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A METHOD FOR DETERMINING SMALL AMOUNTS OF GOLD, AND ITS USE IN ASCERTAINING THE THICKNESS OF ELECTRODEPOSITED GOLD COATINGS

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ABSTRACT

This paper presents a method for the determination of the thickness of gold electroplate, using a punch and die to obtain samples of known small area. Amounts of gold up to 10 micrograms (0.010 mg), corresponding to a thickness of 0.00050 mm (0.00002 in.) or less on 1 mm² (0.00155 in.²) of surface, are determined directly by means of the color produced with *o*-toluidine. Results are reported for thicknesses of gold plate on experimentally plated samples and on commercially plated products.

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I. INTRODUCTION

Many articles of jewelry, such as watchcases, rings, lockets, earrings, tie clasps, ornamental and emblematic buttons, coverings for knife handles, brushes, combs, and insignia for the armed forces, are electroplated with gold. The thickness of the gold may vary from less than one-millionth to more than one ten-thousandth of an inch.

The calculation of the thickness of gold depends on the measurement of a given area, the determination of the total gold on this area, and the known density of gold (19.3). The deposit of gold, usually nonuniform, even on plane surfaces, is still less uniform on curved surfaces, so that the thickness determined by this method is only an average value. The application of this procedure is difficult, because of the uneven contour of the surface, the small size of many articles, and the small amount of gold involved. One square centimeter (0.155 in.²) of surface plated with 0.00025 mm (0.00001 in.) of gold contains only 0.49 mg of gold. The need exists, therefore, for a precise method that can be applied to a small measured area. By means of a suitable die an area of 1 mm² can usually be cut out from some portion of a commercially electroplated article, and the quantity

of gold involved will generally fall within the limits that can be conveniently determined colorimetrically.

II. COLORIMETRIC DETERMINATION OF SMALL AMOUNTS OF GOLD BY MEANS OF *o*-TOLIDINE

The reagent, *o*-tolidine, 3,3'-dimethylbenzidine, reacts with chlorauric acid, HAuCl_4 , to produce a yellow color. This reaction, which is not new, has been investigated by Pollard.¹ The development of the color depends on the oxidation of the *o*-tolidine, and, consequently, any oxidizing substances, such as ferric ion or chlorine, must be rigidly excluded.

With the visual method of comparison, amounts of gold up to about 8 micrograms (0.008 mg) in 25 ml of solution can be determined, and with a spectrophotometer, as much as 10 micrograms in the same volume. Because the yellow color is unstable, freshly prepared color standards must be used in the visual comparisons, but they are not required in the spectrophotometric method after the relation between concentration and percentage transmittance is determined; hence the latter method is more convenient for routine tests.

1. PREPARATION AND STABILITY OF THE REAGENT SOLUTION OF *o*-TOLIDINE AND OF DILUTE SOLUTIONS OF GOLD

The *o*-tolidine used in the colorimetric determination of gold should be free from impurities that effect the color developed by the reaction. Purification of the commercial product was found necessary to eliminate unidentified impurities that caused the characteristic yellow color to fade rather quickly. A reagent of sufficient purity can easily be prepared by recrystallizing the commercial grade of *o*-tolidine from 2-*N* sulfuric acid. A boiling solution of 2-*N* sulfuric acid is saturated with *o*-tolidine, filtered while hot through porous porcelain or a glass frit to remove insoluble impurities and any undissolved *o*-tolidine, and allowed to cool to room temperature. The *o*-tolidine sulfate that crystallizes is removed by filtration and recrystallized twice more from 2-*N* sulfuric acid. Filter paper should not be used because of the danger of introducing organic matter, which has a deleterious effect on the subsequent development of the yellow color. The final product should be a nearly pure white powdery or finely crystalline mass.

The reagent solution is prepared by saturating *N* sulfuric acid with the purified *o*-tolidine sulfate and diluting 1 volume of the saturated solution with 19 volumes of *N* sulfuric acid. Both the saturated solution and the diluted solution are stable for long periods of time, hence the preparation of fresh reagent solution for each series of determinations is unnecessary.

