The effect of hydrogen peroxide concentration on metal ion release from dental casting alloys

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SUMMARY There are concerns that tooth bleaching agents may adversely affect dental materials. The aim of this study was to test the hypothesis that increasing concentrations of hydrogen peroxide (HP) are more effective than water at increasing metal ion release from two typical dental casting alloys during bleaching. Discs (n = 28 for each alloy) were prepared by casting and heat treated to simulate a typical porcelain-firing cycle. Discs (n = 7) of each alloy were immersed in either 0%, 3%, 10% or 30% (w⁄v) HP solutions for 24 h at 37 °C. Samples were taken for metal ion release determination using inductively coupled plasma-mass spectrometry and the data analysed using a two-way ANOVA followed by a one-way ANOVA. The surface roughness of each disc before and after bleaching was measured using a Talysurf contact profilometer and the data analysed using a paired t-test. With the exception of gold, the differences in metal ion concentration after treatment with 0% (control) and each of 3%, 10% and 30% HP (w⁄v) were statistically significant (P < 0.05). Metal ion release from the two alloys increased with increasing HP concentrations (over 3000% increase in Ni and 1400% increase in Pd ions were recorded when HP concentration increased from 0% to 30%). Surface roughness values of the samples before and after bleaching were not significantly different (P > 0.05). Exposure of the two dental casting alloys to HP solutions increased metal ion release of all the elements except gold.

KEYWORDS: tooth bleaching, metal ceramic alloys, ion release, surface roughness

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Introduction

There is an increasing demand for aesthetic procedures in dentistry to satisfy high patient expectations. Tooth bleaching, in particular, has become popular in recent years. Hydrogen peroxide (HP) is the most common bleaching agent, used either directly or following generation by carbamide peroxide (CP) (1, 2).

While the effects of bleaching agents on oral tissues are relatively well known (3–5), there has been relatively little study of their effects on dental materials. Bleaching agents may come into contact with restorative materials, particularly when using mouth guard bleaching or home kits (6, 7). Amalgam restorations and casting alloys are known to corrode on contact with a strong oxidizing agent such as HP and metal ions may be released into the oral cavity (8–11). Elemental release from dental alloys is related to known biocompatibility issues because of the interaction of these elements with surrounding or systemic tissues (12–16).

The phase structure of an alloy is critical to its corrosion properties and therefore it is also related to biocompatibility (15, 17, 18). Multiple phase alloys tend to release more elements than single phase alloys (17, 19). Certain metallic elements or ions have a tendency to be released (lability) regardless of the alloy composition (14). Copper, nickel and gallium, for example, are labile elements whereas gold, palladium and platinum have low labilities.

A number of studies have shown that environments around the alloy will influence corrosion (12–14, 20), with acidic environments increasing corrosion in some
systems (21, 22). This is more relevant to Ni-based alloys, but not the high noble alloys (23, 24). The corrosion of alloys may be investigated using a variety of techniques including visual observation of the alloy surface, electrochemical tests that measure elemental release indirectly through the flow of released electrons, or by direct measurements of the released elements (14).

For direct measurements of ion release, Tufekci et al. (25) used inductively coupled plasma-mass spectrometry (ICP-MS) to measure the in vitro elemental release from two high palladium alloys into a corrosion medium having a pH-value of 2-24. They reported a significant increase in ion release with increased immersion time. It was also reported that there were significantly more ions released into the solution from the Pd-Cu-Ga alloy compared to the Pd-Ga alloy. The mean measured ion release data for Pd-Cu-Ga alloy at 7 h immersion time was reported to be 0.74 µg cm⁻² for Pd, 0.57 µg cm⁻² for Ga, 1.50 µg cm⁻² for Cu and 0.06 µg cm⁻² for Sn. Wataha et al. (20) also used ICP-MS to investigate the effect of pH on element release from dental casting alloys. High noble, noble and base metal casting alloys were treated in different solutions with pH-values of 1, 4 and 7. High noble and noble alloys were resistant to acidic environments, whereas, Ni-based alloys released large amounts of Ni in solutions of pH-values of 1 and 4. For the Pd-Cu-Ga alloy, they reported ion releases of 0.02 µg cm⁻² for Pd and 0.01 µg cm⁻² for Cu at pH-value of 4. For the base metal alloy, they reported 1.25 µg cm⁻² Ni release.

Clearly, there is a dearth of data in the published literature regarding the effect of bleaching agents on ion release because of corrosion of metallic restorations (26, 27). This study was designed to test the hypothesis that HP bleaching agents (3-30% w/v) are more effective than water in increasing metal ion release from Ni-Cr and Pd-Cu-Ga alloys.

