

# In Vitro Release of Metal Ions from a Gold-Platinum Alloy in Saliva-Simulated Conditions

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## ABSTRACT

*The aim of this study was to evaluate the behavior of high-noble gold-platinum alloy samples (18+8 Rafinerija plemenitih kovina, Zagreb, Hrvatska), in a phosphate buffer pH 6.0. The aim of the study was to determine the type and amount of released metal ions from the alloy, and to evaluate how the time of exposure to the phosphate buffer pH 6.0 influences the release of metal ions from the alloy. Manufacturer samples 8.0×6.5×1.0 mm in size, with a surface area of 133mm<sup>2</sup> were used. The release of metal ions from the tested alloy was measured in ten time periods (after 1, 2, 3, 4, 5, 6, 7, 14, 21 and 30 days). Six samples were used (n=6) for each time period that the alloy was in the solution, which means that a total of 60 samples was analyzed. Solutions, in which the samples were placed, were analyzed with the inductively coupled plasma atomic emission spectrometer (ICP-AES, JY 50P, Jobin-Yvon, France). It was found that four metal ions were released: zinc ions (Zn), chromium ions (Cr), copper ions (Cu) and iron ions (Fe). The most released ions from the gold-platinum alloy were those of zinc (Zn), and the least released were those of iron (Fe) (p<0.01). The results of the study show that the time the tested alloy spent in the phosphate buffer pH 6.0 solution has an effect on the release of ions (p<0.01).*

**Key words:** gold-platinum alloy (Au-Pt), ion release, saliva pH

## Introduction

Prosthetic restorations, either fixed or removable, are inserted into the oral cavity for a longer period. The moment that dental alloys are inserted into the oral cavity they become exposed to the effect of the saliva and other electrolytes, and a process of continuous release of various metal ions begins.

In dentistry, and especially in prosthodontics, a wide array of alloys are used. Those alloys are processed and then inserted into the oral cavity for a longer period. Inside the oral cavity the alloys are exposed to the influence of biological, thermal, mechanical, electrical and chemical factors. These factors have a negative impact on functional and aesthetic characteristics of dental works, diminishing their longevity. An important factor of dental alloy damage is chemical and electrochemical corrosion (metal ion release) as well as mechanical damage. Corrosion is unwanted wear of the metals surface due to chemical reactions and the electrochemical action of the environment. In essence it is the damage of a metal.

Biocompatibility of dental alloys is an important question that should be of interest to all dentists because those alloys stay in close contact with the oral cavity tissues for a long period of time. Many dentists often overlook the biocompatibility of dental alloys because they assume that if an alloy is on the market its biocompatibility should not be questioned. Biocompatibility measures the relation of a particular alloy and the biological medium. It is closely related to corrosion stability. Harmful effects of an alloy on the organism as a whole, begin with the release of metal ions which happens as a result of corrosion<sup>1</sup>.

Prosthetic appliances made out of dental alloys should show stability in the oral cavity without corrosion. Corrosion can

mean a change in the alloys' color, and can cause local changes in the tissue with possible side-effects inside the organism. Because of that, the choice of an optimal dental alloy that is resistant to corrosion, a correct technological process as well as good oral hygiene are important pre-requisites in preventing corrosion<sup>2,3</sup>.

A cast of a gold alloy can also corrode because of an inhomogeneous structure of the crystal system inside the structure of the metal.

It was found that high-noble alloys are more resistant to corrosion than noble alloys. A low pH does not significantly influence the release of ions from high-noble and noble alloys<sup>4-6</sup>.

Some authors have determined that Zn and Ag ions are released from most noble alloys in the presence of artificial saliva<sup>7</sup>.

In some patients gold ions caused an allergic contact gingivo-stomatitis which had an appearance similar to an erosive lichen planus. It is interesting that some patients displayed intolerance to gold jewelry<sup>8,9</sup>.

There are numerous studies in which the release of ions from various medias was studied. It was proven that the release of metal ions from alloys was not always proportional to the amount of elements present in the alloy, but rather that so-called selective release occurs in which certain elements show a greater tendency towards releasing than others<sup>10</sup>.

The aim of this experiment was to study the behavior of a gold-platinum alloy in a phosphate buffer pH 6.0 through a longer period of time (1 to 30 days) and to establish the type and amount of ions which are released from the alloy, as well as to find how different time exposures affect the release of ions.

