

4.3 RESINS

(a) Analysis of Polymers by Gas Chromatography.

Differentiations of some polyethylenes were found possible from the chromatograms of their pyrolysis products. The technique was somewhat modified since the relative peak areas of the chromatograms varied considerably for different samples of the same structure. A mechanical integrator has become available that allows more rapid interpretation of the results.

A more detailed investigation of the sensitivity of the technique is being conducted.

(b) Silica-Reinforced Direct Filling Resins.

Data were obtained on highly reinforced polymers showing decreasing strength with increasing particle size. The strengths of the reinforced resins did not appear to be influenced by the particle shape (spherical vs irregular) or, under the conditions of mixing and testing used, by the percent resin. Irregular fused silica (with 33 volume percent resin) and spherical soda-lime glass (with 25 volume percent resin) both had coefficients of thermal expansion of approximately $20 \times 10^{-6}/°C$.

Clinical studies were continued as planned. Direct anterior fillings utilizing vinylsilane-treated fused silica powder (in place of polymer powder) with a proprietary monomer and initiator appeared equally satisfactory or superior to controls (conventional resin filling materials) after one year.

(c) Adhesion Studies.

Additional data have been obtained supporting the finding that the addition reaction product of N-phenylglycine and glycidyl methacrylate (NPG-GMA) can promote significant bonding between methacrylate polymers and calcified substrates.

4.4 Zinc Oxide-Eugenol Materials

(a) Zinc Oxide Eugenol Type Cements.

The heat rise on setting, setting expansion, coefficient of thermal expansion and film thickness of zinc oxide-eugenol and zinc oxide-fused quartz-o-ethoxybenzoic acid (EBA)-eugenol cements were determined by a number of techniques. The compressive, conventional and centrifugal tensile, and shearing strengths of EBA containing cements were generally two to three times higher than those of non-modified cements. A number of experiments were conducted to develop static and dynamic solubility-and-disintegration and abrasion-resistance tests that more closely correlate with the results obtained in clinical studies. Clinical investigations were conducted on about 75 patients. The materials were found to be non-irritating and sedative even when used in pulp capping. Filling materials employing EBA were more susceptible to abrasion than ZnO-eugenol controls. These results indicate that the modified cements are promising as bases under the metallic fillings since they combine the desirable qualities of both ZnO-eugenol and zinc phosphate cements.

Studies of the mechanism of the setting reaction of EBA and eugenol have been continued. The liquid in ZnO-EBA cement can be extracted quantitatively by methanol or chloroform. The latter extract also contained some unreacted zinc oxide.

The reaction of EBA with zinc oxide can either lead to the formation of a zinc salt or a chelated complex. Possible formation of a chelate was ascertained by (1) titration of an aqueous solution of EBA with base in the presence of zinc ions (2) Job's spectrophotometric method of continuous variations (3) polarographic reduction. The first two methods proved inconclusive. The polarogram showed the absence of the characteristic zinc wave when eugenol or EBA was present in excess, indicating that at least under the experimental conditions, a zinc chelate is formed.

(b) Eugenol Isomers.

p-Allyl- and propenylbenzoic acid have been synthesized and their ionization constants are being determined. Synthesis of pure m-allylphenol and m-allylbenzoic acid was also attempted. To relate structure and reactivity the substituent constants σ of the Hammett equation $\log \frac{Ka}{Ka_o} = \sigma\rho$ have been calculated for the m and p-allyl and propenyl groups from the values of the ionization constants of eugenol isomers and p-allylphenol that have been measured previously.

4.5 Investment for Chromium-Cobalt Alloys

Determination of the physical properties of investment for chromium-cobalt alloys was continued with the measurement of the compressive strength at room temperature. The results indicate that there is much variation among the materials. The silica-type investments which are mixed with an ethyl silicate liquid exhibit very low strength at room temperature, even after having been stored for one hour at room temperature, in 100% relative humidity. Since these investments are not used at room temperature but at the casting temperature of the alloy, it would be of more interest to know the strength at the recommended casting temperatures. An investigation of the possibility of measuring the compressive strength of investment materials at elevated temperatures was initiated, and equipment for this purpose has been designed and constructed. Data are being obtained on strength at casting temperatures.

4.6 Evaluation of Materials

Materials evaluated for the Federal dental services or the American Dental Association by specification or other test methods included alginate impression materials, amalgam alloys, denture base resins, gold casting alloys, inlay waxes, investment, relining resins, repair resins, zinc oxide-eugenol impression pastes and zinc phosphate cements.

