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NEW PROCEDURE FOR THE ANALYSIS OF DENTAL GOLD ALLOYS[1]

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ABSTRACT

From a study of conditions under which certain base metals known to be associated with native grain platinum could be collectively separated from the platinum metals and gold, a new procedure has been developed for analyzing dental gold alloys which differs essentially from that published by W. H. Swanger in 1926.

The procedure as applied to dental gold alloys provides for the separation and gravimetric determination of silver, iridium, tin, gold, indium, copper, zinc, nickel, palladium, rhodium, and platinum. Briefly it is as follows: Silver chloride and metallic iridium are precipitated when the alloy is decomposed by aqua regia. Tin is next separated by a new technic of controlled hydrolysis. Gold is then precipitated by sodium nitrite, and next, by adjusting the alkalinity with sodium hydroxide to the end point of thymolphthalein, indium, copper, zinc, and nickel are collectively separated from rhodium and platinum. At this alkalinity a small proportion of palladium precipitates with the base metals but is recovered from them with dimethylglyoxime. Palladium, rhodium, and platinum are separated from one another by the usual methods of this laboratory. The four base metals are separated, in order, by precipitating indium with ammonium hydroxide, copper, and subsequently zinc, with hydrogen sulfide, and nickel with dimethylglyoxime.

It was found that manganese, iron, cobalt, and chromium are also quantitatively precipitated in a solution containing nitrite at the end point of thymolphthalein, and that it is possible to separate lead from palladium and platinum at the end point of xylenol blue, if the lead is precipitated as carbonate.

Suggestions are made for using the procedure as a refining method for crude material containing gold and the platinum metals.

CONTENTS

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 94th Meeting of the American Chemical Society, held in Rochester, N. Y., September 6 to 10, 1937.

I. INTRODUCTION

Although the primary object of the experiments herein described was the investigation of conditions under which certain base metals known to be associated with native grain platinum could be collectively separated from the platinum metals and gold, the scope of this paper has been restricted to the detailed consideration of those base metals and precious metals which are found in dental gold alloys. Modern dental gold alloys always contain silver, gold, and copper; frequently contain palladium, platinum, tin, and zinc; and occasionally contain iridium, rhodium, nickel, and indium. Indium [2] has been introduced into dental gold alloys recently. In addition, magnesium, aluminum, manganese, and iron have been found in rare instances.

With the exception of indium and zinc, the base metals which have been mentioned, as well as cobalt and chromium, are encountered in the analysis of native grain platinum. Native platinum also contains the two additional platinum metals, osmium and ruthenium.

While the recommended procedure is designed specifically for the analysis of dental gold alloys, it is likewise applicable to native platinum, because, under the conditions specified for the quantitative collective precipitation of indium, copper, zinc, and nickel, the additional metals iron, cobalt, manganese, and chromium are also completely precipitated.

Nearly 12 years have elapsed since Swanger,[3] at the National Bureau of Standards, published the only existing method for the complete analysis of dental gold alloys. Although his method is still reliable, certain analytical improvements in handling some of the constituent elements, and the addition of the rare metal indium to such alloys, make a revision of the analytical scheme desirable. The new procedure differs essentially from that of Swanger, but it necessarily retains certain features of his method. The two procedures are identical up to the point where tin is separated. Swanger's directions are likewise followed for the recovery of palladium and of nickel by dimethylglyoxime and of zinc by hydrogen sulfide. For the determi-

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[2] N. O. Taylor, U. S. Patents 1,987,451 and 1,987,452, January 8, 1935.

[3] W. H. Swanger, *Analysis of dental gold alloys*, BS Sci. Pap. **21**, 209 (1926) S532.

nation of aluminum, iron, manganese, and magnesium, Swanger's procedure is also recommended.

The chief feature of the new method is the collective separation of indium, copper, zinc, and nickel from platinum, palladium, and rhodium by precipitation with sodium nitrite and sodium hydroxide at the end point of thymolphthalein. Another essential feature is the precipitation of gold by sodium nitrite.[4] A third is an improved procedure for the hydrolytic precipitation of tin. It is to be noted that the procedure provides for the separation and determination of indium, and also that it is so designed that a preliminary qualitative analysis of the alloy is unnecessary.

1. THE METHOD OF SWANGER

The essential features of Swanger's method are as follows: The alloy is attacked by diluted aqua regia, which leaves silver chloride as an insoluble residue. If iridium is contained in the alloy, it separates in metallic form and is found with the silver chloride. If the alloy contains much platinum and palladium, the silver chloride will also be contaminated by these two metals, and, if the iridium content is over 0.2 to 0.3 percent, the metallic iridium may be contaminated by a significant amount of platinum. If platinum metals occur in the alloy, it is necessary to dissolve the silver chloride deposit in ammonium hydroxide and to reprecipitate it by adding nitric acid. In this operation the iridium is isolated and can be caught and determined. If the iridium contains a significant amount of platinum, it can be refined by fusion with lead.[5] The small amount of platinum and palladium, recovered from the reprecipitation of the silver chloride, is added to the original filtrate from the removal of silver chloride, after suitable treatment to convert these metals again to chloro-acids.

When the alloy contains tin, it is removed at this stage by the action of sodium acetate. It is usually necessary to refine the stannic acid so obtained by a reprecipitation with ammonium acetate from a solution of its sulfate in sulfuric acid.

Before proceeding with the separation of gold, it is necessary to eliminate the acetate which has been added, because of its interference in subsequent analytical operations. Swanger recommended that this be done by heating the evaporated solution with sulfuric acid until fumes of this acid are evolved. It has been the writer's experience that as much as 2 percent of the gold may be lost in this treatment, presumably through volatilization as gold chloride. Ten or more years of experience with Swanger's method have shown that this is the only apparent defect in the procedure, and is encountered only under the circumstances mentioned. The elimination of acetic acid could probably be accomplished at the temperature of the steam bath with no loss of gold.

Gold is precipitated as metal by sulfur dioxide, and must be reprecipitated by oxalic acid if the alloy contains platinum or palladium, since these two metals contaminate the first gold precipitate. Palladium is next separated, after suitable preparation of the filtrates from the gold precipitations, by means of dimethylglyoxime; but it must be reprecipitated to insure freedom from contamination by platinum.

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[4] E. Leidié, Compt. rend. **131**, 888 (1900). Leidié, in a note presented to the French Academy of Sciences, suggested a scheme for separating gold and the base metals from the platinum metals in native platinum by means of sodium nitrite and sodium carbonate. His paper, however, contains only general directions of procedure and no experimental data.

[5] R. Gilchrist, J. Am. Chem. Soc. **45**, 2820 (1923); BS Sci. Pap. **19**, 325 (1924) S483.

After destruction of residual dimethylglyoxime, copper is precipitated by ammonium thiocyanate from a solution saturated with sulfur dioxide and having a definite acidity. When palladium is absent, copper can be precipitated directly after removing the gold. Platinum contaminates the normally white cuprous thiocyanate so that again a reprecipitation is necessary, if accurate results are desired.

After the removal of copper, the metals remaining are platinum, rhodium, nickel, zinc, (manganese, and magnesium). Platinum and rhodium are precipitated together by hydrogen sulfide and later separated from each other by the hydrolytic method of Wichers,[6] which consists in precipitating the rhodium by means of a suspension of barium carbonate. Nickel, zinc, and manganese are recovered by conventional methods. In the case of magnesium and of iron, neither of which is often encountered in dental alloys, Swanger recommends starting with a fresh sample and removing interfering elements with hydrogen sulfide, before proceeding with their determination.

II. PROCEDURE RECOMMENDED FOR THE ANALYSIS OF A DENTAL GOLD ALLOY

The new procedure provides for the separation and gravimetric determination of silver, iridium, tin, gold, copper, zinc, nickel, palladium, rhodium, and platinum, as does Swanger's procedure, and of indium as well. The order of the various steps is such that a prior qualitative analysis will usually not be necessary because proving the presence or absence of a particular metal, with the exception of indium, involves no delay or change in the orderly procedure.

The procedure as written is designed to yield results of a high degree of accuracy. Whenever results of a lesser degree of accuracy are satisfactory, it will undoubtedly be possible to save time by omitting certain steps, such as some of the double precipitations. An attempt has been made to indicate the magnitude of some of the errors that may result from such a simplification of the procedure, but judgment and experience in the use of the method will be needed to determine how much can be done in this direction.

1. PREPARATION OF THE SAMPLE

Dental gold alloys are usually received for analysis in the form of wires, bands, or plates. To obtain as uniform a sample as possible and to insure complete disintegration of the alloy by acids, it is desirable to roll the specimen to a ribbon or sheet about 0.003 to 0.005 inch in thickness and to cut the rolled specimen into small pieces about one-sixteenth to one-eighth of an inch square. A sample weighing 2 g, composed of the small pieces taken at random, is recommended.

2. THE PROCEDURE

Place 2 g of the prepared sample in a covered 250-ml beaker, add 25 ml of diluted aqua regia,[7] and set on the steam bath. With the exception of silver, which separates as the insoluble chloride, and of

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[6] E. Wichers, J. Am. Chem. Soc. **46**, 1818 (1924).

[7] Throughout this paper, whenever acids are mentioned, hydrochloric acid will mean the concentrated acid of specific gravity 1.18; nitric acid, the concentrated acid of specific gravity 1.42; and sulfuric acid, the concentrated acid of specific gravity 1.84.

Diluted acids will be designated as follows: For example, diluted hydrochloric acid (1+99) will mean 1 volume of the concentrated acid of specific gravity 1.18 diluted with 99 volumes of water.

Diluted aqua regia will mean 4 volumes of hydrochloric acid of specific gravity 1.18 and 1 volume of nitric acid of specific gravity 1.42, diluted with 6 volumes of water.