## Materials and Methods

A gold-platinum alloy labeled 18+8 manufactured by the Rafinerija plemenitih kovina Zagreb with the composition: gold 75.0%, platinum 8.0%, silver 9.5%, copper 5.1%, brass (copper – zinc alloy) 1.5%, trace elements 0.9%.

Standard size samples were used:  $8.0 \times 6.5 \times 1.0$  mm (available on the market) with a surface area of 133 mm<sup>2</sup>. A phosphate buffer pH 6.0 was used to simulate human saliva.

The release of metal ions from the alloy was measured in ten time periods (after 1, 2, 3, 4, 5, 6, 7, 14, 21 and 30 days). For each time period six samples (n=6) were used, which gives a total of 60 analyzed samples.

Standard-size samples, before insertion into the solution, were thoroughly cleaned and dried to remove any kind of surface contamination. The samples were cleaned in ethanol then twice rinsed with sterile deionized water and dried with sterile cotton pellets, and then with a sterile plastic tweezer inserted into the prepared and labeled test-tubes. In 15 ml sterile test-tubes 7 ml of solution was poured. Test samples were inserted into the tubes and then put into a room with a constant temperature of 37 °C to simulate the oral cavity temperature.

The samples were taken out of the test-tubes after 1, 2, 3, 4, 5, 6, 7, 14, 21 and 30 days. The presence of released elements in the extraction solution was measured by means of inductively coupled plasma atomic emission spectrometer (ICP-AES, JY 50P, Jobin-Yvon, France).

The before mentioned device enables concomitant quantitative and qualitative analysis of the released elements. Concomitant analysis is very fast and precise and can be used for every element of the periodical system. ICP spectrometer

scans the wavelength of 190–400 nm in 20 milliseconds. The device is based on atomic emission of certain elements which a 10,000 K temperature plasma induces to emit ions. Emitted electronic spectra are characteristic for every single element, and the intensity of the spectral lines is proportional to the concentration of present elements. The device allows a concomitant analysis of all released ions in an amount greater than 10 µg/L<sup>11</sup>.

A computer-assisted statistical analysis was performed by means of the SPSS program for Windows. Statistical methods used were, descriptive statistical analysis, one-way variance analysis and Friedmans non-parametric test.

## Results

The results are shown on Table 1 and Figure 1. Four elements were released from the solution, those being zinc (Zn), chromium (Cr), copper (Cu) and iron (Fe). Figure 1 shows the release of different ions from a gold-platinum alloy depending on the time of exposure to the phosphate buffer pH 6.0. The highest elemental release was recorded for zinc (Zn) with significant concentrations of the released element measured already at day 3. Iron (Fe) and chromium (Cr) ions leached in small amounts during the entire period of 30 days in the phosphate buffer pH 6.0, while copper (Cu) release in somewhat higher concentrations was found on days 5, 6 and 30.

Table 2 shows the results of analyzed variances. For each released element depending on the time the Au-Pt alloy was exposed to the phosphate buffer pH 6.0 solution there is a statistically significant difference ( $p < 0.01$ ). This means that the time of exposure to the solution significantly influenced the amount of released ions from the alloy.

Friedmans non-parametric test for dependent variables was used for the pur-

**TABLE 1**  
ION RELEASE FROM Au-Pt CASTING ALLOY INTO THE PHOSPHATE BUFFERED SALINE AT pH 6.0  
(SIMULATION OF HUMAN SALIVA)