Standard solutions, containing 1.0 microgram (0.001 mg) of gold per milliliter, were prepared by dissolving 0.1000 g of pure gold, diluting to 1 liter, and then diluting 10 ml of this solution to 1 liter. In each case the liter of solution contained 60 ml of concentrated hydrochloric acid and 40 ml of concentrated nitric acid. The above quantities of acids were added to prevent the separation of gold from such dilute solutions. Experience showed that solutions so prepared remained stable and constant with respect to the gold content.

¹ W. B. Pollard, *Bul. Inst. Mining Met.*, No. 223, 8 p. (1923).

2. PREPARATION AND MEASUREMENT OF THE COLOR OF THE *o*-TOLIDINE-GOLD SOLUTION

A definite amount of the standard gold solution (in the range 0.5 to 10.0 micrograms of gold) was placed in a 50-ml beaker and evaporated nearly to dryness on the steam bath. A drop of aqua regia was added, and evaporation to complete dryness was accomplished by impinging on the surface of the solution a jet of purified air. Evaporation on the steam bath alone usually caused some reduction of the chloroauric acid to aurous chloride or metallic gold. No such reduction occurred when the beaker was held in the hand and the stream of air was used.

To the completely air-dried residue of chloroauric acid 25 ml of the *o*-tolidine reagent was added, and the resulting solution was trans-

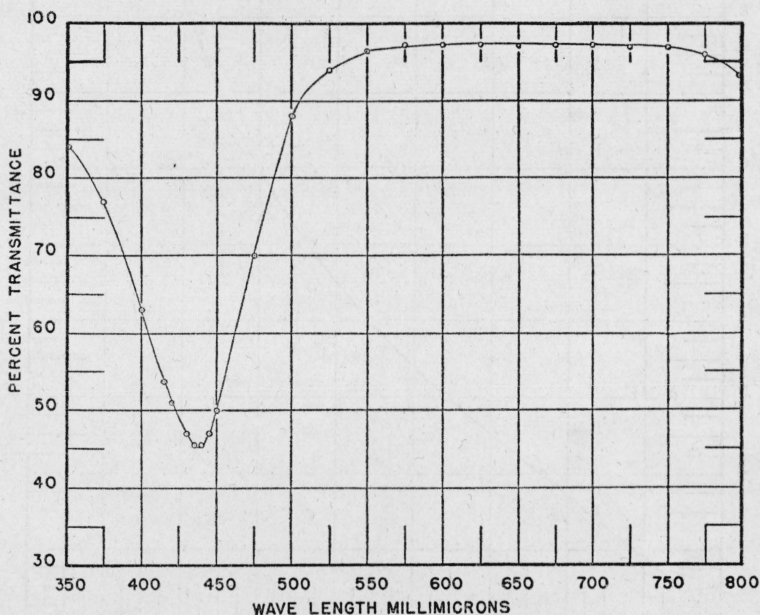


FIGURE 1.—Relation between percentage transmittance and wavelength of light.

ferred to a 25-ml cell for measurement of the percentage transmittance of light by means of a spectrophotometer. The instrument used was a Coleman Universal Spectrophotometer, model 11. The 25-ml cells were cylinders 50.0 mm long.

When the *o*-tolidine solution was added to the dry residue of chloroauric acid, a yellow color developed, the intensity of which reached a maximum in 1 to 3 minutes and remained stable for 10 to 30 minutes. As extensive experience showed that evaporation either of small or large quantities of aqua regia, in the manner described above, left no oxidizing material, 25 ml of the *o*-tolidine reagent was used directly as the solution in the "blank cell."

The relation between percentage transmittance and wavelength of light is shown in figure 1. The solution was found to have a minimum transmittance of light at a wavelength of 437 millimicrons.

The relation between percentage transmittance at 437 millimicrons and the weight of gold contained in 25 ml of solution is shown in figure 2.