Ammonium hydroxide will mean the solution of specific gravity 0.90.

iridium, which separates as metal, all the constituents of the alloy will pass into solution.[8] It is advisable to break up the silver chloride, which usually retains the shape of the original metallic pieces, with a glass rod from time to time, to insure complete disintegration. If the solution contains tin, care must be taken that it does not evaporate to dryness.

When decomposition of the alloy is complete, dilute the solution to a volume of 150 to 200 ml, allow it to stand on the steam bath for about 1 hour, and then set it aside to cool.

(a) DETERMINATION OF SILVER

(1) *In the Absence of Platinum Metals.*—If the alloy is known not to contain platinum metals, either by preliminary qualitative analysis or otherwise, collect the silver chloride by filtering through a porcelain filtering crucible,[9] using suction. Wash the precipitate well with water, dry it at 110° C, weigh it, and calculate its silver content, using the theoretical factor 0.7527.

(2) *In the Presence of Platinum Metals.*—Of the platinum metals only iridium separates quantitatively with the silver chloride, but enough palladium and platinum are also retained to discolor the silver chloride and to necessitate its reprecipitation if an accurate determination of silver is wanted, even if iridium is absent.

If the alloy contains platinum metals, catch the silver chloride on a 9-cm filter of close texture[10] and wash it well with water. Reserve the filtrate.

Dissolve the precipitate of silver chloride with two 25-ml portions of hot diluted ammonium hydroxide (1+1). Wash the beaker, rod, and cover, as well as the filter, with hot diluted ammonium hydroxide (1+99), from a wash bottle. This treatment is probably sufficient to effect the complete removal of silver chloride, but it is advisable to digest the filter itself with an additional 25-ml portion of the diluted ammonium hydroxide, which is then filtered to remove paper pulp, and to recover iridium if present. After a final washing of the filter and paper pulp with hot diluted ammonium hydroxide (1+99), the total volume of the filtrate and washings will be about 200 ml.

Acidify the ammoniacal solution with nitric acid to reprecipitate the silver as chloride, allow it to stand until the supernatant liquid is clear (usually overnight), filter through a porcelain filtering crucible, and finish the determination as previously directed.

If the silver chloride has been dissolved in ammonium hydroxide and reprecipitated, because it was contaminated by platinum and

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[8] Small amounts of rhodium enter into dental gold alloys through the use of impure platinum or palladium. Such amounts, usually only a small fraction of 1 percent, are completely dissolved when the alloy is attacked with diluted aqua regia. There appears to be a limit, however, to the amount of rhodium which can be alloyed with gold and subsequently dissolved when the alloy is treated with acids.

If rhodium is added intentionally to the alloy, even within the limit of subsequent complete solubility, sufficient time of melting may not have been allowed for thorough alloying, and, as a result, some rhodium will be found with the deposit of silver chloride.

In the case of iridium there appears to be no limiting range within which this metal will subsequently be dissolved when the dental gold alloy is attacked. The entire amount of iridium will be found with the deposit of silver chloride.

[9] This type of crucible is manufactured by the State Porcelain Works, Berlin, Germany, and is now available in the United States. A crucible of convenient size is one having a height of 40 mm, a diameter at the top of 35 mm, a diameter at the bottom of 23 mm, a capacity of 25 ml, and a porosity designated by the number "2."

A crucible of this kind is much more convenient to use than the customary Gooch crucible with an asbestos pad. This crucible is likewise excellent for catching the glyoxime precipitates of nickel and palladium. It is especially recommended in the filtration of the hydrolytic precipitates of palladium, rhodium, and iridium, in their separation from platinum, since it avoids the introduction of organic matter, which causes interference in subsequent reprecipitation. No doubt, glass crucibles of suitable porosity could be used.

[10] In the experiments reported in this paper, S. & S. No. 589 blue ribbon filters were used. When solutions were filtered to remove paper pulp or traces of silica, a thinner filter, S. & S. No. 590, was used.

palladium, a filtrate will be obtained which contains the traces of these two metals in the form of ammine-compounds. Although this filtrate will contain no tin, it is as convenient at this stage as later to recover the small amounts of platinum and palladium in suitable form and to unite them with the main solution of the alloy. In order to convert the ammine-compounds of these two metals to their chloro-acids, evaporate the filtrate from the second precipitation of silver chloride, destroy the ammonium nitrate which it contains by treatment with hydrochloric and nitric acids, add 5 ml of sulfuric acid, and heat until fumes of sulfuric acid are evolved. Add a few milliliters of nitric acid and then heat the solution until practically all the sulfuric acid is eliminated. Add a few milliliters of diluted aqua regia to dissolve any metallic deposit, and then add, without filtering, the residual solution to the filtrate and washings from the original silver chloride precipitation. The volume of the combined solutions at this stage will be about 300 ml. Reserve for the determination of tin.

(b) DETERMINATION OF IRIDIUM

Ignite in a porcelain crucible the paper and residue obtained from the extraction of the silver chloride with ammonium hydroxide. Ignite the resulting residue in hydrogen, cool it in hydrogen, and weigh it as metallic iridium.

According to Swanger, if the iridium content is greater than about 0.3 percent, the iridium residue may contain a trace of platinum. If the iridium content of the alloy is substantial, and an accurate determination of it is desired, the two metals can be separated from each other by fusion with lead.[11]

(c) DETERMINATION OF TIN

Heat the solution, which was reserved for the determination of tin, to boiling and neutralize it with a freshly prepared solution of sodium hydroxide until its acidity is decreased to about pH 1.5, as ascertained by means of the indicator thymol blue,[12] which changes color from red to orange. Boil the solution for 5 minutes and then set it on the steam bath for 15 to 20 minutes. If no precipitate is obtained, proceed with the precipitation of gold by sodium nitrite.

If a precipitate of stannic acid is obtained, catch it on a 9-cm filter of close texture, which contains some paper pulp. Wash the filter and precipitate thoroughly with hot water which is acidified with sulfuric acid between the limits of pH 4 (end point of bromphenol blue) and pH 1.5. Return the filter with its contents to the beaker in which the precipitation was made, add 5 ml of sulfuric acid, and destroy organic matter by repeatedly adding nitric acid and subsequently heating to the fuming point of the sulfuric acid. A small amount of

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[11] R. Gilchrist, J. Am. Chem. Soc., **45** 2820 (1923); BS Sci. Pap. **19**, 325 (1924) S483.

[12] Thymol blue, which is thymolsulfonphthalein, undergoes two color changes: one, a change from red to orange, which is utilized here in the precipitation of tin; the other, a change from yellow to blue, which is utilized later in the procedure in the collective precipitation of indium, copper, zinc, and nickel.

Since the solutions being neutralized are usually highly colored or contain precipitates, the method which is used throughout the procedure for determining the end point is to allow a drop of a 0.01-percent solution of the indicator to react with a drop of the solution on the end of a stirring rod. This method is not that of the usual "outside indicator." The operation is performed by lifting the stirring rod above the level of the solution and testing the drop which clings to it. The stirring rod is then replaced in the solution with no loss of material. The end point determined in this way is practically identical with that determined by adding the indicator directly to the main body of the solution. The sulfonphthalein indicators enumerated in this paper were prepared by forming their monosodium salts and then diluting to a concentration of 0.01 percent.

gold which invariably contaminates the first precipitate of stannic acid will separate as metal during the fuming operation. If, however, a purplish cloud appears when the solution is diluted in the next operation, the trace of gold has not been properly coagulated, and the solution must be digested again at the fuming point of the sulfuric acid.

Dilute the concentrated acid solution to 50 ml, and, because of the instability of stannic sulfate, keep it cool and filter it immediately through a 7-cm thin paper of close texture. Wash the filter thoroughly with diluted sulfuric acid (1+99), at room temperature. The recovered gold is treated as is described in the section of the procedure dealing with the collective precipitation of gold, indium, copper, zinc, and nickel.

Dilute the solution of stannic sulfate to a final volume of 200 ml and set it on the steam bath for 1 hour, at a temperature of about 85° C. Catch[13] and wash the resulting precipitate as previously directed. It is to be noted that the precipitate of stannic acid obtained under these conditions differs in character from that obtained during the first precipitation, and that it has a tendency to form a slight film on the glass, which is not always readily removable. This may cause an error of about 0.5 mg in the determination of the tin. It is therefore recommended that clean, unetched glassware be used for the precipitation, and, if a film is formed which can not be removed by wiping, that it be dissolved in 5 ml of sulfuric acid in the manner previously described. From this solution it is recommended that the small amount of tin then be precipitated by adding 15 g of ammonium acetate, which produces stannic acid similar in character to that obtained when tin is precipitated from its chlorostannate compound at pH 1.5. The filtrate obtained in this acetate hydrolysis is thereafter rejected.

It was found experimentally that the two precipitations specified, namely, the one at pH 1.5 and the other by diluting the solution of stannic sulfate, sufficed to free tin from contamination by other metals under the conditions which obtain in the analysis of these alloys.

Ignite the precipitate of stannic acid carefully in a porcelain crucible until carbonaceous matter is eliminated, and finally ignite the residue at a temperature between 1,100 and 1,200° C, taking care that the flame of the burner does not envelop the crucible. Weigh the residue, which should be white when cold, as stannic oxide, SnO_2. Calculate its tin content, using the theoretical factor 0.7877.

(d) COLLECTIVE PRECIPITATION OF GOLD, INDIUM, COPPER, ZINC, AND NICKEL

The next operation in the scheme of analysis is to precipitate the gold as metal by the reducing action of sodium nitrite, and then, without removing the gold, to precipitate the base metals indium, copper, zinc, and nickel.

