Research Journal of Biological Sciences 3 (6): 557-561, 2008
ISSN: 1815-8846

Quantitative Analysis of Ag, Sn and Cu in Dental Amalgam Powder by Gravimetric, AAS and ICP Methods and Comparing their Precisions

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Abstract: Dental amalgam has been the most useful restorative material in dentistry for more than 150 year. Widely pure and applied scientific study has been done in filed of determining amalgam's phases and composition, mechanical and corrosion properties of amalgam alloy. But there are very few reports in quantitative analysis of metals content of powder alloy. The works which have been done is mainly on used amalgam alloy or quantitative analysis of removal metals from the alloy. In this study, determination of silver, copper and tin, as basic components of powder alloy, by three; gravimetric, atomic absorption spectroscopy and Inductive Coupled Plasma atomic spectroscopy (ICP), methods and their precision are studied. The simultaneous solution of the three metals required for AA and ICP methods, is also studied. The statistics is done on basis of ASTM standard methods. As the conclusion, the ICP method for quantitative analysis of silver, copper and tin in powder amalgam alloy with composition 4:2.8:3, respectively, is recommended.

Key words: Amalgam, powder amalgam alloy, determination of Ag, determination of Sn, determination of Cu

INTRODUCTION

Amalgam as restorative material in dentistry was first used in France in 1826 (Svein, 1977) and yet, it is the most used restorative material because it's favorable mechanical properties as well as low cost and it is malleable, durable and affordable; an estimated 80% of all tooth restorations are made of amalgam (Fathi and Mortazavi, 2004). Silver and mercury are the main components of dental amalgam; however, commercial dental alloy has some tin, copper and zinc content in order to improve the mechanical properties for dental use. It is a mixture, rather than a true alloy, of mercury along with other metals like Ag, Sn, Cu and zinc. The results of pure and applied scientific study demonstrated that an alloy having γ phase (Ag_3Sn) composition was a most usable dental alloy and commercial dental alloys contains a mixture of γ and β phases (Svein, 1977; Jensen and Vrijhoef, 1976). While it is accepted that amalgam fillings release mercury, it is generally argued that the amount of mercury released by amalgam fillings is negligible, thus there is no significant danger from mercury leaking from fillings into the body (http://en.Wikinpedia.org/wiki/dental_amalgam_controversy). According to international (ISO, 2004) and national (ISIRI, 1987) standards the component composition of dental amalgam shall comply with Table 1.

Qualitative analysis of element in alloy by x-ray spectroscopy and quantitative analysis of Sn and Ag by gravimetric, respectively as SnO_2 and AgCl and of Cu by weight gain on electrolysis was done (Thomas *et al*., 1971). The energy dispersive spectroscopy coupled with x-ray diffraction analysis as the best method for determination of metal content of amalgam removed from abutment tooth was reported (http://www.ibiblio.org/amalgam/amalgamamtext.html). In this study, the determination of Ag, Sn and Cu in powder amalgam alloy by three methods; gravimetric, atomic absorption and ICP are studied. A sample of powder amalgam alloy is simulated as reference sample by mixing the pure metal powder of the tree elements with composition as Table 1. Determination of gravimetric method was done on solid reference sample and for determination by AA and ICP methods reference sample was solved in sulfuric acid and hydrogen peroxide. The statistics is done on basis of ASTM standard methods (ASTM, 1996).

Table 1: Chemical composition requirements

Metal	Content % (m/m)
Silver	40 min
Tin	32 max
Copper	30 max

MATERIALS AND METHODS

Instrumentation:

- Flame atomic absorption spectrometer- Varian AA - 1275
- ICP spectrometer-Varian Vista-PRO CCD simultaneous ICP-OES

Reagents: Silver, Copper and Tin metal powders(all from Alfa Aesar) were with purity of 99.999%and particle size of (100 mesh) and used without any further purification. Sulfuric acid, hydrochloric acid, nitric acid, ammonium, hydrogen peroxide, sulfurous acid, ammonium thiocynate (all from Merck) were used as received.

The standard stock solution of silver, copper and tin(1000 mg L^{-1})(all from Merck) were used as received.

