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Ion Release from Experimental Au-Pt-based Metal-Ceramic Alloys

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Abstract

Objective The aim of the study was to assess the effect of individual metallic elements within experimental Au-Pt-based dental alloys for porcelain veneering on ion release.

Methods A binary Au-10 at% Pt alloy (AP10) was designed as a parent alloy. Six ternary AP10-X (X = In/Fe/Sn/Zn) and four quaternary (AP10-In₂)-Y (Y = Fe/Sn/Zn) alloys containing oxide-forming elements, X and Y, up to 2 at% were prepared and ion release from the experimental alloys in deionised water and commercial soft drink was examined. For ion release determination samples with size 10X10X0.5 mm³ were immersed in 20 ml of deionized water for 5 min. Samples were then removed and immersed in 20 ml of Sprite Light[®] for a further 5 min, and 2 hours at 37°C. The amounts of ions released in the test solutions were analysed by Inductively Coupled Plasma-mass Spectrometry.

Results When looking at individual elemental ion release, the order of the amount of dissolved ions was Fe>Zn>In>Sn. Among the base metal elements examined, Fe showed significantly higher levels of ion release than the other base metal elements for all three testing conditions (P<0.05). When looking at the effects of test solution on ion release from the alloys, Sprite Light[®] caused significantly higher level of ion release than deionised water, with the exception of In in the ternary AP10-In1.0 and AP10-In1.7 alloys and the quaternary (AP10-In₂)-Sn1.0 alloy, which showed similar or slightly greater amounts of ion release into deionised water.

Significance Significant ion release was only observed from the Fe element. Sn and In elements showed less ion release than the Fe and Zn elements. Accordingly, Sn and In elements should be recommended as oxide-forming elements in Au-Pt-based metal-ceramic systems.

Introduction

Porcelain-fused-to-metal (PFM) restorations are widely used in dentistry because of their excellent clinical properties. Gold alloys for PFM restorations contain small amounts of oxide-forming elements such as In, Sn, Fe and Zn. Oxide layers, formed during the degassing process, are known to improve the bond strength between the metallic frame and the veneering porcelain (1). Although much of the metallic frame is covered with veneering porcelain it is usual for a small collar of alloy to be left uncovered. This is usually highly polished and partially sub-gingival. It is therefore in contact with the tissue and is also open to attack from oral fluids.

Metal ions released from dental alloys interact with metabolic pathways and cell structures causing damage (2). Cation release can provide inflammatory reactions and may modulate the immune response by activation or inhibition of T- and B-cells (3). These responses can be in the form of oral mucositis, gingivitis/periodontitis and alveolar bone resorption (2).

The UK adverse reactions reporting project (4) showed that reactions to precious metals accounted for about 5% of the reactions caused by metals and the number of allergic causes attributed to metals appears to be small. Another study (5) found that in not more than 10% of patients was allergy diagnosed as contributing to a complaint or symptom. However, metal components from almost all cast dental alloys can be detected in adjacent tissue (6).

The single most important property of a dental casting alloy to its biological safety is its corrosion potential (7). Multiple phase alloys increase the risk of elemental release (7). Labile elements within dental alloys have been found to be more likely to be released regardless of the alloy composition with elements such as Zn being more labile than Au (7, 8). Other work has found that ion release is not

generally correlated with the concentration of the individual metal in the alloy or the nobility of the alloy (9).

Most of the alloys used for metal-ceramic systems are high Au and Pd-free alloys based on ternary systems of Au (80-86%), Pt (10-15%) and In (1-2%) (10). Good biocompatibility is obtained by the inclusion of the two high content noble metal elements (Au and Pt) and strength by the In elements (10). Palladium-based alloys have been found to have side effects such as allergies (11). Many case reports exist describing Pd sensitivity and recovery after removal of dental restorations (12). Further, because Pd-containing dental alloys have been identified as a possible source of sensitization, the public should be protected from possible adverse effects by minimizing the use of Pd-containing alloys or the release of Pd from alloys (12). When looking at the elements to be investigated in this study only Zn and In have been cited in the literature as causing adverse reactions to oral mucosa (13, 14, 15). Therefore, we are attempting to develop new Pd-free Au-Pt-based high noble dental alloys for PFM restorations to avoid possible side effects caused by Pd. To make clear the effects of the inclusion of oxide-forming elements, In/Fe/Sn/Zn, on various properties of the above-mentioned Pd-free PFM alloys, we are performing systematic studies including optical properties of a series of experimental alloys (16,17).