The reproducibility of the calibration curve was established by using aliquot portions of independently prepared standard gold

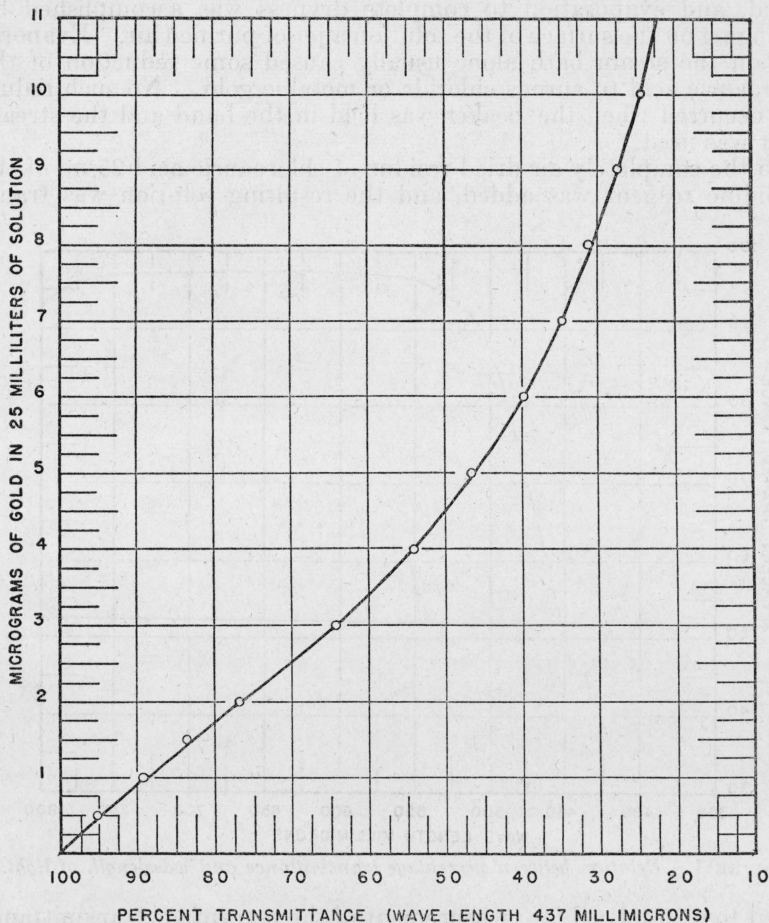


FIGURE 2.—Relation between percentage transmittance at a wavelength of 437 millimicrons and quantity of gold in 25 ml of solution.

solutions. As seen in table 1, the average deviation of the observations is about 4 percent.

In determining very small amounts of gold a few simple precautions must be taken. For instance, the beakers to be used should be cleaned thoroughly with aqua regia to insure removal of any gold or other foreign substances that would affect the color produced with *o*-tolidine. As the determination of gold depends on the oxidation of *o*-tolidine by gold in its trivalent condition, it is necessary to maintain the gold in this state of valency until the *o*-tolidine solution

is added. Simple evaporation of gold solutions causes reduction of some of the chloroauric acid to aurous chloride or metallic gold, but experience has shown that no such reduction occurs if a jet of purified air is used to obtain final dryness. The impurities, ammonia, hydrogen sulfide, and dust, commonly in the air can easily be removed by passing the air through concentrated sulfuric acid, Ascarite, and a fritted-glass filter.

TABLE 1.—*Reproducibility of the calibration curve*

Gold taken	Transmittance, 437 millimicrons	Gold determined	Error
<i>Micrograms</i>	<i>Percent</i>	<i>Micrograms</i>	<i>Percent</i>
1.26	85.0	1.30	+3.1
1.26	86.2	1.20	-4.8
1.58	80.0	1.70	+7.6
1.58	81.0	1.60	+1.3
2.37	70.2	2.52	+6.3
2.37	71.2	2.43	+2.5
2.99	65.8	2.92	-2.3
3.24	61.0	3.35	+3.4
3.24	61.0	3.35	+3.4
4.38	51.8	4.33	-1.1
			¹ ±3.58

¹ Average.

Experiments showed that silver, copper, nickel, and zinc, the metals most commonly used for "coloring" gold deposits, did not interfere with the determination of 5 micrograms of gold, even if present in quantities up to 500 micrograms. Larger amounts of these metals leave, on evaporation, a salt deposit that makes it difficult to ascertain when the solution is evaporated to complete dryness. For this reason, the amount of foreign metals should be kept as small as possible.