In order to unite with the main solution of the alloy the small amount of gold and other metals which contaminated the stannic acid in its first precipitation, add the paper which was used to filter the stannic sulfate solution, and which contains the small amount of recovered gold, to the evaporated filtrate from the second precipitation

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[13] Here and elsewhere throughout the procedure, except in the case of silver chloride or when palladium or nickel is to be determined as its glyoxime compound, whenever a precipitate is quantitatively transferred to a filter, it is recommended that the beaker be wiped with a small piece of ashless filter paper to insure complete removal.

of the tin. Destroy organic matter in the customary manner by repeated addition of portions of nitric acid, and then eliminate practically all the sulfuric acid contained in it by heating. Digest the residue with a few ml of diluted aqua regia, filter the solution, and add it to the filtrate obtained from the first precipitation of the tin.

Concentrate the combined solutions to a volume of about 150 ml, and neutralize with sodium hydroxide to the red-orange end point of thymol blue (about pH 1.5).[14] Heat the solution to boiling and add to it 10 ml of a filtered 10-percent solution of sodium nitrite. Boil the solution for 2 or 3 minutes to coagulate the precipitated gold but take care that the solution does not bump. Neutralize the solution with sodium hydroxide until its acidity again corresponds to the red-orange end point of thymol blue.

Add 20 ml of the nitrite reagent and then neutralize the hot, constantly stirred solution by adding dropwise a diluted solution of sodium hydroxide until the alkalinity reaches that which corresponds to a faint blue color of thymol blue. Boil the solution for 5 minutes, again taking care that the solution does not bump. On boiling, the alkalinity of the solution will tend to decrease and must be restored to the end point of the indicator. Under the conditions just described, gold, and the base metals, indium, copper, zinc, and nickel, will be quantitatively precipitated. The precipitate formed by copper will have changed color from bluish white to brown, and the collective precipitate will have shrunk considerably in volume.

When the solution, after precipitation of gold, is neutralized with sodium hydroxide, its color changes from green, caused by copper, to colorless or pale yellow, depending upon the absence or presence of platinum metals, and, at the same time, the base metals precipitate as hydroxides. Platinum metals in the solution are rapidly converted by the nitrite from chloro-acids to complex nitrites which are soluble and stable at an alkalinity corresponding to the end point of cresol red or of xylenol blue (about pH 8), at which alkalinity the precipitate of base metals suddenly coagulates and settles well. The complex nitrites are also stable at an alkalinity corresponding to the change of color from yellow to blue of thymol blue, with the exception of that of palladium, which begins to decompose. It is simpler not to remove the precipitate of metallic gold until after the base metals have been quantitatively precipitated. In this way the quantity of alkali salts which accumulate is kept at a minimum.

Allow the precipitate to settle for 15 to 20 minutes, and, before filtering the solution through an 11-cm paper of close texture, wash the filter with a 1-percent solution of sodium nitrite neutral to the blue end point of thymol blue. Transfer the base metal precipitate to the filter, but preferably allow the bulk of the gold to remain in the beaker. Wash the beaker, the gold precipitate, and the precipitate on the filter with about 100 ml of the same wash solution. Use the wash solution at room temperature. Reserve the nitrite filtrate and washings, which contain the platinum metals.

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[14] At the acidity designated the solution will be clear. If the solution is neutralized further, before the addition of sodium nitrite, platinum metals are liable to precipitate as hydroxides. In order to insure complete conversion of the chloro-acids of the platinum metals to soluble complex nitrites, it is recommended that sodium nitrite be added at the acidity corresponding to this end point of thymol blue. At acidities greater than this, the nitrite reagent is rapidly decomposed.

(e) DETERMINATION OF GOLD

Although gold is quantitatively precipitated under the conditions just specified, it was found experimentally, in using the method described to dissolve the base metal precipitate, that a small quantity of it appeared on the filter after the base metals had been collectively precipitated a second time and again dissolved. Unless the small amount of gold is recovered, the determination of gold may be low by as much as 1.5 mg, but usually by not more than 0.5 mg.

Wash the gold deposit and the filter containing the base metal precipitate thoroughly with hot water, to remove residual nitrite solution. If residual nitrite is not removed, it reacts with the hot acid in the subsequent operation and causes the gold to dissolve partially. Dissolve the base metal precipitate off the filter with hot diluted hydrochloric acid. For this purpose, use alternately diluted hydrochloric acid (1+99) and acid of greater strength, such as (1+10) or (1+5). Transfer the gold precipitate from its beaker, rinse this beaker with diluted hydrochloric acid to remove any adhering base metal precipitate, and wash the filter, which now contains the gold, first with hot diluted acid and finally with hot water. Place the filter with its contents in a porcelain crucible.

To insure freedom from traces of platinum and rhodium, as well as to recover a small quantity of gold, the base metals, indium, copper, zinc, and nickel, should be collectively precipitated a second time. It is to be noted that palladium will not be completely eliminated at the alkalinity specified because its complex nitrite begins to decompose. That amount of palladium which persists in contaminating the base metal precipitate is subsequently removed by means of dimethylglyoxime. To make the second precipitation, evaporate to a moist residue the solution obtained when the base metal precipitate was dissolved in hydrochloric acid.

Dissolve the residue in 150 ml of water and make sure that the acidity of the resulting solution does not exceed pH 1.5. Heat the solution to boiling, add 20 ml of the nitrite reagent, and proceed with the precipitation of the base metals as previously described. Wash and redissolve the base metal precipitate as previously directed. If a trace of gold accompanied the solution of the first base metal precipitate, it will appear at this stage as a dark stain on the filter.

Combine this filter with that previously obtained, which contains the bulk of the gold, ignite them at about 900° C, and weigh the residue as metallic gold.

Combine the nitrite filtrate with that obtained in the first precipitation and reserve the solution for the separation of the platinum metals from one another.

(f) RECOVERY OF PALLADIUM FROM THE BASE METALS

Before proceeding with the isolation of indium, it is necessary to remove a small but significant amount of palladium from the solution containing the base metals. To do this, first eliminate the excess of acid from the solution containing indium, copper, zinc, and nickel by evaporating to a moist residue; then add 5 ml of hydrochloric acid and dilute to a volume of 200 ml. Precipitate the palladium at room temperature by adding 10 ml of a 1-percent alcoholic solution of dimethylglyoxime. Allow the solution to stand for at least 1 hour and then filter it through a small filter of close texture. Wash the filter and precipitate first with diluted hydrochloric acid (1+99) and then with water, the temperatures of which should not exceed that of the steam bath (about 85° C).

Reserve the filter and palladium precipitate until the main portion of palladium is recovered from the nitrite filtrates.

(g) DETERMINATION OF INDIUM

Evaporate to a moist residue the solution containing indium, copper, zinc, and nickel, from which a small amount of palladium has been removed by dimethylglyoxime. Destroy residual glyoxime reagent by repeated addition of nitric acid and subsequent evaporation, so that no nickel will precipitate when the solution is later made ammoniacal. Finally, evaporate the solution twice with hydrochloric acid, add about 1 g of ammonium chloride, and dilute to 200 ml.

Warm the solution, and add ammonium hydroxide until all the copper hydroxide which precipitates redissolves. Digest the solution, filter it through a 9-cm paper, and wash the filter and precipitate with a hot 1-percent solution of ammonium chloride, which is faintly ammoniacal. Remove and reserve the filtrate and washings.

Dissolve the precipitate of indium hydroxide from the filter by washing it with hot diluted hydrochloric acid. It is best to use first diluted hydrochloric acid (1+10), and then to wash thoroughly with diluted acid of the concentration of (1+99). Dilute the solution of indium chloride to 200 ml and repeat the precipitation of indium hydroxide, to eliminate copper, zinc, and nickel completely. Combine the filtrate obtained with that previously reserved, which contains copper, zinc, and nickel.

It is to be noted that obtaining a precipitate with ammonium hydroxide does not prove the presence of indium, because aluminum and iron precipitate under the same conditions. The identity of indium is established by its subsequent precipitation as a yellow sulfide, under conditions which prevent the precipitation of aluminum and iron.

Again dissolve with hot acid, as before, the precipitate obtained by the second treatment with ammonium hydroxide, add 5 ml of sulfuric acid, evaporate on the steam bath, add a few millimeters of nitric acid, and then heat the solution until fumes of sulfuric acid are evolved. Dilute the resulting solution of indium sulfate to 50 ml, neutralize it with ammonium hydroxide to the end point of methyl red, added directly to the solution, and then add 2 ml of diluted sulfuric acid (1+17). Dilute the solution to a final volume of 150 ml. The desired acidity to be established for the precipitation is approximately 0.02 *N*.

Pass hydrogen sulfide into the solution at room temperature for 1 hour. Allow the solution to stand until the precipitate settles, then filter it through a 9-cm paper of close texture and wash with water containing 1 ml of diluted sulfuric acid (1+17) in a volume of 150 ml (0.01 *N*), at room temperature. Ignite the filter and precipitate carefully at first and finally at a temperature not above 1,000° C. Weigh the residue as indic oxide, In_2O_3, and calculate its metallic content, using the theoretical factor 0.8270.

(h) DETERMINATION OF COPPER

If the alloy contains no indium, add 10 ml of sulfuric acid[15] to the solution containing the copper, zinc, and nickel, and residual glyoxime if palladium had to be removed. Heat the solution until fumes of sulfuric acid are evolved, and destroy organic matter by means of nitric acid, in the usual way.

If the alloy contained indium, concentrate by evaporation to about 50 ml the combined filtrates and washings from the precipitation of indium as hydroxide. Cautiously add nitric acid to the covered beaker to destroy the accumulated mass of ammonium chloride, and then evaporate to dryness. Dissolve the residue in 20 ml of water, add 10 ml of sulfuric acid, and heat the solution until fumes of sulfuric acid are evolved.