The aim of the current study was to assess the effect of individual oxide-forming metallic elements added to experimental Au-Pt-based porcelain-fused-to-metal (PFM) alloys on ion release. The hypothesis being that the oxide-forming elements will show more ion release when compared to the Au-Pt precious metal elements and that the oxide-forming elements would show varying degrees of ion release when compared to each other.

Materials and Methods

Sample preparation

The compositions of alloys are either expressed as weight percentage (wt%) or atomic percentage (at%). Although wt% is the more commonly used description, biological and chemical properties are best understood by knowing the at% as it better predicts the number of atoms available to be released and affect the body (7, 18). Therefore, chemical compositions of the experimental alloys were designed on the atomic percentage basis in the present study. A binary Au-10 at% Pt alloy (referred to as AP10) was designed as a parent alloy. Six ternary AP10-X (X = In/Fe/Sn/Zn) alloys and four quaternary (AP10-In₂)-Y (Y = Fe/Sn/Zn) alloys were designed and the amount of oxide-forming elements X and Y were restricted up to 2 at%.

All the experimental alloys were prepared from high-purity component metals (Ishifuku Metal Industry Co., Ltd., Tokyo, Japan). Appropriate amounts of component pure metals were melted in a high-frequency induction furnace and the ingots obtained were subjected to cold rolling and homogenizing heat-treatments at high temperatures using exactly the same processes used to produce commercial dental alloys. A number of plate samples with size 10X10X0.5 mm³ were obtained. The analyzed composition in atomic percentage of the twelve alloys used in the study can be seen in Table 1. A commercially produced Au-Pt-based alloy BiOcclus 4[®] (DeguDent GmbH, Postfach 1364 63403 Hanau, Germany) was used as a control.

All twelve alloys were then lost wax cast into square plates 10X10X0.5 mm³ and ground smooth. Two samples of each of the alloys were tested. The pieces of alloy were put through the oxidising, opaque and main porcelain firing cycles as would normally be performed during a metal-ceramic restoration construction. All the square plates were then polished to a clinically acceptable state on both sides and on

the edges using fine stones (Meisinger, Germany), rubber wheels (Identoflex AG, Buchs SG, Switzerland) and bristle brushes and fine lambs wool mops (C&LE Attenborough Ltd, Nottingham, UK) loaded with universal polish (yellow and green polish for precious metals, Metrodent, Huddersfield, UK) to replicate the exposed palatal/lingual gingival collars of finished restorations.

Ion release

Each alloy sample was then immersed in 20 ml of deionised water (pH value 7.0) for 5 minutes. The samples were then removed from the water and immersed in 20 ml of Sprite Light[®] (A popular, erosive, sugar free soft drink with a pH value of 2.91 – 2.98, The Coca Cola Co., Uxbridge, UK) for a further 5 minutes or 2 hours at 37°C. Each sample was placed in a tapered centrifuge tube, so that all the surfaces were exposed to the deionised water or Sprite Light[®].

All the test solutions were analysed by Inductively Coupled Plasma-mass Spectrometry (ICP-MS Agilent 4500, Agilent Technologies, Santa Clara, CA 95051, USA). ICP-MS detection limits for the target elements in the 12 alloys are given in Table 2. All the test solutions were acidified with 200µl of nitric acid (for Au determination) or hydrochloric acid (for all other ions). For each analysis the instrument performed 5 measurements and calculated the mean and relative SD (%) for each element. Thus, with the two samples tested in each group, the total number of measurements recorded per element was 10. The surface area of the plates to the volume ratio of Sprite Light[®] solution was 0.055 cm² mL⁻¹, which is below the range 0.5-6.0 cm² mL⁻¹ recommended by the ISO standard 10933 (19). As no biological studies were being performed for the present alloys, ratios of our experimental sample surface area to Sprite Light[®] solution volume were considered acceptable (19, 20).

Statistical analysis

The results were analysed using two-way analysis of variance (ANOVA) at the 95% confidence level ($P = 0.05$). The Newmans-Kuel multiple comparison summary was used to indicate significant differences. Individual comparisons were analysed by using a paired t -test.

Results:

Figures 1 to 4 show the results for the elements Fe (Figure 1), Zn (Figure 2), In (Figure 3) and Sn (Figure 4) in both the ternary, quaternary and control alloys. It should be noted that the scales of the horizontal axis are significantly different from each other reflecting the marked difference in the amount of ions dissolved. Figures 1 to 4 clearly show the order of the amount of dissolved ions, this order being Fe > Zn > In > Sn. When looking at the individual elemental ion release the elements more usually associated with base metal alloys (Fe & Zn) showed significantly more ion release than those more usually associated with the precious or noble alloys (In & Sn). In the current study, we focused our attention on the amounts of base-metal ions released from the experimental alloys into the test solutions. Therefore, the results for Au and Pt ions were not presented in graphs.