For the Director
By
W. T. Sweeney

W. T. Sweeney
Chief
Dental Research Section

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT		NBS REPORT
0708-20-07560	December 31, 1962	7809

Progress Report

on

X-Ray Spectroscopic Analysis of Noble Metal Alloys

by

Barry W. Mulligan*
Harold J. Caul**
Stanley D. Rasberry***

* Chemist, Spectrochemistry Section, National Bureau of Standards, Washington, D. C.

** Research Associate, American Dental Association Research Division, National Bureau of Standards, Washington, D. C.

*** Guest Worker, Spectrochemistry Section, National Bureau of Standards, Washington, D. C.

This work is a part of the dental research program conducted at the National Bureau of Standards in cooperation with the Council on Dental Research of the American Dental Association; the Army Dental Corps; the Dental Sciences Division of the School of Aviation Medicine, USAF, and the Veterans Administration.

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X-RAY SPECTROSCOPIC ANALYSIS OF NOBLE METAL ALLOYS

Abstract

The analysis of noble metal alloys by means of x-ray spectroscopy has been investigated. Alloys were prepared containing gold, platinum, palladium, silver, copper and zinc and then analyzed by wet chemical methods. Specimens were made for x-ray fluorescence measurements by using a dental casting procedure and the surfaces were prepared by wet grinding. The spectrometer operating parameters were then determined. The method is extremely fast when compared to wet chemical methods and appears to be sufficiently precise to be a very useful procedure.

1. INTRODUCTION

The analysis of noble metal alloys for the various constituents is a difficult and time consuming task by wet chemical methods. Fire assay techniques are used chiefly for the determination of gold. If platinum and palladium are present, the alloy has a higher melting point and losses may occur, also further chemical separations are necessary to remove the platinum and palladium before gravimetrically determining the gold. The base metals are not determined by fire assay.

A wet chemical analysis of a noble metal alloy is even much more complex and requires careful, painstaking procedures.

It was thought that x-ray spectroscopy would offer the possibility of increased speed of analysis.

2. EXPERIMENTAL PROCEDURE

Initally, a set of four synthetic standard samples was prepared by melting together in a high frequency furnace the component elements. Since the method was to be applied to the analysis of dental gold alloys the components and concentration ranges were chosen according to Table 1. This range of compositions is representative of dental casting golds.

Disks approximately 1/8 inch thick and 1 1/4 inches in diameter were made by machining so that they fitted the sample holders of the x-ray instrument to be employed. The surfaces of the specimens to be analyzed were precision machined on a lathe, and during the measurement period, the samples were revolved around the axis of the disk by means of the specimen spinner incorporated in the spectrometer.

The instrument was a North American Philips three position spectrometer. It is not as fast an instrument as those employed in production control applications, but since it is possible in this case to use the same crystal and radiation detector for all determinations, a minimum of instrument manipulation was involved.

The compositions of the standard alloys were determined by Charles L. Gordon of the Applied Analytical Research Section of the National Bureau of Standards using wet chemical procedures according to the method of Gilchrist [1]. The results are shown in Table 2.

By using these values and information obtained from x-ray fluorescence measurements with the 1/8 inch thick machined specimens, the resultant analytical curves were found to be linear and the precision of repeated determinations indicated that the method might be a useful analytical procedure. The optimum operating parameters were determined and are shown in Table 3.

For gold the Lβ line rather than the Lα was used, solely because it was found empirically that it consistantly gave better precision.

Since the 1/8 inch thick disk specimens weighed about 35 grams, disks of one composition were cast in thicknesses of 1/16, 3/64, 1/32 and 1/64 inch. The disks were cast using the lost wax process and regular dental procedures. These specimens were mounted in methyl methacrylate resin and the one exposed surface of each specimen was prepared for analysis by wet grinding with a 600 grit as the final abrasive surface. X-ray measurements were made of all the disks including the 1/8 inch machined ones in a statistical sequence and no differences could be detected within the precision of the determinations. Therefore, disks of 1/32 inch thickness were chosen as the best selection between ease of preparation and minimum amount of alloy per sample. No further attempt was made to lessen the quantity of metal per sample, but line-to background intensity ratios of the individual element determinations indicate that it should be possible to reduce disk diameter to about 1/2 inch.

Samples 1/32 inch thick of the four previously analyzed alloys were prepared in duplicate and run on the spectrometer in a statistical sequence to minimize any effects of instrumental drift. The operating parameters were the same as those in Table 3. The analytical curves obtained from these runs for gold, platinum, palladium, silver, copper and zinc are shown in Figures 1 through 6. Each point on the curves is the mean of 4 individual determinations. The coefficient of variation for an individual determination in a group of four variation is shown in Table 4.