	Day	N	X	SD	SE	95% Interval of confidence	
						Lower bound	Upper bound
Zn µg/L	1	6	82.5	26.76	10.93	54.41	110.59
	2	6	111.67	29.51	12.05	80.69	142.64
	3	6	135.83	48.36	19.74	85.08	186.58
	4	6	108.83	25.24	10.3	82.35	135.32
	5	6	150.33	67.61	27.6	79.38	221.29
	6	6	188	28.74	11.73	157.84	218.16
	7	6	143.33	53.89	22	86.77	199.89
	14	6	94	31.32	12.79	61.13	126.87
	21	6	72.33	10.07	4.11	61.76	82.9
	30	6	156.83	51.92	21.2	102.35	211.32
Total	60	124.37	51.34	6.63	111.1	137.63	
Cr µg/L	1	6	10	0	0	10	10
	2	6	10	0	0	10	10
	3	6	16.33	4.97	2.03	11.12	21.55
	4	6	86.33	33.23	13.57	51.46	121.21
	5	6	10	0	0	10	10
	6	6	10	0	0	10	10
	7	6	10	0	0	10	10
	14	6	10	0	0	10	10
	21	6	10	0	0	10	10
	30	6	10	0	0	10	10
Total	60	18.27	24.96	3.22	11.82	24.71	
Cu µg/L	1	6	10	0	0	10	10
	2	6	41	29.09	11.87	10.48	71.52
	3	6	64.33	46.39	18.94	15.65	113.02
	4	6	36.5	11.08	4.52	24.88	48.12
	5	6	95.33	71.58	29.22	20.21	170.45
	6	6	78	53.13	21.69	22.24	133.76
	7	6	42	71.62	29.24	-33.16	117.16
	14	6	11.5	2.35	0.96	9.04	13.96
	21	6	10	0	0	10	10
	30	6	142.5	105.16	42.93	32.14	252.86
Total	60	53.12	63.16	8.15	36.8	69.43	
Fe µg/L	1	6	10	0	0	10	10
	2	6	43.67	31.33	12.79	10.79	76.54
	3	6	48.83	26.93	11	20.57	77.1
	4	6	56.67	14.11	5.76	41.86	71.47
	5	6	55.33	3.01	1.23	52.17	58.49
	6	6	54.5	13.34	5.45	40.5	68.5
	7	6	60.33	17.82	7.27	41.63	79.03
	14	6	96.17	63.87	26.07	29.14	163.19
	21	6	75.33	6.65	2.72	68.35	82.32
	30	6	84.67	51.24	20.92	30.89	138.44
Total	60	58.55	35.96	4.64	49.26	67.84	

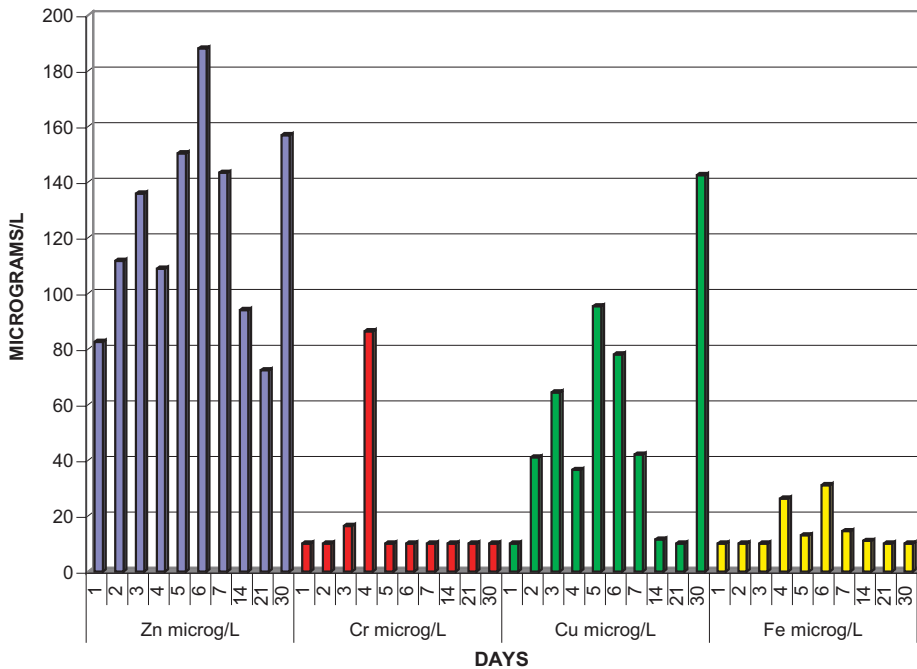


Fig. 1. Ion release from Au-Pt alloy into the phosphate buffered saline at pH 6.0.