Reference sample: To test the proposed methods against a known sample, a reference sample was prepared by mixing metal powder of silver, copper and tin with relative mass of 4: 2.8: 3.

For AA and ICP methods reference sample solution was required, so the solution A, B and C was prepared as fallow:

Twenty milli litter H_2SO_4 (1:1) was added to about 0.2000 g reference sample and heated to boil. $H_2O_2$was added drop by drop (2 mL is sufficient). One milli litter HNO_3 was added to ensure complete solution of metals. After cooling made it to the volume to 50 mL (solution A).The solution A was diluted 10 times with doubly distilled water to prepare solution B and was diluted 100 times with doubly distilled water to prepare solution C.

General procedure for gravimetric method

Step 1: Determination of tin

Twenty milli litter doubly distilled water and 30 mL HNO_3 was added to about 1g (±0.0001g) reference sample and heated to solve. Evaporated it to the volume of 30 mL on water bath. White precipitate of metastannic acid (H_2SnO_3) filtered by filter paper and wash with HNO_3 (1:100).precipitate heated in furnace at 800°C for 30min and after cooling was weight. Then the percent by weight of tin was calculated.

$$Sn + HNO_3 \longrightarrow (H_2SnO_3)_n \longrightarrow SnO_2$$

Step 2: Determination of silver

The solution from step one heated up 70°C. HCl (0.2N) was added drop by drop until precipitation of AgCl was completed. Precipitate was filter by sinter glass filter and washed with HNO_3 (1:100) then dride at 100°C in oven. The percent by weight of silver was calculated from weight of AgCl.

$$\text{Solution from step one} + Cl^- \longrightarrow AgCl\downarrow$$

Step 3: Determination of copper

Six millilitter H_2SO_4 was added to the solution from step two, heated gently to see white cloudy vapor of SO_3. Then it was diluted up to 200 mL with doubly distilled water and neutralized with ammonia. Ten millilitter H_2SO_3 and 2 mL ammonium tiocyanate (10%) was added to precipitate copper as CuSCN. After one night, the precipitate was filtered with sinter glass filter and washed with washing solution (a solution from mixture of 200 mL water, 1 mL NH_4SCN and 5-6 drops of H_2SO_3). Then it was deride at 100-120°C in oven, cooled and weighted. Then percent by weight of copper was calculated.

$$2Cu^{+2} + HSO_3^- + H_2O \longrightarrow 2Cu^+ + HSO_4^- + 2H^+$$

$$Cu^+ + SCN^- \longrightarrow CuSCN\downarrow$$

General procedure for AA and ICP method: The working standard solutions were prepared daily by diluting the stock standard solution with doubly distilled water. The determination of Sn in solution B and the determination of Ag as well as Cu in solution C were performed on AA spectrometer under the recommended condition for each metal ion. The wavelengths used to detect the each were as follow.

λAg = 256 nm; λ Cu = 235 nm; λ Sn = 335 nm

The determination of Sn, Cu and Ag in solution C was performed on ICP spectrophotometer under the recommended condition for each metal ion. The wavelengths used were as follow.

λ Ag = 328.068 nm; λ Cu = 324.754 nm;
λ Sn = 242.950 nm

RESULTS AND DISCUSSION

Determination of Ag, Cu and Sn by ICP methods was done by four different operator in four different laboratory and the results was shown in Table 2-4.The determination of Ag, Cu and Sn by AAS method also was done by four different operator in four different laboratory and the results was shown in Table 5-7. Determination of Ag, Cu and Sn by gravimetric method was done by four different operator in same laboratory and the results was shown in Table 8-10.The statistic analysis of data was done on base of ASTM methodology and the fallowing equations were used.

x = Individual test results (percent by weight) (n = results per cell = 3 number of test).

x = Cell average$\Sigma x_i/n$ (p = Number of laboratories = 4).

$x^{=}$ = Σx-i/p.

s = Cell standard deviation = $\sqrt{\Sigma(x_i - \bar{x})^2/(n-1)}$.