### Materials and methods

#### Materials

Two typical metal alloys were evaluated, a Ni-Cr alloy* and a Pd-Cu-Ga alloy†. The composition (% w/w) for the two alloys is presented in Table 1. Based on the % (w/w) of the elements in Table 1, the Ni-Cr is a base metal alloy and the Pd-Cu-Ga is a noble alloy as classified by the American Dental Association (17). Preparation of test discs (n = 28 for each alloy) was carried out using the lost wax technique. The discs were made in wax from silicone moulds (10 mm × 2 mm for the Ni-Cr discs giving a total surface area of 2.2 cm² for each disc and 5 mm × 1 mm for the Pd-Cu-Ga discs with a total surface area of 0.55 cm²; for each disc), identically sprued and invested in phosphate-bonded investment. Melting and casting of the alloys were carried out using an induction casting machine‡. Castings were allowed to bench cool, devested and sprues with excess alloy ground away. Cast discs were subjected to heat treatment for VITA§ porcelain-firing cycles. Both sides of each disc were polished using fine stones, rubber wheels and bristle brushes loaded with universal polish and finally lambs wool mop. The surface roughness of each disc was determined by using a Talysurf contact profilometer¶ and stored in individually labelled polythene bags. Volumetric analysis based on iodine thiosulphate titration was performed to establish the active concentration of HP in test solutions (28). Five titrations were carried out by using nominally a 30% HP (w/v) solution** and the results recorded as the mean and s.d. The HP solution was diluted to obtain 3% (w/v), 10% (w/v) as well as 30% (w/v) HP solutions with high-purity distilled water as the control (0% HP). The pH of the HP solutions was measured with a pH meter††. The pH meter was first calibrated using two standard buffers of pH 4 and 7.

#### Table 1. Alloy composition

<table>
<thead>
<tr>
<th>Element</th>
<th>% (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cr alloy</td>
<td></td>
</tr>
</tbody>
</table>

*Wiron 99; Bego, Bremen, Germany.
†Cerapall II; Metalor; Technologies SA, CH-2009 Neuchatel, Switzerland.
§Vita Zahnfabrik H. Rauter GmbH & Co., Bad Sackingen, Germany.
¶Mitutoyo Corporation, Kawasaki, Japan.
**Aristar Hydrogen Peroxide, VWP International Ltd, Poole, UK.
††Checker 1; Hanna Instruments, Leighton Buzzard, UK.

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Ion release

The 28 discs, for each alloy, were randomly divided into four equal groups. The discs in a group (n = 7 per group) were immersed in either 0%, 3%, 10% and 30% HP solutions (20 mL for Ni-Cr alloy and 10 mL for Pd-Cu-Ga alloy) for 24 h at 37 °C creating seven samples of each solution (2, 29). This was carried out by placing each disc in a tapered centrifuge tube, with all surfaces exposed to the particular HP concentration in that tube. All the solution samples were analysed by ICP-MS, Agilent 4500. ICP-MS detection limits for the target elements in the samples were analysed by ICP-MS, Agilent 4500. HP concentration in that tube. All the solution

Surface area of ICP-MS detection limits for the target elements in the two alloys are given in Table 2. The surface area of the discs to the volume ratio of bleaching solution was 0.055 cm² mL⁻¹ for the Pd-Cu-Ga alloy and 0.11 cm² mL⁻¹ for the Ni-Cr alloy which are below the range 0.5–6.0 cm² mL⁻¹ recommended by ISO Standard 10933 (30). As no biological studies were being performed, our experimental sample surface area to bleaching solution volume ratios was considered acceptable (25, 30).

For each analysis, the ICP-MS instrument performs five measurements and calculates the mean and relative s.d. (%) for each element. Thus, with the seven discs tested in each group, the total number of measurements recorded per element was 35.

Surface roughness

Following ion release experiments, the surface roughness of the discs was measured again using a Talyssurf instrument (with a conical-shaped stylus measuring 0.830 mm at the base and 0.015 mm at the tip) that was calibrated in accordance with manufacturers instructions. For each disc, the roughness of both polished surfaces was then measured by moving the stylus across its diameter. The procedure was repeated several times for each disc altering the orientation after each measurement.

Table 2. Inductively coupled plasma-mass spectrometry detection limits for elements

<table>
<thead>
<tr>
<th>Elements</th>
<th>Detection limits (ng L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni, Mo, Pd, Sn and Ga</td>
<td>1</td>
</tr>
<tr>
<td>Cr, Cu and In</td>
<td>3</td>
</tr>
<tr>
<td>Au</td>
<td>6</td>
</tr>
</tbody>
</table>

Statistical analysis

A two-way ANOVA (element by concentration) revealed a significant interaction between concentration and elements (P < 0.001) for both alloys indicating that differences between solutions were different across elements. The two-way ANOVA was followed by a one-way ANOVA and Dunnet’s post hoc test for multiple comparisons between solutions for each element. The roughness measurements were analysed by using a paired t-test.