III. APPLICATION OF THE COLORIMETRIC METHOD TO THE DETERMINATION OF THE THICKNESS OF ELECTRODEPOSITED GOLD PLATE

1. METHOD OF OBTAINING SAMPLE OF KNOWN SMALL AREA

To utilize the foregoing colorimetric method to determine the thickness of gold plating, areas of 1.00 mm² (0.00155 in.²)² were cut from experimental gold-plated brass sheets. The punch and die used for this operation was designed and constructed by Charles W. Hyder, of this Bureau, and is shown diagrammatically in figure 3. The punch was designed to cut samples from specimens whose total thickness was 1/32 inch or less.

To remove the gold coating from its affixed base metal layer, the sample cut out by the punch was treated in a 50-ml beaker with from 0.5 to 1.0 ml of a diluted solution of nitric acid, composed of one volume of concentrated nitric acid and one volume of water. It was found that if the gold layer was thicker than 3 millionths of an inch,

² This area was calculated by Charles P. Saylor from measurements, made with a microscope, of the diameters of the pieces which were cut out and of the holes which remained.

the tiny gold disk remained intact during the acid treatment, and could be washed by decantation with water; otherwise, the gold must be collected and washed on a microfilter. A medicine dropper with a fine capillary tip was advantageous in removing the water from the beaker. The gold was then dissolved in aqua regia, and its determination was completed as previously described.

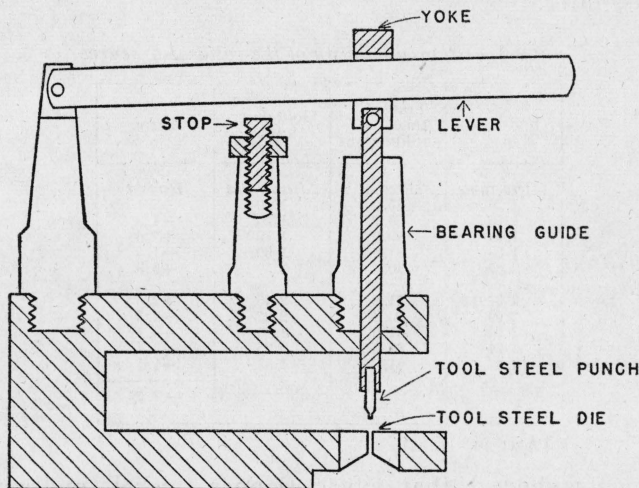


FIGURE 3.—Diagram of punch and die used to cut samples of 1-mm² area.

For converting the determined quantity of gold into thickness of gold layer, a graph was prepared in which the amount of gold, in terms of percentage transmittance of light at 437 millimicrons, was plotted as a function of thickness in millionths of an inch (fig. 4).

2. APPLICATION TO EXPERIMENTALLY PLATED SAMPLES

To prepare the experimental plates, flat sheets of brass approximately 7 cm (2.76 in.) by 8 cm (3.15 in.) were plated on one side with gold by Frances H. Colbert, of this Bureau, under conditions to produce a relatively uniform layer. The average thickness was calculated from the area plated and the amount of gold deposited. Table 2 reports the results obtained by taking from 2 to 5 samples from near the center of each plate and shows that the values determined in this region agreed well with the calculated value for thicknesses up to 0.000005 in.

For layers of greater thickness significant variations are observed between the values determined at the center of the plates and average thicknesses calculated from the areas of the plates and the amounts of gold deposited. As these variations greatly exceed the limits of accuracy of the microdetermination, the values obtained at the centers of the plates must be considered as representing more correctly the actual thickness of the gold layer in the region tested.