In either instance dilute the solution to 100 ml and filter it to remove traces of silica.

Dilute the solution to a final volume of 400 ml, heat it to the temperature of the steam bath (about 85° C), and precipitate the copper by passing in a stream of hydrogen sulfide for 30 minutes. Filter the solution immediately through an 11-cm paper of close texture and wash the filter and precipitate thoroughly, at room temperature, with diluted sulfuric acid (1+300) which is saturated with hydrogen sulfide.

Dry the filter and precipitate and ignite them carefully in a porcelain crucible. Too rapid ignition causes the sulfide to melt, with danger of mechanical loss by spattering. If, however, the initial heating is done very slowly, the sulfide is converted to oxide without melting. Wipe down the walls of the crucible with a piece of moistened ashless filter paper, and then ignite the residue in air and finally in hydrogen. Cool the reduced metal in hydrogen and weigh it as metallic copper.[16]

(i) DETERMINATION OF ZINC

Evaporate the filtrate and washings from the precipitation of copper as sulfide, add a few milliliters of nitric acid, and heat until fumes of sulfuric acid are copiously evolved. Dilute the solution to 50 ml, neutralize the acid in it with ammonium hydroxide to the end point of methyl red, as was done in the case of indium, add 1 ml of diluted sulfuric acid (1+17), and dilute to a final volume of 150 ml. The desired acidity to be established for the precipitation is 0.01 *N*. Precipitate the zinc by passing hydrogen sulfide into the solution for 1 hour, at room temperature.

Allow the solution to stand for about 2 hours and then filter it through a 9-cm paper of close texture, which contains some paper pulp. Wash the filter and white precipitate of zinc sulfide with a filtered 1-percent solution of ammonium sulfate, at room temperature. Dry the filter and precipitate and ignite them carefully in a porcelain crucible. Burn out carbonaceous matter at as low a tem-

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[15] 5 ml of sulfuric acid is sufficient to cover the bottom of a 600-ml beaker, if the bottom of the beaker is flat. Often, however, the bottom of the beaker is not flat and its center becomes dry during the fuming operation. Furthermore, if the accumulated mass of ammonium salts resulting from the removal of indium has not been completely decomposed, the solution may not contain enough sulfuric acid to produce fumes of this acid on heating. Since additional acid has no deleterious effect on the subsequent recovery of zinc and of nickel, and since it is desired to effect a clean separation of copper from zinc in one operation, 10 ml of sulfuric acid is recommended, with precipitation from a volume of 400 ml.

[16] For a discussion of the advantages of this method of determining copper over that in which copper is electrodeposited, see p. 767.

perature as possible, and finally ignite at a temperature between 950 and 1,000° C. Weigh the residue as zinc oxide, ZnO, and calculate its metallic content, using the theoretical factor 0.8034.

(j) DETERMINATION OF NICKEL

Digest on the steam bath the solution containing the filtrate and washings from the removal of zinc sulfide to eliminate most of the hydrogen sulfide. Destroy residual hydrogen sulfide by adding bromine water. Add 5 ml of a filtered 10-percent solution of tartaric acid,[17] and then make the solution slightly ammoniacal.

Precipitate the nickel by adding a 1-percent solution of dimethylglyoxime in 95-percent ethyl alcohol. Approximately 4 g of the solid reagent is required to precipitate 1 g of nickel. To provide an excess of the reagent and to insure complete precipitation, use 5 ml of the alcoholic solution for each 10 mg of nickel. Digest the solution on the steam bath for 10 to 15 minutes, make certain that the odor of ammonium hydroxide in it can be detected, and filter through a filtering crucible of either porcelain or glass. Wash the precipitate well with warm water. Test the filtrate, before discarding it, for complete precipitation of nickel, by adding more ammonium hydroxide and dimethylglyoxime.

Dry the glyoxime precipitate at 110° C for 1 hour, and weigh it. Calculate its nickel content, using the theoretical factor 0.2032.

(k) SEPARATION OF PALLADIUM, RHODIUM, AND PLATINUM FROM ONE ANOTHER [18]

The nitrite filtrates, obtained in the collective precipitation of gold, indium, copper, zinc, and nickel, will contain all the platinum and rhodium, and also that portion of the palladium which did not precipitate with the base metals. The procedure for the separation of these metals from one another and for their recovery will depend upon which ones are absent. If rhodium is absent, it may be more convenient to separate palladium from platinum by precipitation with dimethylglyoxime and to repeat the glyoxime precipitation once. If either palladium or platinum alone is to be recovered, the procedure becomes further simplified.

(1) *When the Alloy Contains Palladium, Rhodium, and Platinum.*—If the nitrite solution contains the three metals, palladium, rhodium, and platinum, decompose the residual nitrite in it with hydrochloric acid in a covered beaker, and evaporate it to dryness. Platinum will impart a yellow color to the residue of salt; palladium, a reddish brown color. These colors will mask the pale rose color of small amounts of rhodium. Treat the residue with hydrochloric acid, and again evaporate to dryness. Repeat this treatment several times, in order to decompose nitroso-compounds which may interfere with the hydrolytic precipitation of palladium and rhodium, and proceed with the separation of these two metals from platinum.

To do this, add 2 ml of hydrochloric acid, dilute the solution to 300 ml, heat it to boiling, add 20 ml of a filtered 10-percent solution of sodium bromate, and then neutralize the hot solution with sodium hydroxide to the end point of bromcresol purple (about pH 6). Add 10 ml more of the bromate reagent, boil for 5 minutes, and further neutralize the solution, this time to the end point of either cresol red

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[17] Tartaric acid is added to prevent the precipitation of the small quantities of iron which the solution may contain if the separation of indium by ammonium hydroxide has not been made.

[18] R. Gilchrist and E. Wichers, J. Am. Chem. Soc. **57**, 2565 (1935).

or of xylenol blue (about pH 8). Add a third 10-ml portion of the bromate reagent and boil for 15 minutes. Under these conditions palladium and rhodium are collectively precipitated as hydrated dioxides, slightly contaminated with platinum.

Filter the solution by suction, using a porcelain filtering crucible. While this method of filtering is recommended, filter paper may be used, since iridium is absent. If the filtering crucible is used, pour the supernatant liquid through first, then transfer the precipitate. Rinse the beaker and wash the precipitate with a hot 1-percent solution of sodium chloride, neutral to cresol red or to xylenol blue. Place the crucible with the precipitate, and also the glass stirring rod, in the beaker used for the precipitation. It may be necessary to remove a small amount of the precipitate which has crept over the lip of the beaker during filtration. This is conveniently done with moistened crystals of sodium chloride on the finger. Replace the watch glass and add 10 ml of hydrochloric acid, pouring most of it into the crucible. Place the covered beaker on the steam bath. Lift the crucible with the stirring rod, wash it with water, and place it in a 250-ml beaker. Leach the porous bottom of the crucible with two 5-ml portions of hydrochloric acid. Combine the leachings with the main portion of the dissolved precipitate, add 2 g of sodium chloride, and evaporate to dryness. Add 2 ml of hydrochloric acid, dilute the solution to 300 ml, and repeat the precipitation of the hydrated dioxides of palladium and rhodium, to insure complete elimination of platinum. Redissolve the precipitate as previously directed.

The separation of palladium from rhodium is accomplished by a single precipitation with dimethylglyoxime. The procedures for the recovery of these three platinum metals are given in the respective sections dealing with their determination.

(2) *When the Alloy Contains Only Palladium and Platinum.*—If the nitrite solution contains only palladium and platinum, decompose the residual nitrite in it as previously directed. Add 10 to 15 ml of hydrochloric acid, dilute the solution to 400 ml, and, after the sodium salts are dissolved, cool the solution to room temperature.

Precipitate the palladium by adding a 1-percent solution of dimethylglyoxime in 95-percent ethyl alcohol. Approximately 2.3 g of the solid reagent is required to precipitate 1 g of palladium. To provide an excess of the reagent and to insure complete precipitation, use 25 ml of the alcoholic solution for each 100 mg of palladium. Allow the solution to stand at room temperature for at least 1 hour and then filter it on an 11-cm paper of close texture. Wash the precipitate and filter with warm diluted hydrochloric acid (1+99). Test the filtrate with additional glyoxime to make certain that a sufficient amount of reagent had been added.

Return the filter with its yellow glyoxime precipitate to the beaker in which the precipitation was made, or, preferably, place it in a 500-ml Erlenmeyer flask which is closed by a short-stemmed funnel. Add 10 ml of sulphuric acid and destroy organic matter by repeated additions of nitric acid, in the usual way. Finally, heat the solution until fumes of sulfuric acid are evolved.

Cool the concentrated acid solution, dilute it with 10 ml of water, and add 5 ml of diluted aqua regia. Warm the resulting mixture to dissolve any platinum which may have separated during the fuming operation, then dilute it to 100 ml and digest it on the steam bath to effect complete solution of any anhydrous palladium salt. Filter the solution through a thin paper of close texture, to remove silica, and wash the filter with hot diluted hydrochloric acid (1+99). Dilute the solution to a final volume of 400 ml and repeat the precipitation of palladium with dimethylglyoxime, as previously directed.

The manner in which the solution is filtered will depend upon how the palladium is to be determined. In any event, reserve the filtrate and washings for recovery of their platinum content.

(*l*) DETERMINATION OF PALLADIUM

Palladium may be determined either by weighing its glyoxime compound or by igniting its glyoxime compound to metal. The method used depends, to a great extent, upon the quantity of palladium being handled. When the quantity is less than 0.1 g, it may be more convenient to determine the palladium as palladium dimethylglyoxime, but when the quantity exceeds 0.1 g, owing to the difficulty in filtering and washing the precipitate in a filtering crucible, it is preferable to determine it as metal.

