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ANALYSIS OF DENTAL AMALGAMS CONTAINING MERCURY, SILVER, GOLD, TIN, COPPER, AND ZINC

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ABSTRACT

The procedure provides for the separation and determination of gold, silver, mercury, tin, copper, and zinc in dental amalgams. The chief feature of the procedure is the simultaneous titration of silver and mercury with thiocyanate. It is this feature which makes the method particularly applicable for the analysis of smaller samples, for example, sections of restorations removed from teeth.

Briefly the method is as follows: The alloy is decomposed with nitric acid and tin is removed from this solution as metastannic acid. If gold is present, it will accompany the tin precipitate and is separated by converting the tin to soluble stannic sulfate. Silver and mercury are collectively titrated with thiocyanate, after which the thiocyanate precipitates are destroyed with nitric and sulfuric acids. The silver is precipitated as the chloride from this solution. The mercury is determined from the thiocyanate titration and the silver determination. Copper and snbsequently zinc are precipitated as sulfides at the proper acidities.

Simplifications of the procedure are presented for use when the composition of the silver alloy is known or when a partial analysis for silver and mercury alone is desired, as is often the case in control work.

CONTENTS

I. INTRODUCTION

The physical properties of dental amalgams depend to a large degree upon the amount of mercury in the hardened alloy. In dental practice, the methods employed for the preparation and insertion of

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amalgam fillings are so variable that it is doubtful whether any two fillings have precisely the same chemical composition, particularly with respect to mercury. Furthermore, some techniques are such that the composition of the amalgam may vary in different sections of the restoration. Such variations may well be responsible for some of the failures encountered in the use of amalgam.

Many techniques have been described in the dental literature for standardizing both amalgamation and methods of packing. Because there has been no convenient chemical method for determining the composition of an amalgam restoration, it has been difficult to study the effect of composition upon its physical properties and the effect of amalgamation and packing techniques upon the composition of the amalgam. Methods in which the composition is determined by weighing the mercury and alloy taken and the mercury removed during packing are rough approximations at best. Certainly no information can be obtained concerning the variations in the distribution of the mercury throughout the alloy by such methods.

It is the purpose of this paper to describe a rapid and convenient procedure for determining the mercury, silver, tin, copper, zinc, and gold in dental amalgams. The chief feature of the method is the simultaneous titration of silver and mercury with thiocyanate after the removal of tin. It is this feature which makes the method particularly applicable for use in the analysis of smaller samples, for example, sections of restorations removed from extracted teeth where nonuniformity in chemical composition is suspected. Methods in which mercury is determined on a separate portion are not applicable for the small samples which are usually available from dental restorations, because of the necessity of crushing, grinding, and using all the available material for one determination.

The procedures described for the separation of tin and gold and the determination of copper are essentially those described by Gilchrist [1],[2] as is also the procedure for determining end points of indicators in colored solution.

II. RECOMMENDED PROCEDURE

1. SOLUTION OF SAMPLE

Place a 0.2- to 0.3-g sample in a 250-ml beaker, add 10 ml of nitric acid (sp gr 1.42), cover and set on the steambath. After the brown fumes disappear and disintegration of the alloy is complete, remove the cover glass and evaporate to incipient dryness. Add 5 ml of freshly boiled nitric acid. Digest 5 minutes on a steambath and dilute with water to 60 ml. Digest 1 hour on a steambath. All the constituents go into solution except tin and gold. Tin will be present as a white precipitate of metastannic acid. Gold, if present, imparts a red or purple color to the precipitate.

2. DETERMINATION OF TIN IN THE ABSENCE OF GOLD

If a precipitate of metastannic acid is obtained by the procedure above, catch it on a 9-cm filter paper 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

[2] Figures in brackets indicate the literature references at the end of this paper.

pH 4 (end point of bromphenol blue) and pH 1.5 (red-yellow end point of thymol blue). Reserve the filtrate and washings for the determination of the remaining constituents. Ignite the precipitate of metastannic acid carefully in a porcelain crucible until carbonaceous matter is eliminated, and finally ignite the residue between 1,100° and 1,200° C, for one-half hour, 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 with the theoretical factor 0.7877.

3. DETERMINATION OF TIN AND OF GOLD

If gold is present, the procedure for the determination of tin must be modified as follows. Return the filter and precipitate of metastannic acid and gold (section II–2) to the beaker in which the tin was precipitated, add 5 ml of sulfuric acid (sp gr 1.84), and destroy organic matter by repeatedly adding nitric acid and subsequently heating to the fuming point of sulfuric acid. The tin precipitate goes into solution, leaving behind the gold, somewhat agglomerated. Cool, dilute the concentrated acid solution to 50 ml with distilled water, and, because of the instability of stannic sulfate, keep it cool and filter immediately through a thin 7-cm paper of close texture. Wash the filter paper and its contents thoroughly with cool diluted sulfuric acid (1+99). The recovered gold is ignited and weighed as metal. Dilute the solution of stannic sulfate to 200 ml and set on a steambath for 1 hour. Catch and wash the resulting precipitate of metastannic acid as described in section II–2. Discard the second filtrate and washings.