Results

The measured pH-values for 0%, 3%, 10% and 30% HP concentrations were 6.41, 5.62, 4.75 and 3.83, respectively. Values for the mean and s.d. of elemental ion release data measured in µg L⁻¹ were converted to units of µg cm⁻² and are shown in Tables 3 and 4 for Ni-Cr and Pd-Cu-Ga alloys, respectively. This was obtained by dividing the total amount of ion release in microgram over a 24-h period for each element by the total surface area of the corresponding disc. Tables 3 and 4 show a steady increase in ion release values from all the constituent elements of the two alloys, except gold, with increasing HP concentration. The constituents with percentage weight of 1% or less in the two alloys were not included in the tables. For each sample tested, the ICP-MS recorded ion release values of all the elements in the periodic table. It was noted that the mean ion release value of Pd from the Ni-Cr alloy was 0.0015 µg cm⁻² and that of Ni from the Pd-Cu-Ga alloy was 0.002 µg cm⁻² at 30% HP concentration. These values are negligibly small which, in turn, adds weight to the accuracy of the recorded data.

The distribution of the recorded ion release data (not shown here) was normal for all elements. The P-values for the one-way ANOVA and Dunnet’s post hoc test are

Table 3. Mean and s.d. Ni-Cr alloy

<table>
<thead>
<tr>
<th></th>
<th>Nickel (µg cm⁻²)</th>
<th>Chromium (µg cm⁻²)</th>
<th>Molybdenum (µg cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>s.d.</td>
<td>Mean</td>
</tr>
<tr>
<td>(HP)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.26</td>
<td>0.08</td>
<td>0.01</td>
</tr>
<tr>
<td>3</td>
<td>0.90</td>
<td>0.16</td>
<td>0.75</td>
</tr>
<tr>
<td>10</td>
<td>5.05</td>
<td>1.50</td>
<td>3.63</td>
</tr>
<tr>
<td>30</td>
<td>8.23</td>
<td>0.49</td>
<td>6.65</td>
</tr>
</tbody>
</table>
shown in Tables 5 and 6 for Ni-Cr and Pd-Cu-Ga alloys, respectively. The difference in metal ion release between 0% HP (control) and all other concentrations (3%, 10% and 30%) was statistically significant ($P < 0.05$) for all elements except gold (the $P$-values for gold are not included in Table 6). Additionally, there was a generally significant change in ion release data at each increase in HP concentration except for Mo (Table 5) where there was no significant difference ($P > 0.05$) when HP concentration was increased from 10% to 30% and indium (Table 6) when HP concentration changed from 3% to 10%. The average roughness values for Ni-Cr and Pd-Cu-Ga alloys before and after treatment is shown in Fig. 1a and b. Paired $t$-tests showed no significant difference ($P > 0.05$) in mean surface roughness values before and after bleaching in all the groups.

### Table 5. Multiple comparisons – $P$-values for Ni-Cr alloy

<table>
<thead>
<tr>
<th>(HP)</th>
<th>Nickel</th>
<th>3</th>
<th>10</th>
<th>30</th>
<th>Chromium</th>
<th>3</th>
<th>10</th>
<th>30</th>
<th>Molybdenum</th>
<th>3</th>
<th>10</th>
<th>30</th>
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<tbody>
<tr>
<td>0</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>3</td>
<td>–</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>–</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>–</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>–</td>
<td>0.001</td>
</tr>
<tr>
<td>10</td>
<td>&lt;0.001</td>
<td>–</td>
<td>&lt;0.001</td>
<td>–</td>
<td>&lt;0.001</td>
<td>–</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>–</td>
<td>&lt;0.001</td>
<td>–</td>
<td>0.840</td>
</tr>
</tbody>
</table>

### Table 6. Multiple comparisons – $P$-values for Pd-Cu-Ga alloy

<table>
<thead>
<tr>
<th>(HP)</th>
<th>Palladium</th>
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<th>10</th>
<th>30</th>
<th>Copper</th>
<th>3</th>
<th>10</th>
<th>30</th>
<th>Tin</th>
<th>3</th>
<th>10</th>
<th>30</th>
<th>Indium</th>
<th>3</th>
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<th>Gallium</th>
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<th>30</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.002</td>
<td>0.003</td>
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</tr>
<tr>
<td>3</td>
<td>–</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>–</td>
<td>0.005</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>–</td>
<td>0.069</td>
<td>0.005</td>
<td>–</td>
<td>&lt;0.011</td>
<td>&lt;0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>&lt;0.001</td>
<td>–</td>
<td>&lt;0.001</td>
<td>0.005</td>
<td>–</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.015</td>
<td>0.011</td>
<td>–</td>
<td>&lt;0.001</td>
<td></td>
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<td></td>
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</table>

### Discussion

With the exception of gold, ion release increased with increasing HP concentration for both alloys. Generally, Pd-Cu-Ga alloys are considered to be more corrosion resistant than non-precious metal-based alloys. In this study, the amount of ion release of all elements from Ni-Cr alloy was higher than those released from the elements in the Pd-Cu-Ga alloy at 3–30% HP concentration. The Ni-Cr alloy used here was a Ni high Cr alloy which is the most resistant of the Ni-based group having a Cr content of 22.5% (w/w). The corrosion of these alloys is far better than the Ni-Cr-Be alloys (as Be lowers the corrosion resistance of these alloys), but not as good as the noble alloy groups (13, 17, 31, 32).