Fe was the most soluble element between the four base metal elements (In/Fe/Zn/Sn) examined (Figure 1), followed by Zn (Figure 2), In (Figure 3) and Sn (Figure 4). The least soluble element was Sn (Figure 4). The Fe, Zn and Sn elements showed much more solubility in the Sprite Light[®] than the deionised water. However, In did not show such a clear trend (Figure 3). The Fe element showed significantly higher levels of ion release than all the other elements for all three testing conditions (deionised water, 5 minutes Sprite Light[®] and 2 hours Sprite Light[®]) ($P < 0.05$). Zn also produced significantly more ion release when compared to Au, Pt ($P < 0.05$). Table 3 shows the details of elemental ion release in the three solutions used and which individual elemental comparisons showed significant differences.

Discussion

This work does agree with the findings of others that the elements more commonly associated with non-precious alloys (Fe and Zn) are the ones more susceptible to ion release compared to those more commonly found in precious or noble alloys (In and Sn). This could be explained by the fact that the non-precious alloys tend to be more heterogeneous in nature than the precious or noble alloys and show increased corrosion rates than the precious and noble alloys (21, 22, 23).

To try to explain the observed order of metal ion release found in this study the following explanations may be helpful: The observed order of metal ion release in this study were basically as follows with a few exceptions Fe > Zn > In > Sn > Pt > Au. According to Pourbaix (24) the order of nobility, according to immunity and passivity, of the elements used in this study is: (noble) Au > Pt > Sn > In > Fe > Zn (less noble). This order explains the experimental results found in this study with the exception of Fe and Zn. To try to explain the remarkable release of Fe ion found in this work three possible reasons could be provided.

Firstly, low pH value of the test solution (Sprite Light[®]), chosen because it is a typical popular, sugar free, non-alcoholic beverage, is suggested to cause increased dissolution of each base metal elements, as the previous studies (10, 25, 26) showed that acidic foodstuffs and drinks contributed to increased ion release. The pH value of Sprite Light[®] was in a range of 2.91 to 2.98 compared to a pH of 7.0 for the deionised water. Fe and Zn were found to be more soluble in the Sprite Light[®] than the deionised water, which would confirm thinking that the more acidic liquids entering the oral environment are more likely to cause damage to metallic restorations. For

these reasons alone it would be prudent to design metal-ceramic restorations to show as little of the metal collar as possible above the gingival margin.

Secondly, if the test solution (Sprite Light[®]) contained chloride ions the protectiveness of Fe oxide may be reduced (24). Fe would then become less “noble” and more “anodic” and more susceptible to ion release. Sprite Light[®] does not appear to contain chloride ions but does contain sodium benzoate and sodium citrate (27), both of which have similar chemical compositions to sodium chloride (sodium chloride = NaCl, sodium benzoate = NaC₆H₅CO₂, sodium citrate = Na₃C₆H₅O₇). Sodium benzoate has been found to cause an oxide less passivity in iron (28), leading to the promotion of Fe ion release in Sprite Light[®].

The third reason relates to the thermodynamics of the solvent element Au and the solute element Fe. That is, the enthalpy of formation, ΔH , is positive at 1123°K for the solid Au phase containing small amounts of Fe in the Au-Fe system (29). This suggests that the Fe atoms tend to segregate themselves in the solvent Au. On the other hand, the enthalpy of formation, ΔH , is negative at 1080°K for the Au-Zn system (30). This suggests that Zn and Au atoms are well mixed and that the surrounding Au atoms may protect the Zn atoms, which would not be the case with the Au-Fe system. The melting range of the present experimental alloys was from around 1040 to 1140°C. This temperature range is significantly higher than the above quoted temperatures at which thermodynamic data are given. Therefore, it is reasonable to consider that the above-mentioned interactions between constituent elements may occur during the solidification process.

The findings from this work proved the hypothesis that the oxide-forming elements did show more tendency to release ions than the noble Au and Pt elements and that certain oxide-forming elements more likely to be found in base metal-

ceramic systems (Fe and Zn) are more likely to release ions than those found in noble metal-ceramic systems (In and Sn). It is noted that the effects of concentrations of the base metal elements added to the parent alloy on the amount of ion release were not prominent compared with those of the element itself in both deionised water and Sprite Light[®]. This implies that the test solution is more sensitive to a base-metal element than their concentrations. This agrees with a previous report by Wataha *et al* (9).