4. COMBINED TITRATION OF MERCURY AND SILVER WITH AMMONIUM THIOCYANATE

Transfer the reserved filtrate and washings (a volume of 200 ml or less) from the tin determination obtained in II–2 to a 600-ml beaker; add a 5-percent solution of potassium permanganate dropwise until the solution remains pink for 5 minutes or more. Add small crystals of ferrous sulfate to destroy the excess permanganate. Add 4 ml of a saturated solution of ferric ammonium sulfate which has been decolorized by the addition of nitric acid. Cool the solution to a temperature below 15° C and titrate with a standardized ammonium thiocyanate solution[3] (approximately 0.05 *N*) until a distinct and permanent pink color is obtained. The solution must be stirred vigorously near the end point. This titration represents the total mercury and silver and will be used as a basis for the determination of mercury (section II–6).

5. DETERMINATION OF SILVER

To the solution containing the precipitates of mercury and silver thiocyanates add 10 ml of sulfuric acid (sp gr 1.84) and evaporate to the fuming point of sulfuric acid. Cool, add 5 ml of nitric acid (sp gr 1.42), and again evaporate to the fuming point of sulfuric acid. Repeat this procedure at least two times in order to decompose the

[3] The ammonium thiocyanate solution may be standardized with pure mercury or silver. The mercury or silver should be dissolved as recommended in II-1, diluted to 200 ml, and then titrated as described in II-4.

thiocyanate. Dilute with distilled water to 300 ml and digest on a steambath until the salts are in solution. Filter to remove any silica and add to the filtrate 10 ml of diluted hydrochloric acid (1+9), digest on a steambath until the silver chloride has coagulated, cool to room temperature, and filter through a glass filtering crucible of fine porosity. Wash the beaker and precipitate with cool diluted nitric acid (1+300). Dry the precipitate in an oven at 120° to 130° C for 1 hour. Cool and weigh as silver chloride. Calculate the weight of silver as metal with the factor 0.7526.

6. DETERMINATION OF MERCURY

From the weight of silver determined calculate the milliliters of standard thiocyanate required to react with the silver to form silver thiocyanate (AgCNS). The difference between the total thiocyanate used (section II–4) and that required to precipitate the silver will represent the thiocyanate required to react with the mercury to form mercuric thiocyanate, $Hg(CNS)_2$.

7. DETERMINATION OF COPPER

Transfer the filtrate and washings from the precipitation of silver chloride (section II–5) to a 600-ml beaker and evaporate to the fuming point of sulfuric acid. Cool, wash the sides of the beaker, and again evaporate to the fuming point of sulfuric acid. Cool, dilute with distilled water to 400 ml, and digest on a steambath until the salts are in solution. Filter to remove silica. Heat the solution on a steambath to approximately 85° C, and precipitate the copper and mercury 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 with cool diluted sulfuric acid (1+300) which is saturated with hydrogen sulfide. Dry the filter and precipitate and ignite them carefully in a porcelain crucible in a hood (mercury is volatilized during ignition). Too rapid ignition causes the sulfide to melt, with danger of mechanical loss by spattering. 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.

8. DETERMINATION OF ZINC

The zinc is precipitated as the sulfide from a buffered solution, as described by H. A. Fales [2].

Evaporate the filtrate and washings from the precipitation of copper and mercury to 50 ml or less. Neutralize with diluted ammonium hydroxide (1+1) to the red-yellow end point of thymol blue [4] (about pH 1.5). Add 25 ml of a 20-percent solution of citric acid and neutralize to the yellow-blue end point of bromphenol blue (about pH 4). Add 25 ml of "formic mixture" (200 ml of formic acid, 90 percent; 30 ml of ammonium hydroxide, sp gr 0.90; and 200 g of ammonium sulfate diluted to 1 liter with distilled water) and 20 ml of formic acid

[4] Because the solutions are colored by iron, a procedure recommended by Gilchrist [1] was used for determining the indicator end points. A drop of the indicator (0.01 percent) is permitted to react with a drop of the solution on the end of a stirring rod.