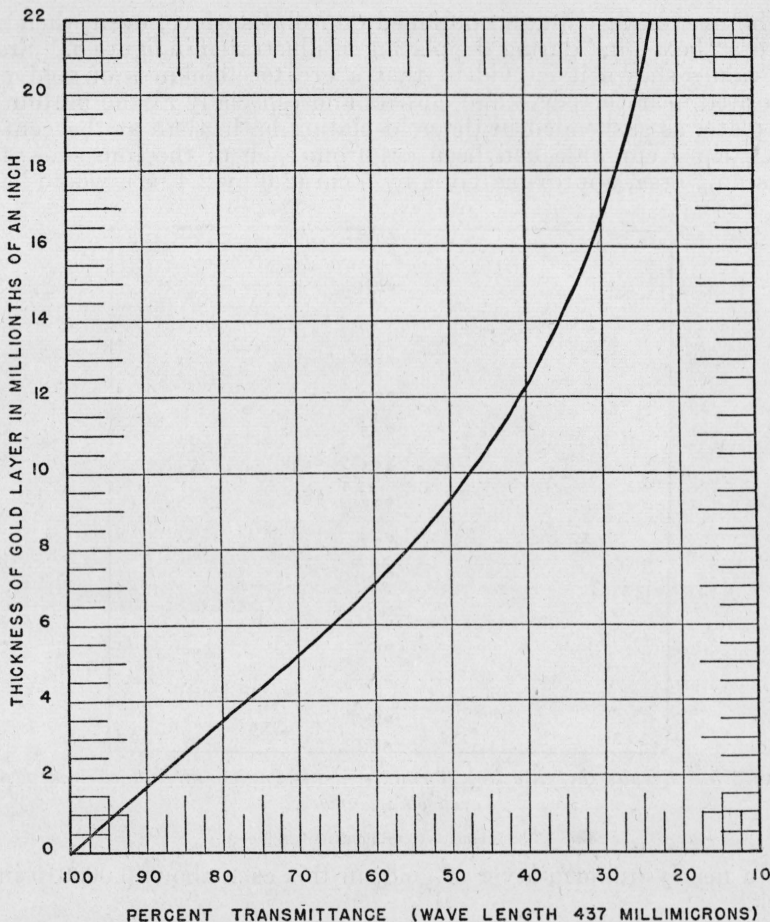


FIGURE 4.—Graph for converting amount of gold per 1-mm² area (in terms of percentage transmittance at a wavelength of 437 millimicrons) to thickness of gold layer.

TABLE 2.—Comparison of thickness of gold layer determined near center of specimen and the average thickness calculated from the area plated and the amount of gold deposited

Plate number	Thickness of gold, millionths of an inch						
	Determined						Calculated from weight of deposit
	1	2	3	4	5	Average	
1	1.5	1.5	-----	-----	-----	1.5	1.0
2	3.2	2.5	2.2	2.2	2.5	2.5	2.5
3	4.5	4.4	4.4	4.1	4.0	4.3	4.3
4	4.5	4.4	4.4	4.5	4.7	4.5	4.5
5	6.9	6.1	5.9	6.9	6.9	6.8	8.6
6	8.2	8.0	8.4	8.4	8.3	8.3	10.6
7	9.5	9.0	9.0	9.4	-----	9.2	11.0
8	20.0	21.5	20.5	20.0	20.5	20.5	25.0

The uneven distribution obtained on a flat surface, even when the plate is "boxed in" during the plating, is illustrated in figure 5. From the values shown it is evident that a greater thickness of gold was deposited near the edges and corners and especially at the bottom of the plate, as suspended in the gold-plating bath, than at the center. If a strip 1 cm wide had been cut from each of the four sides, the remaining area, approximately 5 by 6 cm (2.0 by 2.4 in.), would have

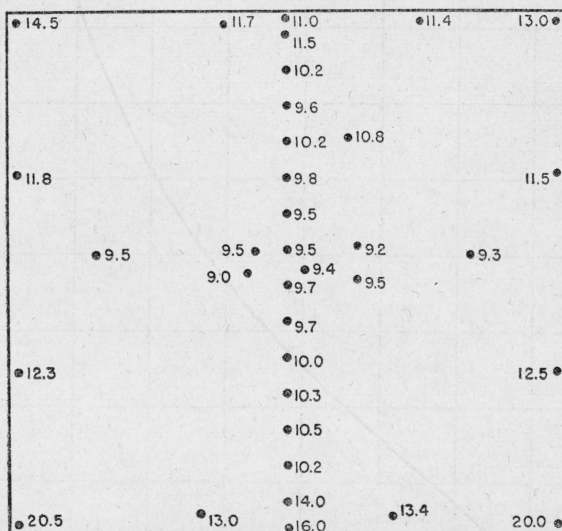


FIGURE 5.—Results that illustrate the uneven distribution of gold electrodeposited on a plane surface.