3. DISCUSSION

The observed precision for an individual determination in a group of four may be compared with the theoretical precision of the counting of x-ray quanta. The standard counting error for such a process is equal to the square root of the total number of counts. The best precision possible, therefore, would give a coefficient of variation equal to the square root of the total number of counts divided by the total number of counts or the reciprocal of the square root of the total number of counts. In the case of gold, silver and copper, where 256,000 counts were obtained per determination this would be 0.20%. In the case of platinum, palladium, and zinc, where 186,000 counts were obtained per determination, this would be 0.23%. It can be seen that the theoretical precision was approached in the gold and silver determinations but not in the case of the other four elements possibly due to the greater influence of background variation when the line-to-background ratio is low.

If one can assume that the data in Table 2 showing the composition of the 4 alloys are the true values then the accuracy of analysis by x-ray fluorescence would be comparable to the precision. If this is the case then results given in Table 4 indicate that the amount of gold or copper may be determined to about 0.2% and for the other elements to 0.1% or less.

As to the question of the number of standards required for actual determinations of unknowns it is doubtful that more standards would be required for the ranges already investigated. The zinc range should cover the composition of most dental alloys. For more complete coverage of these alloys the ranges for copper, silver and gold need to be extended in both directions, while the platinum and palladium ranges should be increased to handle dental wrought gold wires.

In spectrochemical analysis the greatest accuracy is obtained when the unknown is closely bracketed by two standards nearly identical to that of the unknown. The minimum number of required standards, therefore, will be determined by the accuracy desired and by the number of alloy compositions to be analyzed.

The estimated time for preparing 6 specimens is 3 hours and the time required for determining the 6 elements should be less than 2 hours. This method reduces the time element for determining chemical composition of this type of alloy from man weeks to man hours.

4. CONCLUSION

The results indicate that the x-ray spectroscopic method is sufficiently precise for analysis of dental gold alloys and has marked advantages of speed and simplicity compared to chemical analysis.

5. REFERENCES

1. R. Gilchrist, J. Res. N.B.S., 20, 745 (1938)

2. H. A. Liebhafsky, H. G. Pfeiffer, and P. D. Zemany, Anal. Chem., 27, 1257 (1955).

TABLE 1

Concentration Range of the 4 Standards

Element	Range
Gold	68 - 79%
Platinum	0 - 6
Palladium	0 - 3
Silver	8 - 14
Copper	6 - 12
Zinc	0 - 2

TABLE 2

Compositions of the Standards

Element	No. 1	No. 2	No. 3	No. 4
Au	68.27%	72.01%	78.08%	79.08%
Pt	6.34	3.76	2.17	0.00
Pd	0.00	1.97	2.84	1.04
Ag	11.63	10.86	8.13	13.88
Cu	11.88	9.95	7.86	6.01
Zn	1.87	1.44	0.94	0.00
Total	99.99%	99.99%	100.02%	100.01%

TABLE 3

Operating Parameters

Element	Atomic Number	Line	LiF 2θ	X-Ray Source		Total Counts* Per Determination
				KV. -	MA.	
Au	79	L_β	31.19	50	30	256,000
Pt	78	Lα	38.05	50	45	128,000
Ag	47	Kα	15.95	50	45	256,000
Pd	46	Kα	16.70	50	45	128,000
Zn	30	Kα	41.74	50	45	128,000
Cu	29	Kα	44.96	50	45	256,000

* A scintillation counter was used in all cases.

TABLE 4

Reproducibility of Single Determinations

Standard Number	Au. %	CV.* %	Pt. %	CV. %	Pd. %	CV. %
1	68.27	0.43	6.34	1.15	0.00	2.24
2	72.01	0.23	3.76	1.63	1.97	1.32
3	78.08	0.41	2.17	2.64	2.84	1.18
4	79.08	0.30	0.00	1.36**	1.04	1.19

Standard Number	Ag. %	CV. %	Cu. %	CV. %	Zn. %	CV. %
1	11.63	0.17	11.88	2.07	1.87	0.73
2	10.86	0.66	9.95	2.32	1.44	0.81
3	8.13	0.30	7.86	2.60	0.94	0.62
4	13.88	0.63	6.01	1.74	0.00	2.15

* CV. = Coefficient of variation for an individual determination in a group of four.