(90 percent). Dilute to 200 ml. Precipitate the zinc by passing in a stream of hydrogen sulfide for 1 hour. Let the solution stand 2 hours and filter through a paper of close texture. Wash the filter and precipitate thoroughly with a diluted formic acid solution (1+250) which is saturated with hydrogen sulfide. Without removing the filter or precipitate from the funnel, dissolve the precipitate by successive washings with hot diluted hydrochloric acid (1+1). Evaporate to 5 ml and dilute to 50 ml. Adjust the acidity, reprecipitate, and wash the precipitate as before. Carefully ignite the precipitate and paper in a porcelain crucible with a final temperature between 950° and 1,000° C for one-half hour. Weigh as zinc oxide and calculate the weight of zinc as metal with the factor 0.8034. Blank runs must be carried through all the steps of this zinc procedure because of the large quantities of reagents used.

III. DISCUSSION OF THE METHOD

1. PREPARATION AND SOLUTION OF THE SAMPLE

If an amalgam restoration which has been in service is to be analyzed, it is essential that surface tarnish and coatings be removed. This can be done by using a fine file or dental burr operated in such a manner as to prevent local heating and loss of mercury.

No loss of mercury will occur through volatilization if the sample is dissolved in nitric acid as recommended. Weighed samples of pure mercury and mercury-silver mixtures were dissolved in nitric acid and evaporated to dryness on a steambath. When the samples were titrated with thiocyanate, the results were correct for both silver and mercury. See experiments 3, 4, 5, 6, and 7 in table 1.

2. INTERFERING ELEMENTS

Chlorides, bromides, or iodides interfere when the thiocyanate titration is made. These elements form precipitates with silver and complex salts with mercury which would give a low titer. Bromides and iodides would also interfere with the silver chloride determination.

Cuprous copper and mercurous mercury interfere with the thiocyanate titration because they form insoluble thiocyanates. They must be oxidized as indicated in the procedure.

Oxides of nitrogen interfere because they decompose the thiocyanate ion. The solution obtained by dissolving the sample in nitric acid is evaporated to dryness for this reason. Freshly boiled nitric acid should be used where indicated.

3. THIOCYANATE END POINT

The color change in the combined titration of silver and mercury with thiocyanate is sharp and can be readily obtained if the solution is maintained below 15° C and is vigorously stirred near the end point. Titration should be continued until a permanent and distinct rose-brown color is observed. A slight straw color is often observed before the end point; this should not be mistaken as the end point. The rose-brown color can best be observed by permitting the precipitate to settle and observing the color through the supernatant liquid.

4. SIMPLIFICATION OF PROCEDURE FOR CONTROL WORK

The foregoing procedure may be simplified and shortened when an approximate analysis is desired. For example, entire specimens or sections of specimens on which physical tests have been made can be weighed and dissolved as described in II–1. The mercury and silver are simultaneously titrated with thiocyanate without removing the metastannic acid precipitate. From this value and a knowledge of the silver content of the original alloy (determined by titrating a weighed sample with thiocyanate), the amount of mercury or silver in the amalgam may be calculated from the following equations.

Equation 4 is used to calculate the amount of silver. This value for silver is used in eq 3 to calculate the mercury.

In the following equations

a=percentage of silver in the silver alloy divided by 100.
b=weight (mg) of sample of amalgam.
Hg=weight (mg) of mercury in the amalgam.
Ag=weight (mg) of silver in the amalgam.
S=weight (mg) of silver alloy in the amalgam.
N=normality of the ammonium thiocyanate solution.
ml=the volume (ml) of thiocyanate used for the titration.

$$\frac{Hg}{100.3}+\frac{Ag}{107.88}=N\,ml \tag{1}$$

$$Hg+Ag+\left(\frac{1-a}{a}\right)Ag=b \tag{2}$$

$$Hg+Ag\left[1+\left(\frac{1-a}{a}\right)\right]=b$$

$$Hg+\frac{Ag}{a}=b$$

$$Hg=b-\frac{Ag}{a} \tag{3}$$

Substituting Hg in eq 1,

$$\frac{b}{100.3}-\frac{Ag}{100.3a}+\frac{Ag}{107.88}=N\,ml$$

$$\frac{Ag}{100.3a}-\frac{Ag}{107.88}=\frac{b}{100.3}-N\,ml$$

$$Ag=\frac{\frac{b}{100.3}-N\,ml}{\frac{1}{100.3a}-\frac{1}{107.88}}=\frac{0.009970\times b-N\,ml}{0.009970\times\frac{1}{a}-0.00927} \tag{4}$$

From eq 2

$$S=Ag+\left(\frac{1-a}{a}\right)Ag=Ag\left[1+\left(\frac{1-a}{a}\right)\right]$$

$$S=\frac{Ag}{a} \tag{5}$$

The weights of tin, copper, zinc, and gold can be calculated if the chemical composition of the silver alloy is known, from the weight of alloy used in the amalgam, as determined by eq 5.