Conclusions

Within the limitations of the study, only 2 test pieces per alloy being available for testing, the following conclusions were made:

- The oxide-forming base metal elements showed significantly more ion release than the precious or noble metal elements.
- When looking at the individual elemental ion release, the order of the amount of dissolved ions was Fe>Zn>In>Sn.
- Fe showed significantly higher levels of ion release than the other base metal elements (Zn, In, Sn) for all three testing conditions ($P<0.05$).
- When looking at the effects of test solution on ion release from the alloys, Sprite Light[®] caused significantly higher level of ion release than deionised water for Fe and Zn elements.
- Sn and In elements showed less ion release than the Fe and Zn elements. Accordingly, from the viewpoint of chemical stability in the oral environment, Sn and In elements should be recommended as oxide-forming elements in Au-Pt-based high noble metal-ceramic systems.

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Figure and Table Legends

Figure 1

The absolute amount of Fe ions released from the ternary and quaternary Au-Pt-based noble alloys tested in the study when immersed in deionised water followed by Sprite Light[®] (SL) for 5 minutes or 2 hours.

Figure 2

The absolute amount of Zn ions released from the ternary and quaternary Au-Pt-based noble alloys tested in the study when immersed in deionised water followed by Sprite Light[®] (SL) for 5 minutes or 2 hours.

Figure 3

The absolute amount of In ions released from the ternary and quaternary Au-Pt-based noble alloys tested in the study when immersed in deionised water followed by Sprite Light[®] (SL) for 5 minutes or 2 hours.

Figure 4

The absolute amount of Sn ions released from the ternary and quaternary Au-Pt-based noble alloys tested in the study when immersed in deionised water followed by Sprite Light[®] (SL) for 5 minutes or 2 hours.

Table 1

The chemical composition (at%) of the 12 Au-Pt-based noble alloys used in the study.

Table 2

Inductively coupled plasma-mass spectrometry detection limits for the individual elements used in the 12 alloys used in the study.

Table 3

The individual elemental comparisons after immersion in deionised water followed by Sprite Light[®] for 5 minutes or 2 hours.

Significant differences were seen between the following elements ($P < 0.05$):

Deionised water: j-adgmpsv, m-adgpsv, p-dgsv, g-adv.

Sprite Light[®] 5 minutes: k-behnqtw, n-behqtw, h-betw, q-betw.

Sprite Light[®] 2 hours: l-cfirux, o-cfirux, i-cfrux, c-rux, f-rux, r-ux.