** Coefficient of variation for zero percent is the value of the background radiation.

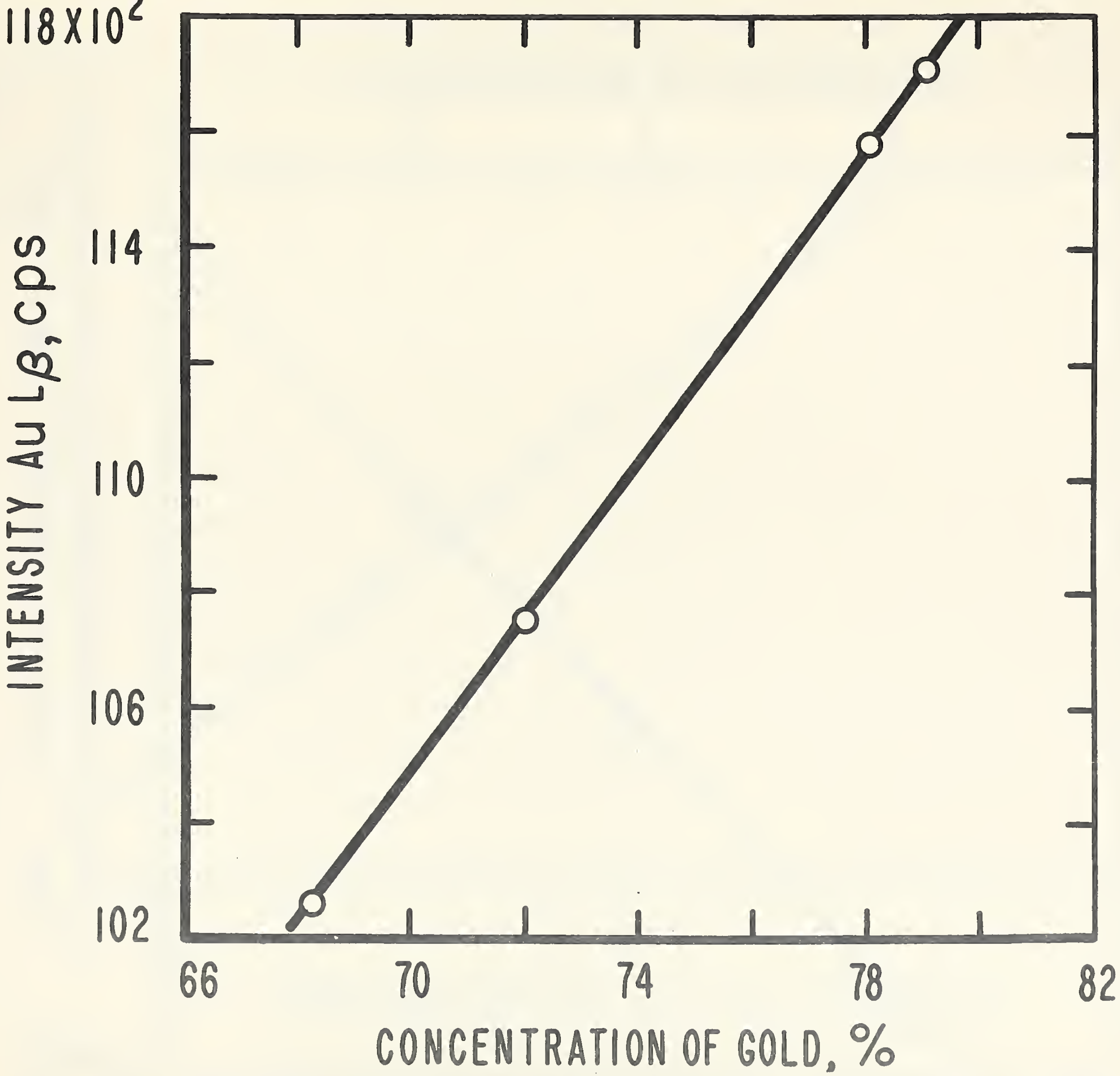