**TABLE 2.**  
 VARIANCE ANALYSIS FOR SIGNIFICANT DIFFERENCE IN ION RELEASE DEPENDING ON DIFFERENT TIME OF EXPOSURE Au-Pt CASTING ALLOY TO THE PHOSPHATE BUFFER AT pH 6.0

		Sum of squares	df	Mean square	F	p
Zn µg/L	Between groups	72322.6	9	8035.84	4.828	<0.01
	Within groups	83215.3	50	1664.31		
	Total	155538	59			
Cr µg/L	Between groups	31101.1	9	3455.67	30.61	<0.01
	Within groups	5644.67	50	112.893		
	Total	36745.7	59			
Cu µg/L	Between groups	99079	9	11008.8	4.038	<0.01
	Within groups	136309	50	2726.18		
	Total	235388	59			
Fe µg/L	Between groups	3144.4	9	349.378	4.246	<0.01
	Within groups	4114.33	50	82.287		
	Total	7258.73	59			

pose of comparing the released amount of ions for different metals, and also to find out if there is a significant difference between the released amounts of ions (Table 3). In all time-periods a difference in releasing different ions was noticed ( $p < 0.001$ ). Most released were zinc ions (Zn), slightly lower were copper ions (Cu), and the least released were chromium (Cr) and iron (Fe) ions.

**TABLE 3**  
FRIEDMAN'S NON-PARAMETRIC TEST FOR  
CORRELATED SAMPLES

	Mean rank
Zn $\mu\text{g/L}$	3.93
Cr $\mu\text{g/L}$	1.76
Cu $\mu\text{g/L}$	2.5
Fe $\mu\text{g/L}$	1.81

$N = 60$ ;  $\chi^2 = 129.303$ ;  $df = 3$ ;  $p < 0.001$

## Discussion

Various conditions occur inside the oral cavity. Numerous biological factors, including organic acids and enzymes which are formed by microorganisms can contribute to lower saliva pH values. The intake of acid foods and drinks, smoking, alcohol, use of various drugs, formation of lactic, citric and other acids as well as the composition of the saliva itself can contribute to lower pH values of the saliva. It is also well-known that poor oral hygiene contributes to the formation of dental plaque on the surfaces of dental casting alloys.

The tested samples predominantly released four elements: An, Cr, Cu, and Fe. This does not mean that other elements were not released from the alloy, but that was not within detectable limits of the ICP-AES, JY 50P. Although the manufacturer of the alloy does not declare the presence of iron (Fe) and chromium (Cr), certain amounts of these elements are

present. It could be possible that these elements are added to the alloy in small amounts inside the 0.9% of the trace elements.

Interesting results were obtained pertaining to the release of zinc (Zn) and copper (Cu) elements into the extraction solution. After one day of exposure to the extraction solution a significant amount (100  $\mu\text{g/L}$ ) of Zn leached from the alloy, reaching its peak at day six (150  $\mu\text{g/L}$ ). A continuously rising release of Cu elements was detected from day one to day five after which there was no significant difference in the amount released. The maximum value of released ions for Cu was 150  $\mu\text{g/L}$  at day 30.

The release of metal ions from dental casting alloys is a constant occurrence which cannot be avoided. It begins the very day the alloy is, as a prosthetic appliance, inserted into the oral cavity. More stable alloys that will not show signs of biodegradation are constantly being sought. Because of this a number of researchers are studying the biocompatibility of dental casting alloys. Their aim is to find such alloys that display biological tolerance for each element inside the alloy, and to find the means by which the release of elements can be held within the recommended limits. The bigger the surface of the alloy inside the oral cavity, the greater the number of various types of alloys with a different technological and surface finishing, the lower the pH value of the saliva and the poorer the oral hygiene, the greater are the conditions for electrocorrosion and subsequent leaching of ions from an alloy.

Bearing in mind the fact that fixed prosthodontic appliances stay inside the oral cavity for several years, some studies took this fact into consideration by monitoring the release of elements from various alloys over several months (10 months). It was concluded that the maximum amount of released elements oc-

curred after one month, even mimicking elemental release which happened after 72 hours. The amount of released ions over the first few days and weeks reaches high levels, subsequently leveling in relation to the time the samples were immersed in the extraction solution<sup>12</sup>.

Wataha et. al.<sup>12,13</sup> analyzed the release of elements after 7, 14, 21 and 28 days. They concluded that the initial release of elements occurs within the first seven days, and is actually the highest for most elements, although that period is not sufficient to determine the overall amount of released elements, so they suggest a period of 30 days.

In this study a significant release of zinc (Zn) ions from a gold-platinum alloy was noticed, suggesting that zinc is a labile element inside the alloy<sup>12</sup>.

