NATIONAL BUREAU OF STANDARDS REPORT

6826

Progress Report

on

A PROCEDURE FOR THE DETERMINATION OF THE NOBLE METAL CONTENT OF DENTAL GOLD ALLOYS

by

Harold J. Caul
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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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A PROCEDURE FOR THE DETERMINATION OF THE NOBLE METAL CONTENT OF DENTAL GOLD ALLOYS

Abstract

A procedure for determining the noble metal content (gold and platinum metals) of dental gold alloys is described. In this procedure silver, gold and platinum metals content may be determined separately if desired. This method for noble metal content is accurate to within 0.1 per cent.

I. INTRODUCTION

The determination of the noble metal content of a dental gold alloy is important because of its correlation with the corrosion resistance of the alloy. The term "noble metal content" as used here means the amount of gold and metals of the platinum group. The chief platinum metals encountered are platinum and palladium, but small amounts of rhodium and iridium may be present in the alloy, introduced as impurities in the metals used to make the alloy.

The procedure described here makes use of certain portions of a method published by Gilchrist [1] for the complete analysis of a dental gold alloy. It differs, however, in that glass electrodes, instead of indicator solutions, are used to establish acidities and alkalinities, and no attempt is made to separate the individual noble metals.

2. METALS USED

In preparing the synthetic mixtures for the experiments, the following metals were used:

gold, purified by the authors, estimated by spectrochemical analysis to have a purity of 99.99 per cent;

palladium, estimated to have a purity of 99.96 per cent;

silver, prepared by the U. S. Mint, known to have a purity of 99.98 per cent;

platinum, by thermoelectric measurement, 99.999 per cent;

copper, standard melting point copper, by chemical analysis, 99.997 per cent.

3. REAGENTS USED

The reagents used were those that conformed to the specifications of the American Chemical Society for reagent grade chemicals.

Throughout this paper, whenever the use of an acid is prescribed with no indication of strength or dilution, the acid to be used is the concentrated acid. Dilutions are indicated by the volumes of acid and water mixed to prepare a diluted reagent. Diluted acid (1 + x) means a diluted acid prepared by mixing 1 volume of the concentrated acid with x volumes of distilled water. Similar designations are used for ammonium hydroxide.

Concentrated sodium hydroxide solution was prepared by dissolving from 30 to 40 grams of solid sodium hydroxide in about 100 milliliters of distilled water.

Ten per cent solutions of sodium hydroxide, sodium carbonate and sodium nitrite were prepared by dissolving 10 grams of each of the solid reagents in distilled water and diluting each such solution to a volume of 100 milliliters. It is to be noted that the sodium nitrite solution should be filtered before using it.

The solution of dimethylglyoxime was prepared by dissolving 1 gram of the solid reagent in 100 milliliters of 95 per cent ethyl alcohol.

The sodium formate solution was prepared by dissolving 25 grams of the solid reagent in water and diluting it to a volume of 100 milliliters.

The ammonium formate solution was prepared by diluting 10 milliliters of formic acid with about 500 milliliters of distilled water, adjusting the resulting solution to pH 8.5 with ammonium hydroxide (1 + 1), and diluting to a final volume of 1 liter.

4. APPARATUS FOR MEASUREMENT OF HYDROGEN ION CONCENTRATION

A pH meter with a standardized glass-calomel electrode system, capable of measurement over a wide range of temperature and pH, was used to measure the pH of the various solutions.

5. PROCEDURE

Preparation of Sample. Roll the sample into a ribbon 0.005 to 0.010 inch thick. This is done to insure more rapid and complete disintegration and solution of the sample. A 0.5-gram sample is recommended.

Decomposition of Sample. Place the 0.5-gram sample, accurately weighed, in a 250-milliliter beaker, cover the beaker with a watch glass, and add 5 milliliters of distilled water, 2 milliliters of nitric acid and 6 milliliters of hydrochloric acid. Heat this solution on a steam bath. It is necessary to break up the silver chloride with a stirring rod from time to time. If disintegration is not complete in a reasonable length of time, add more hydrochloric and nitric acid in the ratio of 3 to 1. If additional acids were added, the solution should then be evaporated to dryness and the original amounts of distilled water and acids then added. After decomposition is complete, add 150 milliliters of distilled water and continue to heat the solution on the steam bath until the silver chloride precipitate has coagulated. Cool the solution and set it aside for at least 1 hour.

Elimination of Silver. Filter the solution through a 9-centimeter filter paper of close texture[1] and wash the precipitate and paper

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[1] Whatman no. 42 paper may be used.

at least 10 times with diluted hydrochloric acid (1 + 99) at room temperature. Reserve the filtrate and washings for the determination of gold and platinum metals.

Dissolve the silver chloride with hot diluted ammonium hydroxide (1 + 1) and wash the filter well with water. The filter may contain iridium and because of this should be placed in a porcelain crucible reserved for the determination of the platinum metals or noble metals.