Table 2: Determination of Ag in powder amalgam by ICP method

	(x_i)					
Lab.	X_1	X_2	X_3	$\bar{X}$	S	d
1	42.18	41.75	41.52	41.8167	0.3350	0.6875
2	39.71	40.08	40.35	40.0467	0.3213	-1.0825
3	40.63	40.82	41.02	40.8233	0.1950	-0.3059
4	41.40	42.19	41.90	41.8300	0.3996	0.7008
$x^{=} = 41.1292$	$S_{x^2} = 0.8620$					
$S_r = 0.2831$	r = 0.79					
$S_R = 0.8925$	R = 2.50					

Table 3: Determination of Cu in powder amalgam by ICP method

	(x_i)					
Lab.	X_1	X_2	X_3	$\bar{X}$	S	d
1	29.28	29.07	29.85	29.4000	0.4036	0.6308
2	28.85	28.90	28.52	28.7567	0.2065	-0.0125
3	29.10	29.18	29.24	29.1733	0.0702	0.4041
4	27.76	28.16	27.32	27.7467	0.4202	-1.0225
$x^{=} = 28.7692$	$S_{x^-} = 0.7319$					
$S_r = 0.3111$	r = 0.87					
$S_R = 0.6001$	R = 1.68					

Table 4: Determination of Sn in powder amalgam by ICP method

	(x_i)					
Lab.	X_1	X_2	X_3	$\bar{X}$	S	d
1	31.48	31.00	31.92	31.4667	0.4601	1.2542
2	29.42	30.18	29.35	29.65	0.4603	-0.5625
3	29.92	30.03	29.79	29.9133	0.1201	-0.2992
4	29.52	29.87	30.07	29.82	0.2784	-0.3925
$x^{=} = 30.2125$	$S_{x^-} = 0.8432$					
$S_r = 0.3590$	r = 1.00					
$S_R = 0.8927$	R = 2.50					

Table 5: Determination of ag in powder amalgam by AAS method

	(x_i)					
Lab.	X_1	X_2	X_3	$\bar{X}$	S	d
1	40.56	40.21	40.06	40.2767	0.2566	1.9100
2	37.28	37.68	36.39	37.1167	0.6603	-1.2500
3	39.22	38.23	38.92	38.79	0.5076	0.4233
4	38.18	37.48	36.19	37.2833	1.0095	-1.0834
$x^{=} = 38.3667$	$S_{x^-} = 1.4791$					
$S_r = 0.6668$	r = 1.8670					
$S_R = 1.5761$	R = 4.4131					

Table 6: Determination of Cu in powder amalgam by AAS method

	(x_i)					
Lab.	X_1	X_2	X_3	$\bar{X}$	S	d
1	28.51	28.36	28.56	28.4767	0.1041	0.8442
2	25.33	25.88	26.13	25.78	0.4093	-1.8525
3	28.76	28.16	28.01	28.31	0.3969	0.6775
4	28.76	27.86	27.27	27.9633	0.7504	0.3308
$x^{=} = 27.6325$	$S_{x^-} = 1.2534$					
$S_r = 0.4740$	r = 1.3272					
$S_R = 1.3118$	R = 3.6730					

s_{x-} = Standard deviation of cell average = $\sqrt{\Sigma d^2/(p-1)}$.

d = Cell deviation = $x^{-} - x^{=}$.

S_r = Repeatability standard deviation = $\sqrt{\Sigma s^2/p}$.

S_R = Reproducibility standard deviation = larger of S_r and $\sqrt{(S_x-)^2 (S_r)^2 (n-1)/n}$.

r = NinEty five percent repeatability limit (within a laboratory) =1.960 v2 S_r = 2.8 S_r.

R = Reproducibility limit (between laboratories) = 1.960 √2 S_R = 2.8 S_R the percentage of metal in reference sample) = x_T) Bais = $x^{=} - x_T$.