If the palladium is to be determined as the glyoxime compound, catch the precipitate in a filtering crucible of either porcelain or glass, wash it first with warm diluted hydrochloric acid (1+99) and finally with warm water. Dry the precipitate at 110° C, weigh it, and calculate its palladium content, using the theoretical factor 0.3167.

If the palladium is to be determined as metal, catch the precipitate on paper, and, after washing, ignite it slowly in a porcelain crucible, first in air and then in hydrogen. Finally, ignite the residue in carbon dioxide for 2 minutes, cool it in an atmosphere of this gas, and weigh it as metallic palladium.

The palladium to be determined will consist of that portion which was recovered from the solution containing indium, copper, zinc, and nickel and the remaining portion which was recovered in the separation of palladium from rhodium and platinum, or from platinum alone.

If the palladium is to be determined as metal, ignite the two filters with their precipitates and finish the determination. If it is desired to determine palladium as its glyoxime compound, it is necessary to redissolve the small quantity of palladium dimethylglyoxime first obtained and to reprecipitate it. For this purpose use 5 ml of sulfuric acid, in the manner previously described, and precipitate the palladium from a volume of 100 ml. Finish the determination as directed.

(m) DETERMINATION OF RHODIUM

If the alloy contains rhodium, the procedure described for the collective separation of palladium and rhodium from platinum should be followed. The filtrate obtained in the subsequent single precipitation of palladium by dimethylglyoxime will contain all the rhodium in the alloy.

To recover rhodium, evaporate the filtrate from the precipitation of palladium, destroy with aqua regia the residual glyoxime contained in it, and decompose nitroso-compounds by evaporating with hydrochloric acid. It should be noted that residual glyoxime must be destroyed before attempting to precipitate the rhodium quantitatively with hydrogen sulfide. Add 10 ml of hydrochloric acid, dilute the solution somewhat, filter it, and wash the filter with diluted hydrochloric acid (1+99). Dilute the solution to a final volume of 200 ml, heat it to boiling, and pass in a rapid stream of hydrogen sulfide for 30 minutes. Allow the solution to cool somewhat with the hydrogen sulfide still passing through it, to insure complete precipitation of the rhodium.

Catch the precipitate on a filter and wash with diluted hydrochloric acid (1+99). Ignite the dried filter and precipitate in a porcelain crucible, first in air and then in hydrogen. Allow the residue to cool in hydrogen and weigh it as metallic rhodium.

(n) DETERMINATION OF PLATINUM

All the platinum which the alloy contains will be found in the nitrite filtrates resulting from the collective precipitation of indium, copper, zinc, and nickel. After the removal of palladium and rhodium, it is recovered by precipitation with hydrogen sulfide.

If palladium and rhodium have been collectively separated from platinum by hydrolysis in a solution containing sodium bromate, add 20 ml of hydrochloric acid to each of the filtrates obtained from the precipitation of the dioxides of palladium and rhodium. Carefully warm the solutions until they become quiescent, partially concentrate them, combine them, and then evaporate to dryness. Make certain that all bromate is destroyed, by evaporating with hydrochloric acid. Add 20 ml of hydrochloric acid, dilute the solution to 200 ml, and filter it. Wash the filter with diluted hydrochloric acid (1+99). Finally, dilute the solution to about 400 ml, heat it to boiling, and pass in a rapid stream of hydrogen sulfide for 30 minutes. Allow the solution to cool somewhat with the hydrogen sulfide still passing through it, to insure complete precipitation of the platinum. Filter the solution and wash the precipitate with diluted hydrochloric acid (1+99).

If only palladium has been separated from platinum, by a repeated precipitation with dimethylglyoxime, evaporate the filtrate obtained in the second precipitation of palladium with glyoxime reagent. Destroy organic matter in it by adding nitric acid to the hot solution, and then evaporate until about 2 ml of sulfuric acid remains. Add 10 ml of diluted aqua regia, to redissolve any platinum which separates, and combine the resulting solution, without filtering it, with the filtrate obtained in the first precipitation of palladium with dimethylglyoxime. Evaporate the combined solutions, and destroy the glyoxime which it contains with nitric acid. Finally, repeatedly evaporate the solution with hydrochloric acid until oxides of nitrogen are no longer observed when the dried mass of salt is treated with hydrochloric acid. Dissolve the evaporated salt residue in 100 ml of water, filter the solution, wash the filter with diluted hydrochloric acid (1+99), add 10 ml of hydrochloric acid, and dilute to a final volume of 400 ml. Recover the platinum by precipitation with hydrogen sulfide as previously directed.

Ignite the dried filter and precipitate of platinum sulfide in a porcelain crucible. Leach the metallic residue with diluted hydrochloric acid (1+10), to extract sodium salts, transfer it to a filter, and wash it thoroughly with hot water. Ignite the filter and metal again in air, and weigh the residue as metallic platinum.

The metal so obtained will usually contain a small but significant amount of sulfur, the quantity of which ranges from 0.0 to 1.0 mg, with portions of platinum weighing 0.25 g. If the highest accuracy is desired, dissolve in aqua regia the metallic platinum, obtained by ignition of the sulfide. Destroy nitroso-compounds by evaporating with hydrochloric acid, filter the solution into a clean, unetched beaker, and wash the filter with diluted hydrochloric acid (1+99). Dilute the solution to 100 ml, heat it to boiling, and add to it a solution containing 3 g of sodium acetate and 1 ml of formic acid for each 0.25 g of platinum. Boil the resulting solution gently until the precipitated metallic platinum is well coagulated and the supernatant liquid is colorless. Filter the solution and wash the metallic deposit with a hot 1-percent solution of ammonium chloride. Ignite the filter and residue. Leach and wash as previously directed, and ignite again. Weigh the final residue as metallic platinum, which will now be free from sulfur.

(o) DETERMINATION OF MANGANESE, IRON, ALUMINUM, AND MAGNESIUM

Although manganese and iron are quantitatively precipitated under the conditions specified for the collective precipitation of indium, copper, zinc, and nickel, this alkalinity is too great for the complete precipitation of aluminum and probably not great enough for that of magnesium. As these four metals are so rarely encountered in dental gold alloys, provision for their determination has not been made, but tests have shown that their presence in no way interferes in the procedure described. If occasion arises for determining them, it is recommended that a separate portion of the alloy be taken and that those metals which are precipitated by hydrogen sulfide in acid solution first be collectively removed. By operating on the resulting filtrate, the four metals in question can then be separated and determined by conventional methods.

(p) SUGGESTED SIMPLIFICATION OF THE PROCEDURE

The procedure which has just been given was designed to obtain the highest degree of accuracy and to include all the metals likely to be encountered in the analysis of dental gold alloys. In many instances a lower degree of accuracy may suffice for practical purposes, particularly when economy of time is an all-important factor. To meet this requirement, the procedure can be simplified to some extent. First of all, the procedure naturally becomes shortened through the absence of a number of metals in the particular alloy being analyzed. A further shortening can be made by eliminating certain steps, such as those involving reprecipitation.

With modern methods of refining the platinum metals, iridium and rhodium will not occur in most alloys, or will be present only to the extent of a few hundredths of a percent. Unless these two metals are added intentionally, the steps involving their separation and determination may usually be disregarded. At the present time only a few alloys contain indium. Unless the alloy is known to contain indium, the portion of the procedure dealing with its isolation and determination drops out. If indium is present and disregarded, a portion of it will be precipitated with the copper and the remainder of it with the zinc. Nickel is now less frequently added than formerly. Although aluminum made its appearance as an alloying constituent for a short time, its addition to dental gold alloys seems to have been abandoned. Manganese and magnesium have infrequently been found in the alloys, but ordinarily they are not regarded as alloying constituents. Iron is encountered only as an impurity.

The metals most commonly encountered are silver, gold, tin, copper, zinc, palladium, and platinum. Many alloys do not contain both palladium and platinum, and some contain neither. With alloys containing only silver, gold, copper, zinc, and nickel, the procedure is reduced to a very simple form. In the analysis of such an alloy, the procedure can be modified with respect to the end point at which the collective precipitation of base metals is made. If the nitrite filtrate from the collective precipitation is combined with the solution produced by redissolving the base metals, it will not be necessary to neutralize beyond the end point of xylenol blue. The combined solutions will contain all the copper, zinc, and nickel in the alloy.

As previously mentioned, the procedure can be further shortened by the deliberate elimination of steps involving reprecipitation. In this connection, however, it may not be advisable to dispense with the second precipitation of the tin, because of the variable amount of gold which may contaminate the first precipitate. The second precipitation of tin does not involve much time.

If the alloy contains palladium and platinum, time can be saved, at the expense of accuracy, by dispensing with the reprecipitation of the silver as chloride, the reprecipitation of the base metals, and the reprecipitation of palladium in its separation from platinum by dimethylglyoxime. Although no attempt was made to ascertain exactly the effect of eliminating these reprecipitations, a few observations were made during the development of the complete procedure. When 0.1 g of copper was hydrolytically precipitated at the end point of xylenol blue, and thus separated from a similar quantity of either palladium or platinum, the copper precipitate retained not more than 1 mg of the particular platinum metal. At the end point of thymol blue, the alkalinity specified in the procedure, a greater amount of palladium contaminated the collective base metal precipitate, but this was the result of decomposition of the complex nitrite of palladium, and provision for its recovery is made in the procedure.

The principal cause of contamination of the precipitate of palladium dimethylglyoxime by platinum, when these two metals are so separated, is the gradual reduction of quadrivalent platinum to bivalent platinum, which then forms a compound similar to that of palladium. As this reduction is favored by heating the solution, it is recommended that palladium be precipitated at room temperature. Under such conditions the amount of platinum retained probably is not much greater than about 1 mg.