If it is desirable to determine the silver content, acidify the ammoniacal solution with nitric acid, dilute it to 200 milliliters and add 2 milliliters of hydrochloric acid. Heat the solution on the steam bath until the silver chloride has coagulated. Cool the solution and set it aside for at least 1 hour. By means of suction, filter the solution through a glass filtering crucible of fine porosity. Again wash the precipitate with diluted hydrochloric acid (1 + 99) at room temperature. Dry the precipitate at 110°C. (230°F.) for 2 hours, weigh it and calculate its silver content by means of the factor 0.7526.

If the silver content is not to be determined, discard the ammoniacal solution containing the silver. No significant losses of noble metals have been observed by discarding this solution, unless the original silver chloride was extremely highly colored. To recover the small amount of noble metals which contaminated the silver chloride, the method described by Gilchrist may be used. After the silver has been reprecipitated and filtered from the

ammoniacal solution by acidifying it with nitric acid, the filtrate is evaporated and the ammino compounds are destroyed by treatment with hydrochloric and nitric acids. A few mililiters of sulfuric acid are added and the solution heated until fumes of sulfuric acid are given off. Any metallic residue is dissolved by aqua regia. The solution is diluted with 50 to 100 milliliters of water, then filtered to remove silica before adding the solution to the main filtrate containing the rest of the alloy in solution.

Precipitation of Gold. After heating the filtrate from the silver chloride precipitation to approximately 80°C. (176°F.) on the steam bath, increase its pH to between 1.5 and 2.0 by means of a concentrated sodium hydroxide solution. Add 10 milliliters of 10 per cent filtered sodium nitrite solution to precipitate the gold and again heat the solution on the steam bath to coagulate the precipitate. Coagulation usually occurs in less than 15 minutes. Increase the pH to 3.0 by adding either concentrated or 10 per cent sodium hydroxide solution and add 5 milliliters more of the filtered sodium nitrite solution to insure complete precipitation of the gold. Heat the solution again for 1/2 hour on the steam bath.

Filter through a 9-centimeter filter paper of close texture, leaving the bulk of the gold in the beaker. Wash the stirring rod, beaker, gold and filter paper at least 10 times with hot distilled water. Reserve the filtrate and washings for the precipitation of platinum metals.

Next, wash the gold and original beaker 5 times with hot diluted hydrochloric acid (1 + 9). Transfer the gold to the filter and wash it thoroughly with hot distilled water.

If it is desirable to determine the gold separately, place the filter paper and its contents in a porcelain crucible. Char and ignite the filter slowly. Finally, ignite the gold at red heat in air for at least 1/2 hour, cool it and weigh it as metal.

If the total noble metal content is to be determined, place the filter and its contents in the crucible in which the insoluble residue obtained from redissolving the silver chloride was placed. Slowly char and ignite the filter. Reserve this crucible and its contents for the addition of the precipitate of platinum metals.

Removal of Base Metals. To the hot filtrate and washings reserved from the gold precipitation, add 10 grams of sodium chloride and 5 milliliters of filtered 10 per cent sodium nitrite solution. The large amount of sodium chloride helps to keep the palladium nitrite complex in solution when palladium is present in large amounts. The sodium chloride may be added as the solid salt or as a solution. Adjust the pH to 5 with 10 per cent sodium hydroxide solution. Then adjust the pH to 7.5 ± 0.1 with 10 per cent sodium carbonate solution to completely precipitate the base metals. Heat the solution for 2 hours on the steam bath. Readjust its pH to 7.5 ± 0.1, if necessary, at the end of the first hour of heating by adding more 10 per cent sodium carbonate solution.

Filter the solution through a 9-centimeter paper of close texture and wash the precipitate of base metal at least 10 times with hot distilled water. Reserve the filtrate and washings for the determination of the platinum metals.

Dissolve the base metals by means of several washings with hot diluted hydrochloric acid (1 + 9) and again wash the filter thoroughly with hot water. Dilute these washings with distilled water to a volume of 150 milliliters. Cool the resulting solution to room temperature and add 10 milliliters of 1 per cent alcoholic dimethylglyoxime solution to precipitate any traces of palladium. Set the solution aside for 2 hours. If a yellow precipitate has formed, filter the solution through a filter paper of close texture and wash the filter and precipitate thoroughly with distilled water at room temperature. Discard the filtrate and washings.

If palladium was present, slowly char and ignite the filter and precipitate in the crucible reserved for the determination of the noble metals.