Figure 1. Analytical Curve for Gold

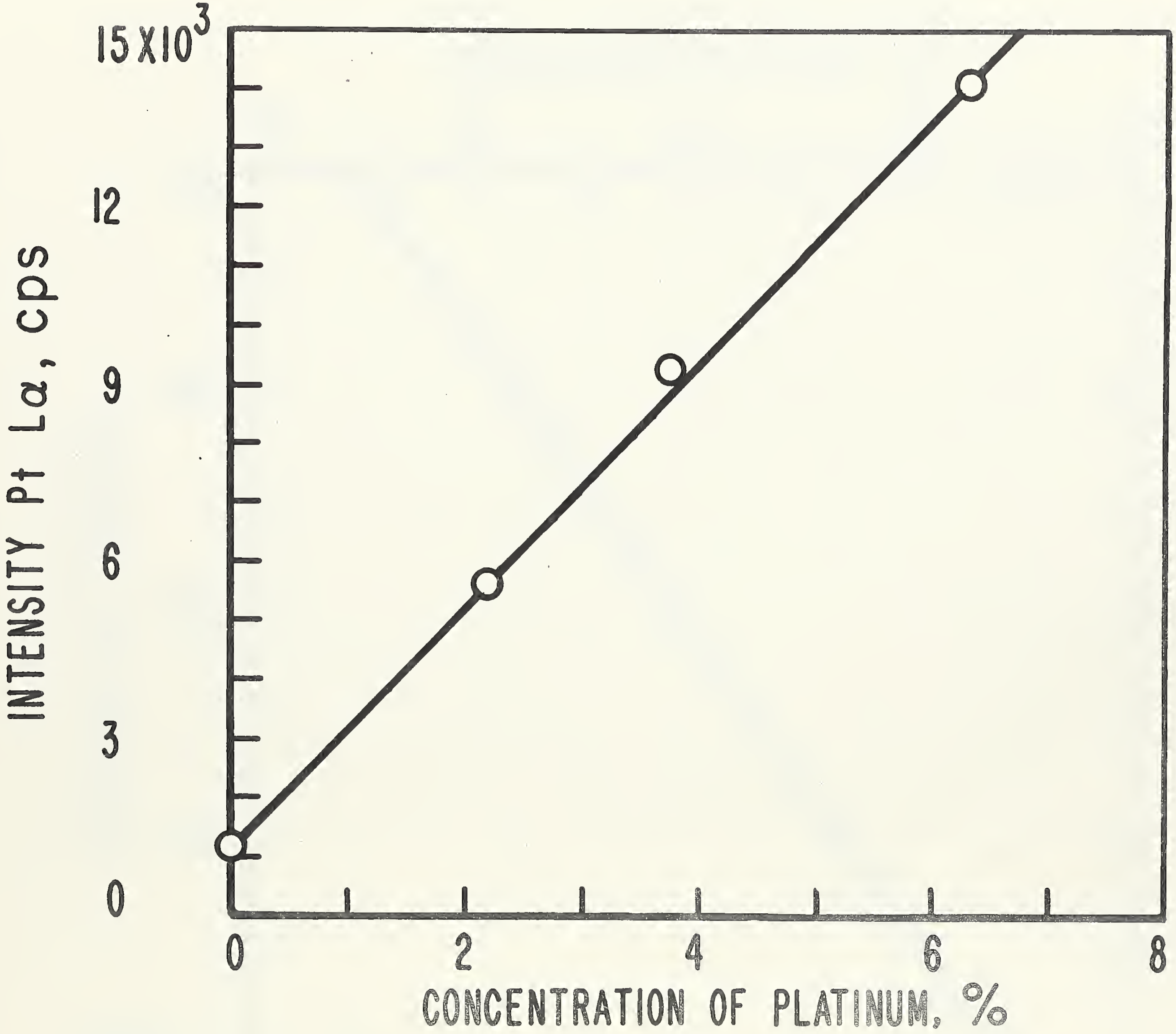

Figure 2. Analytical