[Measurements in millionths of an inch.]

had a nearly uniform layer of gold, in this case about 0.000010 inch thick.

3. APPLICATION TO COMMERCIALY PLATED OBJECTS

To apply the method of testing to commercially plated objects, 16 prewar gold-plated articles of jewelry were obtained through the courtesy of Byron L. Shinn, counsel, Jewelers' Vigilance Committee, and W. H. Blake, associate secretary, New England Manufacturing Jewelers' & Silversmiths' Association. Some of the articles were labeled "electroplated precious metal," some "24k fine gold finish", and some bore no identification as to whether they were gold plated or not.

The results of determination of thickness of the gold layer are given in table 3.

TABLE 3.—Thickness of gold on commercially plated articles

Article	Portions tested	Thickness of gold (millionth of an inch)	Remarks
			Avg
1. Ladies compact	Top, bottom, sides		Was not gold plated.
	End clamps	1.6, 1.4	1.5
	Tongue of clasp	3.1, 3.5	3.3
	Top of clasp	3.1	3.1
2. Chain watch band	Bottom of clasp	6.2	6.2
	Chain part	6.3, 6.9, 6.0, 7.1, 7.1	6.7
3. Earring	Each of four petals		Gold too thin to determine.
4. Earring	do		Do.
5. Tie clasp	Two samples from each side	2.5, 3.2, 3.7, 3.0	3.1
6. Sport watch chain	(Swivel	13.5, 15.0	14.2
	Chain	10.7, 11.0	10.8
7. Tie clasp	Two sides of front bar	7.5, 7.3, 7.7, 7.8	7.6
	Monograms	2.5, 2.5, 1.9, 1.9	2.2
8. Tie clasp with chain and monograms.	Monogram bar holder	2.7	2.7
	Shirt bar	1.5, 2.0	1.8
	Chain	1.0, 0.8	0.9
9. Tie clasp	Front and back	5.0, 6.0, 4.0, 5.7	5.2
10. Tie clasp	do	7.0, 6.0, 4.2, 4.5	5.4
11. Tie clasp	do	5.5, 5.0, 3.7, 3.5	4.4
12. Collar clasp	do	3.8, 3.3, 4.0, 4.3	3.8
13. Collar clasp	do	3.0, 3.5, 4.5, 4.0	3.8
14. Collar clasp	do	4.7, 4.2, 5.0, 4.2	4.5
15. Key chain	Belt clamp	9.5, 10.5, 10.3	10.1
	Key ring	9.5, 10.0	9.8
	Chain	13.2, 14.3	13.8
	Snap catch	2.7, 3.2	3.0
	Center ornament	2.6	2.6
16. Ladies compact	Top metal case	Less than 1.0	Attached outside of enamel cover.
	Bottom of metal case	do	Metal case inside of enamel cover.
			Do.

The chain parts of articles 2 and 15 were tested by measuring the respective diameters and cutting a piece of the required length to give an area of 1 mm². Articles that were too thick for the punch were ground down on one side to reduce the total thickness to less than 1/32 inch, precautions being taken not to disturb the gold layer on the side to be tested.

Articles that have gold layers thicker than 20 millionths of an inch can be tested either by using a larger volume of *o*-tolidine-sulfuric acid reagent solution for dissolving the air-dried residue—or by diluting the aqua-regia solution of the gold obtained in the test and evaporating an aliquot of this solution to dryness for the colorimetric determination of the gold.

The data in tables 1 and 2 and in figure 5 show that the determination of thickness by the method described is accurate well within ±10 percent. This degree of accuracy is greater than that of the uniformity of thickness usually attained in commercial plating.

WASHINGTON, November 14, 1945.