Precipitation of Platinum Metals. Add 35 milliliters of diluted sulfuric acid (1 + 1) to the filtrate from the precipitation of the base metals and evaporate the resulting solution to dryness on the steam bath. Allow the residue to cool and add 6 milliliters of sulfuric acid. Heat the beaker and its contents gently by swirling it over an open flame until liquefaction occurs and boiling has stopped. Then heat it more strongly until the white

fumes of sulfuric acid are formed. Allow it to cool and wash down the sides of the beaker with distilled water. Reheat the solution, boil it gently, and then heat it strongly to produce fumes of sulfuric acid. Cool the resulting salt cake, add 200 milliliters of diluted hydrochloric acid (1 + 99), and dissolve the salts by heating on the steam bath. Filter the solution to remove silica derived from the glass during the fuming operation.

Adjust the acidity of the hot solution with concentrated and, finally, with 10 per cent sodium hydroxide solution to a pH of 4. Then raise the pH to 5.0 with a 10 per cent sodium carbonate solution. Add 10 milliliters of 25 per cent sodium formate solution to precipitate the platinum metals. Place the solution on a steam bath for several hours or overnight to coagulate the precipitate.

Filter the hot solution containing the coagulate precipitate through a filter of close texture and wash the precipitate at least 10 times with a 1 per cent ammonium formate solution (pH = 8.5) at room temperature.

Place the filter and its contents in the crucible reserved for the determination of the noble metals. Slowly char and ignite the filter and precipitate in air. Finally, ignite the residue in hydrogen, cool it in carbon dioxide and weigh it as metal.

To obtain as correct a value as possible for the amount of the noble metals, it is necessary to take into account the small amount of impurities introduced through the reagents and analytical operations. Therefore, blank determinations should be made and the

foregoing weight of metal corrected.

6. RESULTS

The results obtained when known mixtures of silver, gold, palladium, platinum and copper were handled by the foregoing procedure age given in Table 1. The determination of the noble metal content is found to be accurate within 0.1 per cent.

7. DISCUSSION OF THE PROCEDURE

When copper was used to represent the base metals, there was no apparent interference.

The precipitation of gold by sodium nitrite was found to be quantitative at pH 3.0.

The optimum pH for rapid and complete precipitation of the platinum metals was found to be between 5 and 6. When precipitation occurred at a pH of 5 and the solution was heated, the pH gradually increased to about 8.5 and coagulation occurred. If the pH remained less than 7, little or no coagulation resulted. If, on the other hand, the original pH was greater than 8, the precipitation was inhibited. At a pH of 10, precipitation was delayed for several hours.

The progress of coagulation of the platinum metals could be followed by stirring the solution and observing its appearance. Immediately after precipitation the solution was black and opaque. When coagulation of the precipitate began, some of the opacity of the solution was lost. The solution gradually became more transparent and had a bluish tinge when the coagulation of the

precipitate was nearly completed. Finally, the solution became clear and colorless.

It was necessary to wash the precipitate of the platinum metals with an ammonium formate solution adjusted to pH 8.5 to prevent the formation of a colloidal suspension. This wash solution was completely volatile. Since the platinum metals had already been precipitated completely, no trouble was encountered from complexing by the ammonium ion. The presence of formate resulted in a reducing solution and the ammonium ion adjusted the pH to that of the filtered solution. This wash solution of ammonium formate solved many of the problems encountered in washing the platinum precipitate free of sodium salts. Washing with dilute formic acid was useless because the precipitate would often be washed through the filter paper.

The need of a reagent blank was readily understood when one realized that about 40 grams of sodium salts were present in the solution when the platinum metals were precipitated. A spectrochemical analysis of the precipitate from the reagents indicated that nickel, aluminum, silicon and iron were the major constituents.

8. CONCLUSION

A procedure for determining the noble metal content (gold and platinum metals) of dental gold alloys is described. In this procedure silver, gold and platinum metals content may be determined separately if desired. This method for noble metal content is considered to be accurate to within 0.1 per cent.

REFERENCE

1. Gilchrist, R. New Procedure for the Analysis of Dental Gold Alloys. J. Research NBS 20:745 June 1938.

Table 1

Analysis of Mixtures of Typical Components Occurring in Dental Gold Alloys

Sample Number	Silver		Gold		Palladium	Platinum	Total Platinum Metals		Copper	Noble Metals	
	Original	Recovered	Original	Recovered	Original	Original	Original	Recovered	Original	Original	Recovered
	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg	mg
1	47.8	47.8	426.2	426.2	---	---	---	---	26.2	426.2	426.2
2	60.8	60.8	400.4	400.4	15.6	---	15.6	15.4	25.2	416.0	415.8
3	51.9	51.8	250.3	250.4	125.1	---	125.1	125.1	75.4	375.4	375.5
4	61.3	61.3	376.8	376.8	---	17.0	17.0	16.9	50.5	393.8	393.7
5	50.0	49.9	250.9	250.9	---	125.7	125.7	125.6	75.7	376.6	376.5
6	50.8	50.6	300.3	300.4	35.4	65.7	101.1	101.0	50.6	401.4	401.4

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