Curve for Platinum

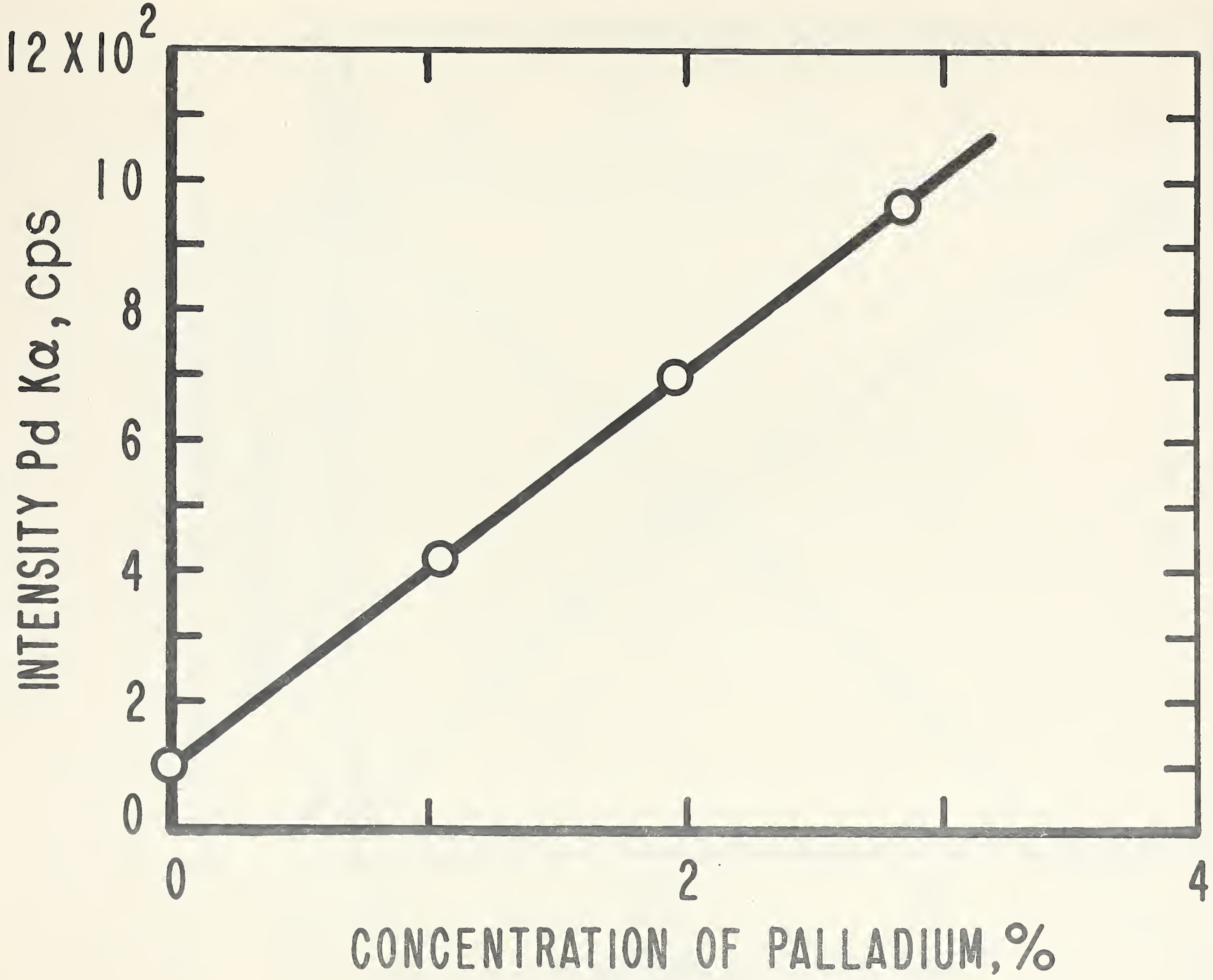

Figure 3. Analytical Curve for Palladium