It was found that the amount of gold which dissolved when the collective base metal precipitate was treated with hot diluted hydrochloric acid, as recommended in the procedure, ranged from 0.0 to about 1.5 mg, but usually did not exceed about 0.5 mg.

III. DEVELOPMENT OF THE PROCEDURE AND DISCUSSION OF THE EXPERIMENTS

In the following experiments the copper, zinc, tin, and aluminum used were those metals issued by the National Bureau of Standards as materials with standard melting points. The iron was likewise one of the Bureau's standard samples. The silver was stated to have a purity of at least 99.97 percent, and the gold, refined by the U. S. Assay Office, contained an extremely small amount of copper and silver. The platinum, palladium, and rhodium, prepared at the National Bureau of Standards, were found to be free from impurities, by spectrochemical analysis. Likewise by spectrochemical analysis, the indium was found to contain not more than faint traces of impurities. The nickel used was that obtained from nickel sulfate of reagent quality which had a very low cobalt content.

The results of 33 experiments, performed in the development and testing of the procedure, are compiled in table 1, while additional experimental data are given in the text in connection with the discussion of these experiments.

TABLE 1.—*Results which illustrate the accuracy of the separations involved in the analysis of dental gold alloys*

Experiment	Silver		Tin		Gold		Indium		Copper		Zinc		Nickel		Palladium		Platinum	
	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered
	g	g	g	g	g	g	g	g	g	g	g	g	g	g	g	g	g	g
1	------	------	0.0555	0.0556	------	------	0.0100	0.0100	------	------	------	------	------	------	------	------	------	------
2	------	------	.0525	.0525	------	------	.0100	.0101	------	------	------	------	------	------	------	------	------	------
3	------	------	.0623	.0622	------	------	.0100	.0100	------	------	------	------	------	------	------	------	------	------
4	------	------	------	------	0.1297	0.1298	------	------	------	------	------	------	------	------	------	------	0.1183	0.1183
5	------	------	------	------	.1196	.1196	------	------	------	------	------	------	------	------	------	------	.1129	.1129
6	------	------	------	------	.1175	.1174	------	------	------	------	------	------	------	------	0.1117	0.1116	------	------
7	------	------	------	------	.1158	.1158	------	------	------	------	------	------	------	------	.1141	.1141	------	------
8	------	------	------	------	------	------	------	------	0.1069	0.1068	------	------	------	------	.1092	.1095	------	------
9	------	------	------	------	------	------	------	------	.1048	.1047	------	------	------	------	.1054	.1054	------	------
10	------	------	------	------	------	------	.0100	.0102	.2064	.2064	0.0405	0.0404	0.0201	0.0201	------	------	------	------
11	------	------	------	------	------	------	.0100	.0101	.2036	.2036	.0405	.0404	.0201	.0201	------	------	------	------
12	------	------	------	------	------	------	.0100	.0101	.2024	.2025	.0405	.0405	.0201	.0201	------	------	------	------
13	0.1367	0.1366	.0189	.0185	1.4108	1.4104	.0200	.0203	.2047	------	.0203	------	.0201	.0200	.0893	.0892	.0888	------
14	.1339	.1338	.0208	.0203	1.4026	1.4022	.0200	.0200	.2037	------	.0203	------	.0201	.0200	.0928	.0927	.0926	------
15	.1375	.1373	.0220	.0220	1.4006	1.4004	.0200	.0201	.2022	------	.0203	------	.0201	.0200	.0882	.0882	.0906	------
16	------	------	.0839	.0839	.7023	.7023	------	------	------	------	------	------	------	------	------	------	------	------
17	------	------	.0745	.0744	.6592	.6592	------	------	------	------	------	------	------	------	------	------	------	------
18	------	------	.0750	.0749	.6910	.6911	------	------	------	------	------	------	------	------	------	------	------	------
19	------	------	------	------	------	------	------	------	.2066	.2061	.0200	.0199	.0200	.0200	------	------	------	------
20	------	------	------	------	------	------	------	------	.2002	.1993	.0200	.0199	.0200	.0200	------	------	------	------
21	------	------	------	------	------	------	------	------	.2037	.2026	.0200	.0199	.0200	.0200	------	------	------	------
22	------	------	------	------	------	------	------	------	.2022	.2017	.0200	.0199	------	------	------	------	------	------
23	------	------	------	------	------	------	------	------	.2046	.2042	.0400	.0397	------	------	------	------	------	------
24	------	------	------	------	------	------	------	------	.2017	.2018	.0200	.0199	------	------	------	------	------	------
25	------	------	------	------	------	------	------	------	.2018	.2019	.0400	.0399	------	------	------	------	------	------
26	------	------	------	------	1.6294	1.6295	------	------	.2076	.2078	------	------	------	------	.1246	.1248	------	------
27	------	------	------	------	1.3825	1.3825	------	------	.2005	.2006	------	------	------	------	.1272	.1271	------	------
28	------	------	------	------	------	------	------	------	.2065	.2066	.0200	.0199	------	------	.1073	.1073	------	------
29	------	------	------	------	------	------	------	------	.2062	.2063	.0200	.0199	------	------	.1158	.1157	------	------
30	------	------	------	------	------	------	------	------	.2035	.2037	.0200	.0198	------	------	.1060	.1059	------	------
31	------	------	------	------	1.3980	1.3978	.0202	------	.2011	------	.0200	------	.0200	------	.1006	.1007	.1026	.1027
32	------	------	------	------	1.4202	1.4204	.0202	------	.2006	------	.0200	------	.0200	------	.1035	.1035	.1049	.1050
33	------	------	------	------	1.4138	1.4139	.0202	------	.2058	------	.0200	------	.0200	------	.1045	.1043	.1017	.1018

NOTE.—In experiments 19, 20, 21, 22, and 23 copper was determined electrolytically and the results are low. By treating the electrolyzed solutions with hydrogen sulfide, small black precipitates were recovered. In experiments 19, 20, and 21, after ignition in hydrogen, the residues weighed 0.4, 0.8, and 0.7 mg, respectively. In experiments 22 and 23 the small amount of copper was determined colorimetrically by comparison with known amounts of copper. The quantities found were 0.3 and 0.4 mg, respectively.

1. EXPERIMENTS ON THE SEPARATION AND DETERMINATION OF TIN

To avoid the introduction of acetate into the solution, the subsequent elimination of which may cause loss of gold, and to effect a separation from indium and iron, conditions were investigated for the hydrolytic precipitation of tin by controlling the acidity in other ways. It was found that tin is completely precipitated at an acidity not greater than about pH 1, from a boiling solution containing chlorostannic acid, the form in which tin exists when a dental gold alloy is dissolved in diluted aqua regia. Three experiments were made in which 0.1018, 0.0879, and 0.0782 g of tin, each quantity dissolved in 25 ml of diluted aqua regia, were precipitated by neutralizing with sodium bicarbonate the hot solutions, 150 ml in volume, to an end point established by means of quinaldine red and thymol blue. Quinaldine red changes from colorless to red at about pH 1 and thymol blue changes from red to orange at about pH 1.5. The end point chosen was that acidity at which each indicator was red. The solutions were boiled for 5 minutes, filtered, and the precipitates washed with hot water which was acidified with hydrochloric acid to a range between the end points of bromphenol blue (pH 4) and thymol blue (pH 1.5). The precipitates were ignited to stannic oxide, from which were calculated the quantities of tin 0.1024, 0.0886, and 0.0789 g, respectively. The positive errors may possibly be attributed to the retention of a small amount of sodium chloride. Of primary significance was the fact that no tin was detected in the hydrolytic filtrates.

Because the precipitate of stannic acid so obtained is liable to be slightly contaminated by other metals, a second precipitation is necessary. As a repeated precipitation at pH 1.5 did not appear to be sufficiently effective, conditions were investigated for the hydrolytic precipitation of tin by mere dilution and warming of solutions containing stannic sulfate in sulfuric acid, since the simplest and usual way of dissolving precipitates of stannic acid is by means of hot sulfuric acid. It was found that tin is completely precipitated from such solutions if the quantity of sulfuric acid does not exceed 5 ml in a volume of 100 ml (1.8 N). Three experiments were made in which 0.1054, 0.1087, and 0.1017 g of tin were taken. The solutions, each 200 ml in volume and containing 5 ml of sulfuric acid, were boiled for 5 minutes, then set on the steam bath for about 20 minutes, filtered, and the precipitates washed with hot water containing hydrochloric acid (pH 4 to 1.5). The quantities of tin recovered were 0.1055, 0.1088, and 0.1018 g, respectively, and no tin was detected in the filtrates and washings. The precipitate obtained by hydrolysis of stannic sulfate differs somewhat in character from that obtained by the hydrolysis of chlorostannic acid, and it has a tendency to adhere to the walls of the beaker. To avoid a tendency of the solution to bump when boiled, it is recommended in the final procedure that hydrolysis of the sulfate compound be accomplished by heating at the temperature of the steam bath (about 85° C) for 1 hour. It is further recommended, to avoid the remote possibility of a loss of tin when the precipitate is ignited, that washing be done with hot water acidified with sulfuric acid (pH 4 to 1.5).

The isolation of tin required a knowledge of the behavior of the other metals which were liable to contaminate the precipitate of stannic acid. Indium begins to precipitate as an opalescent colloid at an acidity slightly greater than pH 4, and is completely precipitated between the limits pH 6 (end point of chlorphenol red) and about pH 10 (end point of thymolphthalein). To ascertain whether repeated precipitation of stannic acid from sulfate solution would eliminate indium, three experiments were made in which 0.1044, 0.1171, and 0.1000 g of tin were taken. The quantities of indium taken were 0.0988, 0.1166, and 0.1172 g, respectively. The tin was precipitated four times from a volume of 200 ml, containing 5 ml of sulfuric acid, and the precipitates were washed with hot water acidified with hydrochloric acid (pH 4 to 1.5). The quantities of tin recovered were 0.1045, 0.1177, and 0.0995 g, respectively. The amounts of indium recovered were 0.0994, 0.1165, and 0.1184 g. In these experiments the indium was recovered by precipitation with ammonium hydroxide and the precipitates were washed with a hot 1-percent solution of ammonium chloride neutral to bromcresol purple.