Bumgardner et. al.<sup>14</sup> studied the toxic effect that copper and zinc from gold alloys have on human gingival fibroblasts. They noticed that only copper and zinc ions from the alloys cause morphological changes of the cells, while every tested alloy inhibited the 3H-thymidine uptake by proteins inside the cell-culture medium.

In this study we have used labeled gold-platinum alloys made by a manufacturer for subsequent use in prosthetic dentistry. It can be concluded that the uneven release of metal ions was caused by the disturbance inside the crystal structure of the metal during the process of making an alloy. Although there is a smaller amount of copper (Cu) and zinc (Zn) ions within the alloy than of gold, platinum or silver, they were released in greater amounts (Au, Ag and Pt ions were not at detectable levels) showing that the percentage of elements inside the alloy is not significant for their release.

Because of this it is of great importance to respect the manufacturers guidelines when handling with these alloys.

Today dentists have to insert into the oral cavity an alloy with a regular structure in order to obtain quality characteristics.

Relatively low concentrations of metal ions measured in this study, which were released from the gold-platinum alloy, cannot have adverse effects on oral cavity tissues and other body organs. The amount of released ions were in concentrations far below the dietary daily recommended uptake of these elements<sup>15,16</sup>. The released elements can be resorbed intestinally, and they can be an addition to other sources of these elements (food, water). There is no possibility of a systemic toxic effect<sup>17</sup> either although one should not neglect the possibility of local side-effects on tissues adjacent to the alloy. As technological procedures can undesirably act on the crystal structure of the alloy, future studies should analyze how these procedures (polishing, casting) affect the release of ions from the alloy.

## Conclusions

Although the tested samples are high-noble gold-platinum alloys, they too, due to the electrochemical forces inside the oral cavity, release various metal ions into the saliva and the surrounding tissues from the day they are put into the cavity.

1. From the samples with a surface area of 1.33 cm<sup>2</sup>, four metal ions were released: zinc (Zn), chromium (Cr), copper (Cu) and iron (Fe) under the influence of phosphate buffer pH 6.0 and a period of 30 days.

2. The most released ions were zinc (Zn), the least released were chromium (Cr) and iron (Fe) ions.

3. The tested samples released chromium (Cr) and iron (Fe) ions which are not declared by the manufacturer, however they could be within the 0.9% of trace elements.

4. The time of exposure to the extraction solution affects the amount of released ions.

5. All released ions were below the daily dietary level of need for these elements.

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## OTPUŠTANJE METALNIH IONA IZ ZLATNO – PLATINSKE LEGURE U IN VITRO UVJETIMA SIMULIRANE SLINE

### S A Ž E T A K

Svrha ovog istraživanja bila je ispitati ponašanje uzoraka visoko plemenite zlatno – platinske legure (18+8, Rafinerija plemenitih kovina Zagreb, Hrvatska), u fosfatnom puferu pH 6.0. Svrha rada bila je ustanoviti vrstu i količinu otpušanih metalnih iona iz legure, te kako na otpuštanje metalnih iona utječe vrijeme izloženosti legure fosfatnom puferu pH 6.0. Korišteni su uzorci tvorničkog lijeva 8.0×6.5×1.0 mm. površine 133 mm<sup>2</sup>. Otpuštanje metalnih iona iz ispitivane legure mjereno je nakon deset vremenskih razdoblja (nakon 1, 2, 3, 4, 5, 6, 7, 14, 21 i 30 dana). Korišteno je po šest uzoraka (n=6) za svako vremensko razdoblje boravka legure u otopini, što znači da je ukupno analizirano 60 uzoraka. Otopine u kojima su bili uronjeni uzorci analizirane su pomoću atomskog emisijskog spektrometra s induciranom združenom plazmom (ICP–AES, JY 50P, Jobin-Yvon, Francuska). Pronađeno je da su se otpustile četiri vrste metalnih iona i to: ioni cinka (Zn), ioni kroma (Cr), ioni bakra (Cu) i ioni željeza (Fe). Najviše se iz zlatno – platinske legure otpustilo iona cinka (Zn), a najmanje iona željeza (Fe) (p<0.01). Rezultati istraživanja pokazuju da na otpuštanje iona iz ispitivane legure utječe vrijeme izloženosti legure fosfatnom puferu pH 6.0 (p<0.01).