The $P$-values (Tables 5 and 6) showed that there were significant differences ($P < 0.05$) between the
control and each of the three HP concentrations for the elements in the two alloys given in these tables. There was also a significant change in ion release data every time the HP concentration changed (except for molybdenum between 10% and 30% HP and indium between 3% and 10% HP). This indicated an increase in corrosion with increasing HP concentrations. The statistical tests for the surface roughness data showed no statistically significant differences before and after bleaching ($P > 0.05$).

It is difficult to compare our data with those in the published literature because of lack of standardization in previously reported testing procedures. There are differences in the units of the data presented, exposure times, pH of the treatment solutions and HP concentration. To facilitate meaningful comparison, it was necessary first to convert the units of our measured ion release data from $\mu$g L$^{-1}$, as recorded by the ICP-MS instrument to $\mu$g cm$^{-2}$ to correspond to the units quoted, for example, in references (20) and (25). Secondly, it was necessary to account for the differences in the exposure times. For this purpose, an attempt was made to calculate the ion release data by Tufekci et al. (25) at 24 h exposure time by applying a linear interpolation to their recorded data at 7 and 70 h. This resulted in ion release data of 5.67, 4.50, 4.69, 0.15 and 0.05 $\mu$g cm$^{-2}$ for Pd, Cu, Ga, Sn and In, respectively, when treated with a solution of pH 2.24. Our ion release data expressed in $\mu$g cm$^{-2}$ per surface area at 30% HP (w/v) are much lower than the corresponding values reported by Tufekci et al. (25). The differences can be attributed, in part, to differences in pH-values, as Tufekci et al. investigated corrosion under more acidic conditions (pH 2.24 compared with 3.83). Wataha et al. (20) reported ion release data of about 0.02 $\mu$g cm$^{-2}$ for Pd and 0.01 $\mu$g cm$^{-2}$ for Cu from a Pd-Cu-Ga alloy exposed to a solution of pH-value of 4 for a period of 30 min. Data presented here show much higher release figures than the corresponding ones reported by Wataha et al. The differences may be partly because of differences in exposure times and pH-values. Further work is needed in this area, particularly regarding the standardization of the testing procedures.

The surface area for typical restorations fabricated from dental alloys vary from about 0.33 cm$^2$ for the exposed palatal metal collar of a metal ceramic crown to about 1.50 cm$^2$ for a full coverage metal crown. Estimates of daily intake in the diet of some of the elements in dental alloys which are of interest to the present work are 400 $\mu$g for Ni and Mo, 240 $\mu$g for Cr, and 3110 $\mu$g for Cu (14). With regard to Ni release, based on our measured data, the daily diet figures equate to ion releases from about 147 metal ceramic crowns or 32 full coverage crowns treated with 30% HP concentration over 24-h period. The corresponding numbers for the other three elements quoted are 262 and 58 crowns for Mo, 109 and 24 crowns for Cr, 104 714 and 23 037 crowns for Cu. There are a large number of other elements taken daily in the diet which are also released from dental alloys. A number of these elements are needed for normal body function (e.g. Zn), whereas others (e.g. Pd), if introduced in excess, could become toxic. The route, however, by which an element gains access to the body is critical to its
biological effects. Elements released from a casting alloy enter the oral cavity rather than the body. Similarly, the elimination of an element from the body also depends on its route of access to the body. Elements released from casting alloys introduced through the oral cavity are believed to be eliminated from the body in a relatively short space of time (14). Whereas the risk of systemic adverse reactions due to elements released from dental alloys though clearly elevated is, however, unlikely to constitute a health hazard (33). A dental crown can, however, extend below the level of the gingival margin, forming a sulcus between the gingiva and the alloy (14). If elements from the alloy are released into the sulcus, they may reach high enough concentration to cause a local adverse reaction (34).

Conclusions

Metal ions were released from both dental alloys following all treatments. The rate of ions released for all elements except Au increased with increasing HP concentrations and was statistically significant ($P < 0.05$). Differences in surface roughness values before and after bleaching were not statistically significant ($P > 0.05$). An increase in elemental ion release into the oral cavity from dental casting alloys following bleaching can trigger allergic reactions and caution need to be exercised in particular when applying HP at high concentrations.

References


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