As the indium oxide so obtained is liable to be contaminated, three experiments were made in which 0.1214, 0.0886, and 0.1183 g of indium were taken and subsequently recovered by precipitation with hydrogen sulfide at room temperature. The indium was converted to indium sulfate and precipitated from 150 ml of solution, which was adjusted to an acidity of 0.02 *N* with respect to sulfuric acid. The sulfide precipitates were washed at room temperature with 0.01 *N* sulfuric acid and ignited at a temperature not above 1,000° C. The quantities of indium recovered were 0.1218, 0.0888, and 0.1186 g. In this connection it was of interest to ascertain whether a single precipitation of indium by hydrogen sulfide, according to the recommended procedure, sufficed to separate this metal from small amounts of iron and aluminum. In each experiment 0.0100 g of indium, 0.0045 g of iron, and approximately 4 mg of aluminum were taken. The recovery of aluminum was not attempted. The indium recovered in each instance was 0.0100 g, and the quantities of iron found in the filtrates, determined by titration with potassium permanganate, were 0.0044, 0.0045, and 0.0046 g.

To ascertain whether repeated precipitation of stannic acid from sulfate solution would eliminate iron, a single experiment was made in which 0.1186 g of tin and 0.1121 g of iron were taken. The tin was hydrolytically precipitated four times. The second filtrate contained 6 mg of iron, and the fourth, only a trace. The quantity of tin recovered was 0.1192 g, but the oxide was very slightly discolored. Two such precipitations of tin, in an experiment in which approximately 0.1 g of tin and 0.1 g of copper were taken, sufficed to eliminate copper. Only a very small amount of copper was detected in the second filtrate with potassium ferrocyanide, and no copper was detected in the filtrate obtained by dissolving the second tin precipitate and removing the tin by ammonium hydroxide.

Stannic acid, obtained by precipitation from a chloride solution containing gold, will always be contaminated by gold, and, if ignited, will be discolored. When the precipitate of stannic acid is dissolved in sulfuric acid and the resulting solution gently fumed, however, the gold which was adsorbed by the precipitate separates and agglomerates. If the solution of stannic sulfate is not diluted too much and is not allowed to become hot, it can be filtered and thus freed from gold, as well as from silica. If, on dilution, a purple colloid appears, the solution should again be digested at the fuming temperature of the sulfuric acid, in order to coagulate the colloidal gold.

In the case of a dental gold alloy, two precipitations of the tin, in the amounts usually encountered, were found to be sufficient to free it from contamination, provided the first precipitation is made from a chloride solution at about pH 1.5 and the second by diluting a sulfate solution containing 5 ml of sulfuric acid to a volume of 200 ml. The nine results given in table 1 under the heading "Tin" were obtained by following the recommended procedure. The errors in experiments 13 and 14 were the result of mechanical loss in attempting to recover a trace of gold, before this detail of the procedure was fully established.

2. EXPERIMENTS ON THE SEPARATION OF BASE METALS FROM GOLD AND THE PLATINUM METALS, AND OF THESE METALS FROM ONE ANOTHER

It was found that gold is precipitated as metal in well coagulated form by sodium nitrite from a chloride or aqua regia solution over a considerable range of acidity. At an acidity of pH 4 precipitation of gold did not appear to be quite complete, but at about pH 8, the end point of cresol red or of xylenol blue, it was found to be quantitative.

In experiments 4, 5, 6, and 7, gold was precipitated twice from acid solution, with final neutralization with sodium bicarbonate to the end point of cresol red. Washing was done with a hot 1-percent solution of sodium nitrite neutral to cresol red.

In experiments 8 and 9, copper and palladium were separated from each other under the conditions just described for the separation of gold from palladium and from platinum. Two experiments were also made in which copper was separated from platinum, but the recoveries of copper were low by 0.5 and 0.3 mg, respectively. In these experiments copper was recovered by precipitation as cuprous thiocyanate and ignited to metal. It was observed, in general, that errors up to about 1 mg were to be expected if this method of recovering copper were used. Copper could always be detected in the thiocyanate filtrates. It was found that the amount of palladium or of platinum which contaminated the first precipitate of copper under the conditions of these particular experiments did not exceed 1 mg.

As zinc and nickel likewise appeared to precipitate quantitatively in a solution containing sodium nitrite, it was necessary to provide for the subsequent separation of indium, copper, zinc, and nickel from one another. Experiments 10, 11, and 12 show the results obtained by following that part of the recommended procedure which deals with the separation of these four metals from one another. It was found experimentally that indium must be removed before precipitating copper with hydrogen sulfide. When 0.2 g of copper was precipitated, as directed in the procedure, from a solution also containing 10 mg of indium, the amount of indium which contaminated the precipitate of copper sulfide, and which was subsequently recovered from it, was 6.0 mg. In a similar experiment in which 20 mg of indium was added, the quantity of indium which accompanied the copper was 8.3 mg.

In experiments 13, 14, and 15, it was found that copper and zinc failed to precipitate quantitatively when the collective precipitation of the four base metals was made with sodium bicarbonate at the end point of cresol red. In these particular experiments, however, a considerable quantity of sulfuric acid, obtained from the reprecipitation of the tin, had been neutralized. As the effect of accumulated salts on sulfonphthalein indicators is such that, in general, the true pH of the solution is less than that shown by the indicator, a series of three experiments in which copper, zinc, and nickel were precipitated by sodium bicarbonate, and a series in which they were precipitated by sodium hydroxide, were made. In both series, the quantity of accumulated salt was kept at a minimum. Neutralization was controlled to an end point between those indicated by cresol red and xylenol blue. Xylenol blue changes from yellow to blue just on the alkaline side of the color change of cresol red. Using approximately the same quantities of copper, zinc, and nickel as in experiments 13, 14, and 15, it was found that the errors in the copper determinations were 0.0000, −0.0003, and −0.0001 g in the bicarbonate series, and a trace of copper was detected in the hydrolytic filtrates. In the series with sodium hydroxide the errors were −0.0006, −0.0014, and −0.0011 g, but these were caused by faulty ignition of the copper sulfide precipitates rather than by incomplete precipitation, because no significant amount of copper was detected in the filtrates. In the bicarbonate series the error in each zinc determination was −0.0014 g; in the series with sodium hydroxide the errors were −0.0019, −0.0025, and −0.0009 g. Approximately these quantities of zinc were detected in the filtrates. There was no error in the nickel determination in the experiments using sodium hydroxide, and no significant amount of nickel was detected in the hydrolytic filtrates. In the bicarbonate series errors of as much as −0.0003 g were found and the corresponding filtrates showed a trace of nickel. Additional experiments in which approximately 0.1 g of zinc was precipitated by sodium hydroxide at the cresol red-xylenol blue end point, and only the filtrates investigated, showed definitely that precipitation of zinc was not complete and that quantities of zinc ranging from about 1.5 to 2.5 mg remained in solution.

It was found, however, that copper, zinc, and nickel were completely precipitated if the alkalinity of the solution was increased with sodium hydroxide to that corresponding to the end point of thymolphthalein, an indicator which changes from colorless to blue in the range pH 9.4 to 10.6. Neither copper nor zinc could be detected in the entire evaporated filtrates with either potassium ferrocyanide or potassium mercuric thiocyanate, under the appropriate conditions for such tests. Dimethylglyoxime revealed no nickel.

In experiments 19, 20, and 21, copper, zinc, and nickel were collectively precipitated twice at the end point of thymolphthalein and washed each time with about 100 ml of a 1-percent solution of sodium nitrite neutral to this indicator, at room temperature. It is to be noted that the copper was determined electrolytically and that the results are low. By treating the electrolyzed solutions with hydrogen sulfide, small black precipitates were recovered, which, when ignited, weighed 0.0004, 0.0008, and 0.0007 g, respectively.

Experiments 22, 23, 24, and 25 were accordingly made to compare the method of recovering copper electrolytically with that in which copper is precipitated as sulfide and ignited to metal. In these four experiments copper was first separated from zinc by precipitation with hydrogen sulfide as directed in the recommended procedure. The sulphide precipitates in experiments 24 and 25 were carefully ignited to oxide and reduced to metallic copper, whereas those in experiments 22 and 23 were redissolved and the copper was precipitated electrolytically. A small amount of copper was recovered from the electrolyzed solutions by precipitation with hydrogen sulfide, but determined in this instance colorimetrically with potassium ferrocyanide in acetic acid solution by comparison with known amounts of copper. The amounts found were 0.3 and 0.4 mg, respectively.

To ascertain whether a significant amount of zinc contaminated the precipitates of copper sulfide, under the conditions of separation specified in the recommended procedure, the electrolyzed solutions in experiments 22 and 23, after removal of the small amounts of copper just mentioned, were evaporated until the sulfuric acid which they contained was eliminated. The residues were taken up in 10 ml of water, but the resulting solutions were not filtered. Potassium ferrocyanide produced a turbidity in each about comparable to that of 0.1 mg of zinc.

It was observed that when the base metals were precipitated by either sodium bicarbonate or sodium hydroxide, a sudden coagulation of the precipitate occurred at the cresol red-xylenol blue end point, leaving a clear mother liquor. The copper precipitate was usually bluish white with a slight tendency to darken on boiling. At this alkalinity the complex nitrites of palladium, platinum, rhodium, and iridium are stable and pass into the nitrite filtrates from the hydrolytic precipitates of the base metals, as was found to be true in experiments 4, 5, 6, 7, 8, 9, 13, 14, and 15.