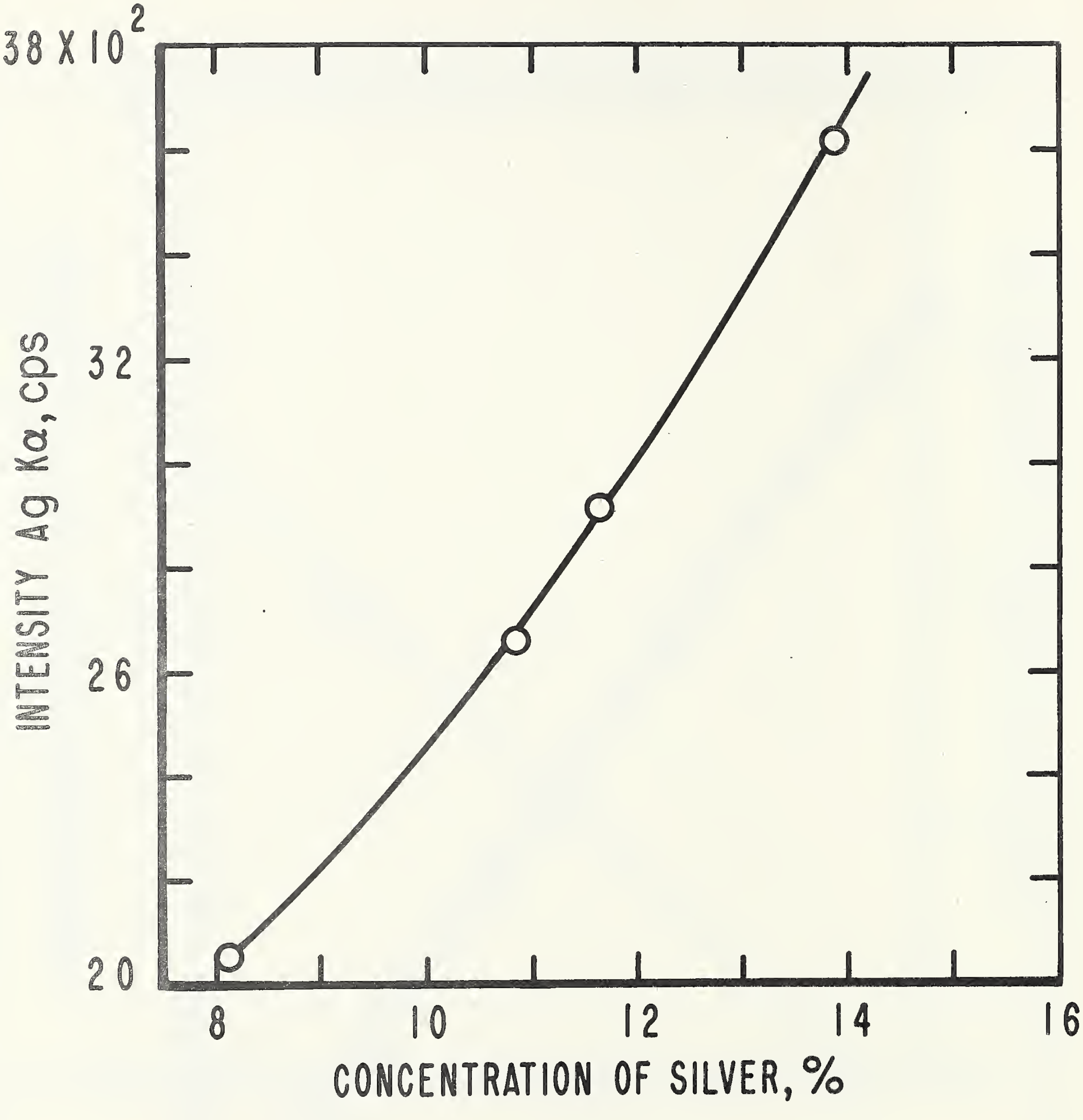

Figure 4. Analytical Curve for Silver

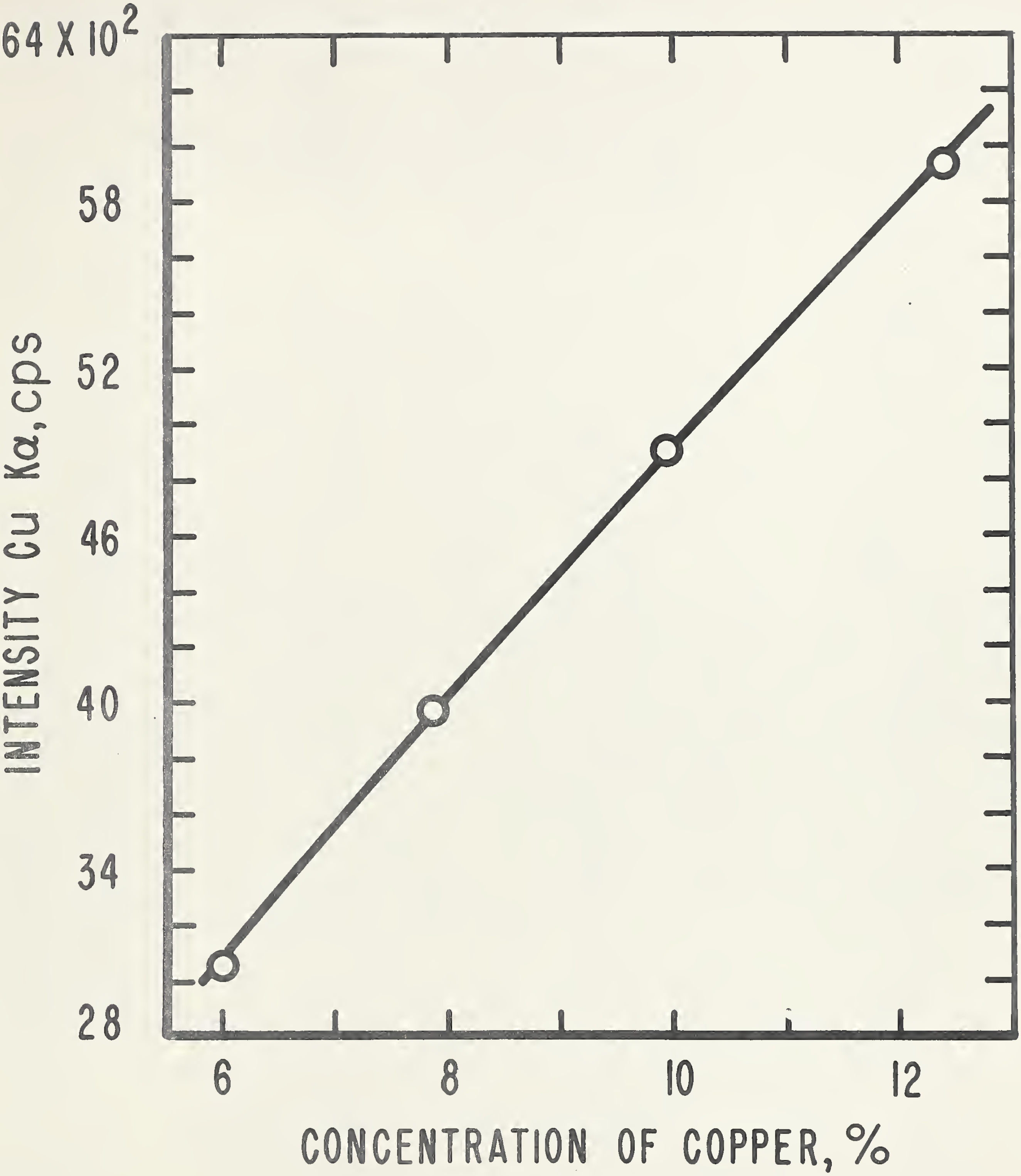