The values from these calculations (eq 3, 4, and 5) will be subject to error caused by the small amount of the alloy removed with the excess mercury during packing. (See Souder and Sweeney [3].)

IV. EXPERIMENTAL RESULTS

The results of 19 experiments, performed in the development and verification of the recommended procedure, are compiled in table 1. Experiments 1 through 7 show the accuracy in titrating weighed portions of pure silver and mercury with ammonium thiocyanate. Experiments 8 through 17 illustrate the accuracy of separations involved in the analysis of dental amalgams. Experiments 18 and 19 demonstrate that mercury and silver may be titrated in the presence of metastannic acid with ammonium thiocyanate.

Table 2 illustrates the accuracy of the calculations used in the modified procedure. The data given for experiments 10 through 17 in table 1 were used for these calculations.

TABLE 1.—*Results illustrating the accuracy of the procedure*

Experiment	Mercury		Silver		Tin		Copper		Zinc	
	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered
	Grams	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*
1	-------	-------	0.1005	0.1004	-------	-------	-------	-------	-------	-------
2	-------	-------	.1192	.1193	-------	-------	-------	-------	-------	-------
3	0.0733	0.0733	-------	-------	-------	-------	-------	-------	-------	-------
4	.2150	.2150	-------	-------	-------	-------	-------	-------	-------	-------
5	.1143	.1140	-------	-------	-------	-------	-------	-------	-------	-------
6	.1146	.1141	.1319	-------	-------	-------	-------	-------	-------	-------
7	.2275	.2272	.0666	-------	-------	-------	-------	-------	-------	-------
8	.0819	.0811	.1321	0.1321	0.0524	0.0524	0.0087	0.0089	-------	-------
9	.0876	.0874	.1304	.1304	.0517	.0516	.0086	.0086	-------	-------
10	.1824	.1822	.0535	.0534	.0208	.0209	.0035	.0035	0.0008	0.0009
11	.1170	.1170	.0348	.0345	.0135	.0138	.0023	.0024	.0005	.0002
12	.0826	.0827	.0567	.0562	.0221	.0224	.0038	.0039	.0008	.0008
13	.1070	.1070	.0727	.0726	.0284	.0283	.0048	.0048	.0011	.0012
14	.0663	.0665	.1073	.1072	.0418	.0412	.0071	.0075	.0016	.0019
15	.0565	.0566	.0900	.0897	.0351	.0348	.0059	.0060	.0013	.0015
16	.0115	.0119	.1495	.1492	.0583	.0587	.0099	.0100	.0022	.0020
17	.0172	.0176	.2215	.2212	.0863	.0866	.0147	.0147	.0032	.0031
18	.1596	.1596	.2211	-------	.0876	-------	.0145	-------	-------	-------
19	.1057	.1056	.2402	-------	.0952	-------	.0158	-------	-------	-------

TABLE 2.—*Calculations illustrating the accuracy of the modified procedure* [1]

[The composition of the silver alloy used in these experiments is: Tin, 26.5 percent; silver, 68.1 percent; copper, 4.5 percent; zinc, 1.0 percent]

Experiment	Sample of amalgam	Volume of ammonium thiocyanate [2] (NH_4CNS)	Silver		Mercury	
			Taken	Calculated	Taken	Calculated
	Milligrams	*Milliliters*	*Milligrams*	*Milligrams*	*Milligrams*	*Milligrams*
1	261.0	46.45	53.5	53.8	182.4	182.0
2	168.1	29.87	34.8	35.2	117.0	116.4
3	166.0	27.08	56.7	57.2	82.6	82.0
4	214.0	34.96	72.7	73.2	107.0	106.5
5	224.1	33.28	107.3	107.4	66.3	66.4
6	188.8	28.04	90.0	90.5	56.5	55.9
7	231.4	30.17	149.5	149.9	11.5	11.3
8	342.9	44.71	221.5	222.0	17.2	16.9

[1] These values were determined on experimental mixes of amalgam from which the excess mercury was not expressed and are, therefore, not subject to the error caused by the removal of small amounts of metal with the mercury normally expressed during packing.

[2] Ammonium thiocyanate (NH_4CNS) = 0.0498 *N*.

V. REFERENCES

[1] R. Gilchrist, *New procedure for the analysis of dental gold alloys*, J. Research NBS **20**, 745 (1938) RP1103.
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[3] W. Souder and W. T. Sweeney, *Is mercury poisonous in dental amalgam restorations?* Dental Cosmos **73**, 1145 (1931).

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