When the precipitation of the base metals is made at the end point of thymolphthalein, however, the nitrite complex of palladium begins to decompose and deposit hydrated palladium oxide, so that palladium is not readily eliminated by repeated precipitation of the base metals but must be recovered from them by precipitation with dimethylglyoxime. It was found that the complex nitrates of platinum and of rhodium are stable at the end point of thymolphthalein and do not contaminate the base metal precipitate.

Some difficulty was encountered in using the indicator thymolphthalein, particularly if the solution contained considerable palladium. The indicator is readily soluble in alcohol, but not in water. In using this indicator a drop of a 1-percent solution of it in ethyl alcohol was added directly to the solution in which the precipitation was being made. The complex nitrite formed by 0.1 g of palladium imparts a rather intense yellow color which interferes with the judging of the end point by producing a green color with the indicator. Because of this the end point may be overrun, with the result that nearly all of the palladium will be precipitated. Furthermore, the character of the base metal precipitate obtained by boiling the solution at the end point of thymolphthalein differs from that obtained at the end point of cresol red-xylenol blue. The increase in alkalinity causes the precipitate to shrink noticeably and changes that formed by copper from blue to brown. The finely divided precipitate settles more slowly and interferes with the detection of the end point.

It was found that thymol blue, which is thymolsulfonphthalein, changes from yellow to blue at practically the same alkalinity as that at which thymolphthalein changes from colorless to blue, under the conditions which obtain in these analyses. As the sulfonphthalein compounds are soluble in water, dilute solutions of their monosodium salts furnish an easier means of establishing a desired pH by using them to test a drop of the solution which clings to the end of a stirring rod.

Experiments 26 to 33, inclusive, were made according to the recommended procedure. In each instance a small amount of palladium was recovered by dimethylglyoxime from the redissolved second precipitate of base metal. An amount of zinc not exceeding about 0.1 mg was detected with potassium ferrocyanide in the evaporated filtrates resulting from the precipitation of the main quantity of palladium in experiments 28, 29, and 30. In experiments 31, 32, and 33 no zinc was detected by hydrogen sulfide in the filtrates resulting from the removal of platinum. In these same experiments palladium was separated from platinum by two precipitations with dimethylglyoxime. In experiments 13, 14, and 15, palladium and platinum were first separated from each other by precipitating the palladium as its hydrated dioxide.

In experiments 13, 14, 15, 26, 27, 31, 32, and 33 the precipitate of base metals was separated from the precipitated gold by means of hot diluted hydrochloric acid, according to the recommended procedure. In this connection, it should be remarked, however, that danger of mechanical loss may result if the base metals have been precipitated as carbonates, because of effervescence. No danger attends the dissolving of a precipitate formed by sodium hydroxide. It was observed that an error ranging from −0.0002 to −0.0017 g, but usually about −0.0005 g, occurred in the determination of gold, and that these small quantities of gold appeared on the filter when the base metal precipitates were redissolved after the second precipitation. In the case of experiments 13, 14, 15, 31, 32, and 33, this small amount of gold was identified by dissolving it and precipitating it with sulfur dioxide. It was finally recovered by digestion with hot sulfuric acid. In experiments 26 and 27 the filter containing the trace of gold was ignited with that containing the bulk of gold, as in the recommended procedure.

The determination of silver offers no particular difficulty. In connection with its determination experiments were made to simplify the recovery of traces of palladium and platinum which contaminate. the original precipitate of silver chloride, and which are converted to ammine-compounds when the silver chloride is dissolved in ammonium hydroxide. In one experiment 0.0146 g of platinum was dissolved in aqua regia; in the other, 0.1164 g of palladium. The solutions were made ammoniacal and boiled to convert these metals to the ammine-form. To each solution was added 5 ml of sulfuric acid and a few milliliters of nitric acid. The solutions were then heated to the fuming point of sulfuric acid for about 30 minutes. The amount of platinum recovered by precipitation with hydrogen sulfide was 0.0148 g. The amount of palladium recovered by precipitation with dimethylglyoxime, and determined as the glyoxime compound, was 0.1159 g. Each filtrate was heated for an additional 30 minutes at the fuming point of sulfuric acid, but the one yielded no precipitate upon further treatment with hydrogen sulfide, and the other, no precipitate with dimethylglyoxime.

IV. EXPERIMENTS ON THE BEHAVIOR OF OTHER BASE METALS

Under the conditions specified in the recommended procedure for the collective precipitation of indium, copper, zinc, and nickel, a number of other metals also appear to precipitate quantitatively. In the following experiments, about 0.1 g of metal was taken and precipitated, from a solution containing nitrite and having a volume of 200 ml, at the blue end point of thymol blue. The time of boiling was 5 minutes, and the quantity of wash solution used was 100 ml of a 1-percent solution of sodium nitrite neutral to the indicator.

Cobalt, which forms a complex nitrite and is only partially precipitated at the end point of cresol red, produced a dirty brown precipitate. The filtrate and washings were separately evaporated to dryness with hydrochloric acid. In a volume of 15 ml, made slightly ammoniacal, hydrogen sulfide produced no precipitate in either instance. In a second experiment in which only the filtrate was investigated, an extremely faint dark precipitate was obtained with hydrogen sulfide, but, when it was dissolved in diluted aqua regia and the resulting solution evaporated to dryness with hydrochloric acid, no cobalt could be detected microchemically with potassium mercuric thiocyanate.

Bivalent manganese was precipitated in one experiment at the end point of thymolphthalein, and, in the other, at the end point of thymol blue. The filtrate and the wash water in the first experiment and the filtrate only in the second experiment were separately evaporated and tested with potassium periodate. Neither filtrate produced a color of permanganate. The wash solution developed a faint pink color which was not as intense as that produced by 0.05 mg of manganese.

Iron and tervalent chromium were likewise found to be quantitatively precipitated at the end point of thymol blue, but at this alkalinity a considerable amount of aluminum remained in solution. Although the behavior of cadmium and of bismuth was not thoroughly investigated, it appeared that neither metal was quite completely precipitated either at the end point of cresol red or of thymol blue.

It was not found possible to precipitate lead completely with sodium hydroxide at any alkalinity. However, a few experiments in which 0.1 g of lead, taken as lead chloride, was precipitated with sodium bicarbonate from a boiling solution containing nitrite, at the end point of xylenol blue, indicated the possibility of separating it from the platinum metals. In experiments in which only lead was taken, no lead was detected in the filtrates resulting from the precipitation with bicarbonate. The filtrates were tested by evaporating them to dryness with hydrochloric acid, diluting to 50 ml, and passing in a stream of hydrogen sulfide for 1 hour.

Three experiments were made in which 0.1123, 0.1089, and 0.1066 g of palladium were respectively separated from 0.1 g of lead by twice precipitating the lead with bicarbonate, in a solution containing nitrite, at the end point of xylenol blue. The precipitate in each instance was washed with about 100 ml of a 1-percent solution of sodium nitrite neutral to the indicator, at room temperature. Palladium was recovered by precipitation with dimethylglyoxime and determined as metal. The recoveries of palladium were 0.1122, 0.1088, and 0.1065 g, respectively. The precipitates of lead carbonate were dissolved in diluted hydrochloric acid, and the resulting solutions were evaporated to dryness. The dry residues of lead chloride were white. They were subsequently dissolved in 100 ml of water containing 2 to 3 ml of hydrochloric acid and tested for palladium with dimethylglyoxime. No palladium was detected.

Four experiments were made in which 0.1126, 0.1041, 0.1142, and 0.1159 g of platinum were likewise respectively separated from 0.1 g of lead. Platinum was recovered by precipitation with hydrogen sulfide and the sulfide ignited to metal for determination. The metal residues were not reprecipitated to eliminate sulfur, and the recoveries were slightly high. The recovered metal weighed 0.1127, 0.1048, 0.1149, and 0.1162 g, respectively. The absence of platinum in the precipitates of lead carbonate was proved by dissolving the precipitates in hydrochloric acid, evaporating the solutions to dryness, and eliminating the lead by precipitating it with potassium iodide, in slight excess. The resulting mother liquors, even when filtered, were colorless.

In the preceding experiments, the metallic residues were not tested for lead. Additional experiments on the separation of lead from the platinum metals are in progress, and a complete report will be made in a subsequent paper.

V. ADAPTATION OF THE PROCEDURE TO THE REFINING OF CRUDE MATERIAL CONTAINING GOLD AND THE PLATINUM METALS

The procedure which has been given for the analysis of a dental gold alloy may be used, with slight modification, for recovering the precious metals in materials of the general type of dental gold scrap.

If it is to be so used, a few suggestions are in order. The procedure should be altered with respect to the conditions for precipitating gold and also for precipitating base metals. It was found experimentally that no gold was precipitated by nitrite in a solution containing 10 percent of concentrated hydrochloric acid by volume. At half of and at quarter of this acid concentration, gold is precipitated as well-coagulated, clean-looking metal which, when washed, is free from impurities. In separating the gold the acidity of the solution should not be allowed to become less than that corresponding to the end point of thymol blue (about pH 1.5). A small amount of gold will remain in solution but it is recoverable when the base metals are subsequently precipitated.

It is recommended that the base metals be precipitated with sodium hydroxide at the end point of xylenol blue (about pH 8), in order that the platinum metals shall pass entirely into the nitrite filtrates.

It is further recommended that platinum be separated from other platinum metals by hydrolytically precipitating the latter as hydrated oxides in a solution containing sodium bromate, at the end point of xylenol blue.

WASHINGTON, March 15, 1938.