Table 7: Determination of Sn in powder amalgam by AAS method

	(x_i)					
Lab.	X_1	X_2	X_3	$\bar{X}$	S	d
1	28.57	30.69	30.16	29.81	1.1033	1.105
2[*]	23.63	21.42	24.79	23.28	1.7120	-
3[*]	22.66	21.10	23.30	22.35	1.1316	-
4	27.27	27.91	27.62	27.6	0.3205	-1.105
$x^{=} = 28.705$	$S_{x^-} = 1.5627$					
$S_r = 1.1489$	r = 3.2169					
$S_R = 3.3220$	R = 9.30					

•This Row is deleted from calculation because of it's large deviation from the theory value and the other results

Table 8: Determination of Ag in powder amalgam by gravimetric method

Operator	$\bar{X}$	S	D
1	39.066	0.3610	-0.633
2	40.20	0.3610	0.501
3	39.64	0.3610	-0.059
4	39.89	0.3610	0.191
$x^{=} = 39.699$	$S_{x^-} = 0.4802$		
$S_r = 0.3610$	r = 1.01		
$S_R = 0.5634$	R = 1.58		

Table 9: Determination of Cu in powder amalgam by gravimetric method

Operator	$\bar{X}$	S	D
1	26.88	0.4467	-0.3275
2	27.69	0.4467	0.4825
3	26.75	0.4467	-0.4575
4	27.51	0.4467	0.3025
$x^{=} = 27.2075$	$S_{x^-} = 0.4622$		
$S_r = 0.4467$	r = 1.25		
$S_R = 0.5888$	R = 1.65		

Table 10: Determination of Sn in powder amalgam by gravimetric method

Operator	$\bar{X}$	S	D
1	29.311	1.2581	-0.6753
2	30.183	1.2581	0.1968
3	29.711	1.2581	-0.2753
4	30.74	1.2581	0.7538
$x^{=} = 29.99$	$S_{x^-} = 0.6161$		
$S_r = 1.2581$	r = 3.52		
$S_R = 1.2581^{\prime}$	R = 3.52		

•The value calculated for S_R is smaller than S_r

Table 11: Results of determination of Ag in powder amalgam by the three methods

Method	True value (x_T)	Test result ($x^{=}$)	s_r	s_R	r	R	Bais
Gravimetry	41.41	39.70	0.3610	0.5634	1.01	1.58	-1.71
AAS	41.70	38.37	0.6668	1.5761	1.87	4.41	-3.33
ICP	41.70	41.13	0.2831	0.8925	0.79	2.50	-0.57

Table 12: Results of determination of Cu in powder amalgam by the three methods

Method	True value (x_T)	Test result ($x^{=}$)	s_r	s_R	r	R	Bais
Gravimetry	27.94	27.21	0.4967	0.5888	1.25	1.65	-0.73
AAS	27.89	27.63	0.4740	1.3118	1.33	3.67	-0.26
ICP	27.89	28.77	0.3111	0.6001	0.87	1.68	0.88

Table 13: Results of determination of Sn in powder amalgam by the three methods

Method	True value (x_T)	Test result ($x^{=}$)	s_r	s_R	r	R	Bais
Gravimetry	30.15	29.99	1.2581	1.2581	3.52	3.52	-0.16
AAS	30.41	28.71	1.1489	3.3220	3.20	9.30	-1.70
ICP	30.41	30.21	0.3590	0.8930	1.00	2.50	-0.20

Repeatability and reproducibility are the preferred types of precision statements for ASTM test methods. The preferred index for each of these types is the 95% repeatability limit (r) and 95% Reproducibility limit (R). The index is expressed in the same units as those of the test result. The larger the index, the less precise the measurement process. The repeatability limit and the reproducibility limit reported for AAS and ICP methods

are within a laboratory and between laboratories, but for gravimetric methods they are operator-to-operator, within a laboratory. The percentage of metal in prepared reference sample was subtracted from the average of average cell ($\bar{x}$) to determine the bias of each test method. The obtained results of determination of each metal by three methods (Table 11-13) indicated lower r, R and bias, so better precision, for ICP method.

CONCLUSION

Between three proposed methods, the ICP method is more precise method. Because it is also provided simultaneous determination of three elements, The ICP method is recommended as preferable method for determination of Ag, Cu and Sn in amalgam powder.

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