Figure 5. Analytical Curve for Copper

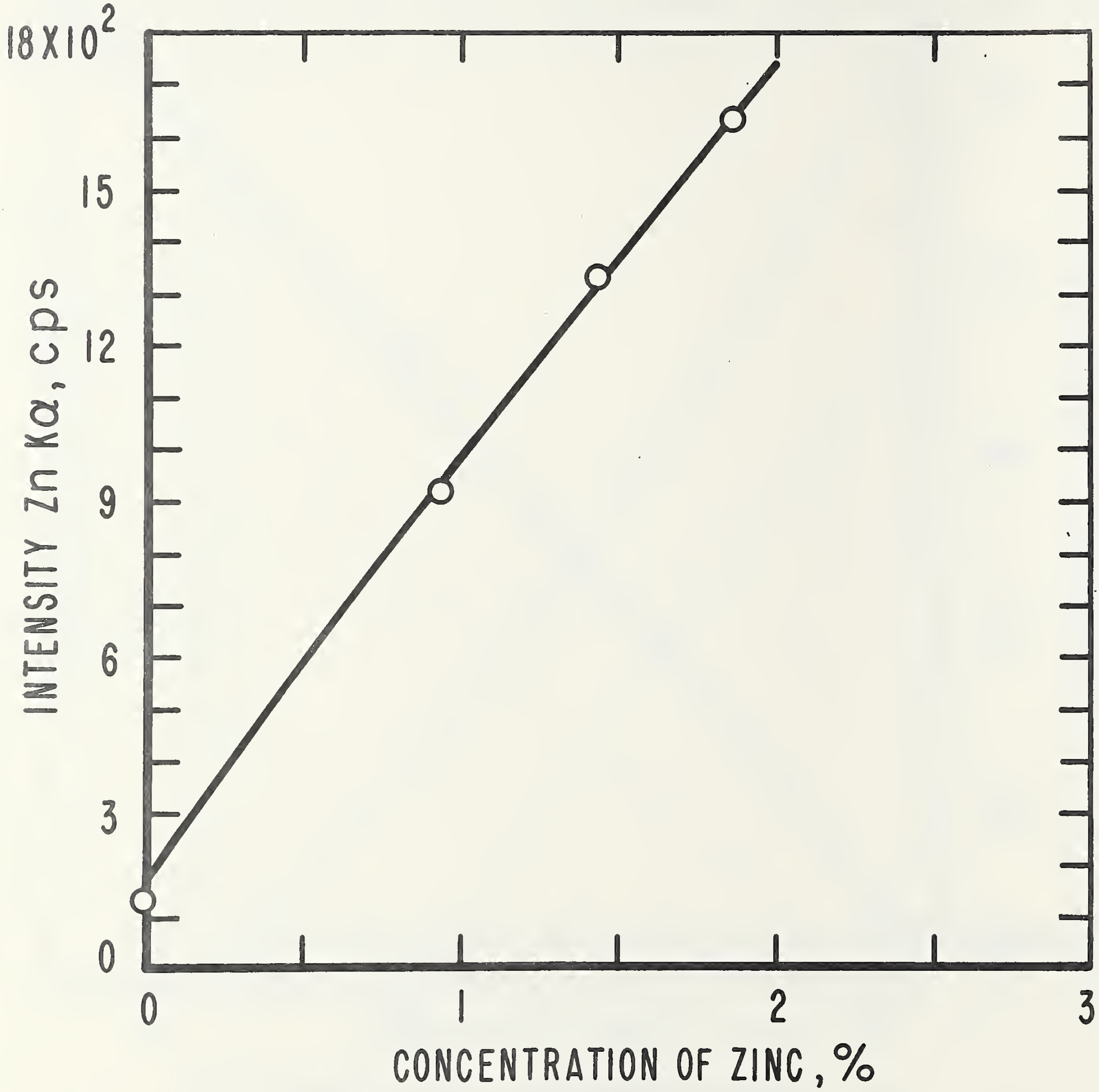

Figure 6. Analytical Curve for Zinc