Figure 1

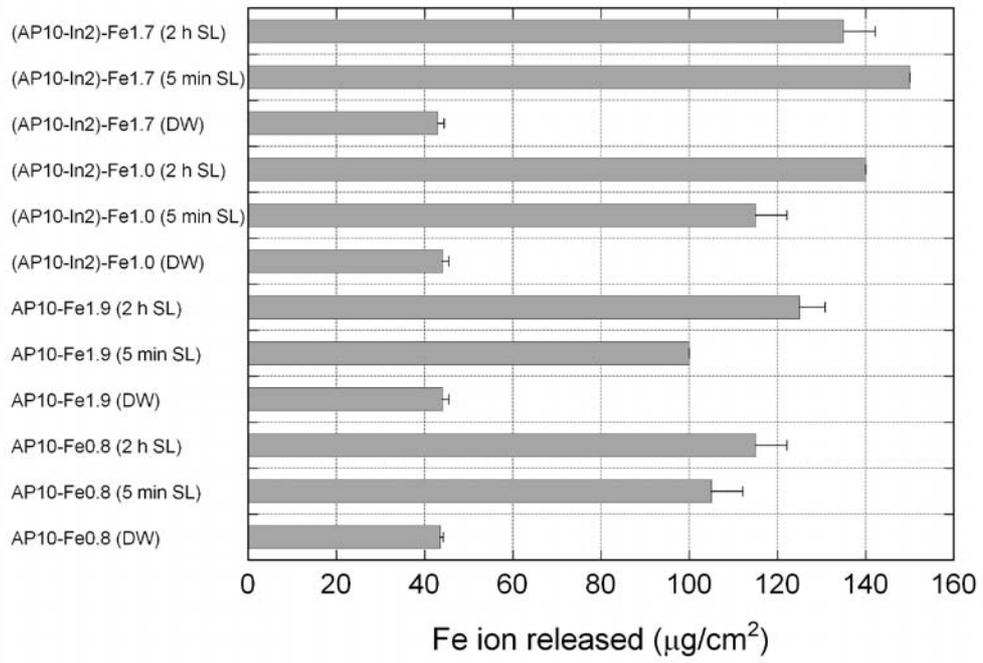


Figure 2

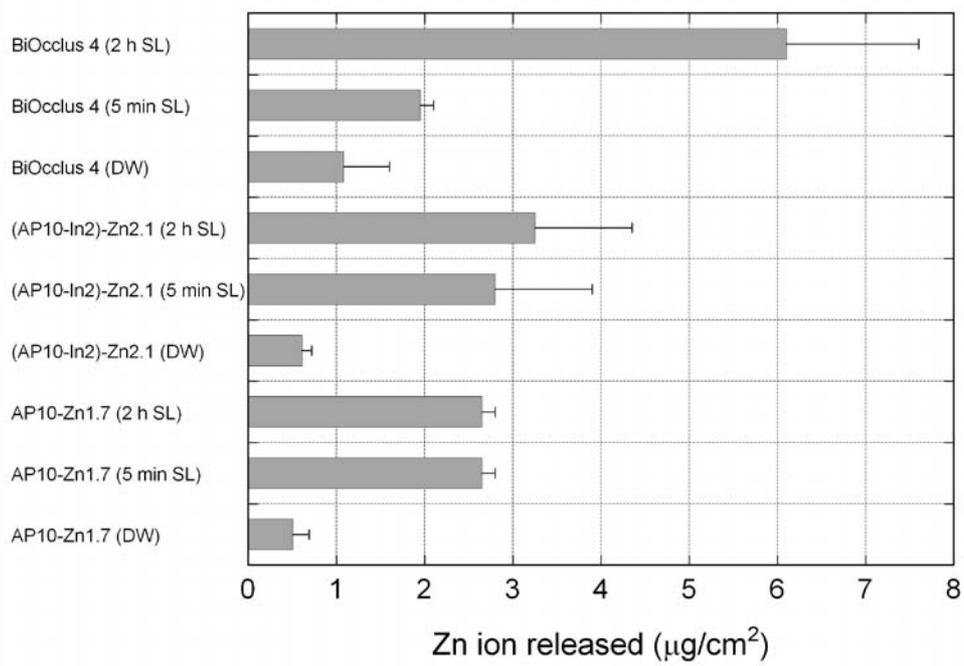


Figure 3

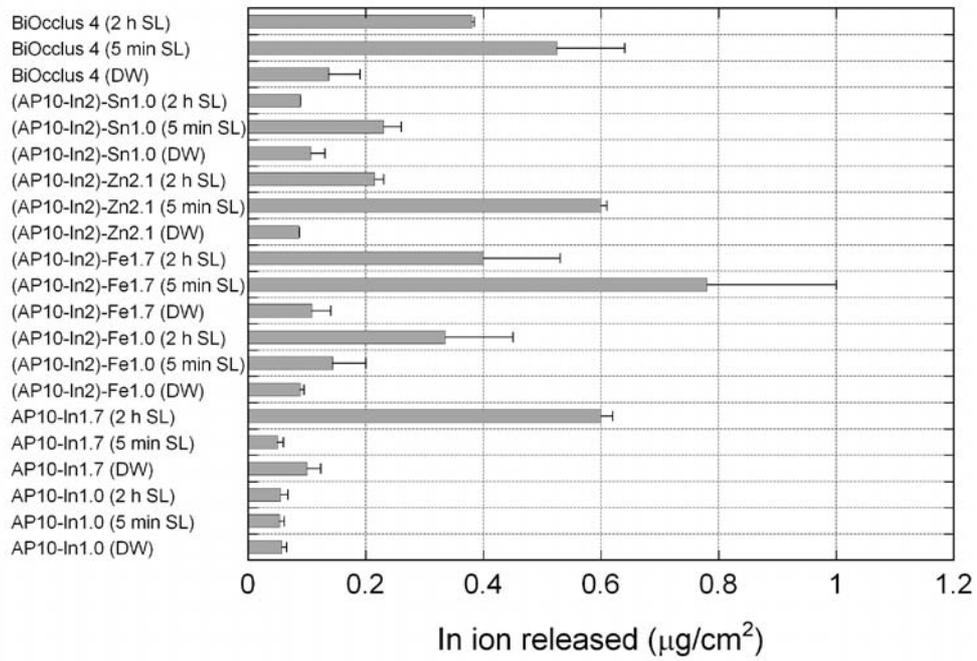


Figure 4

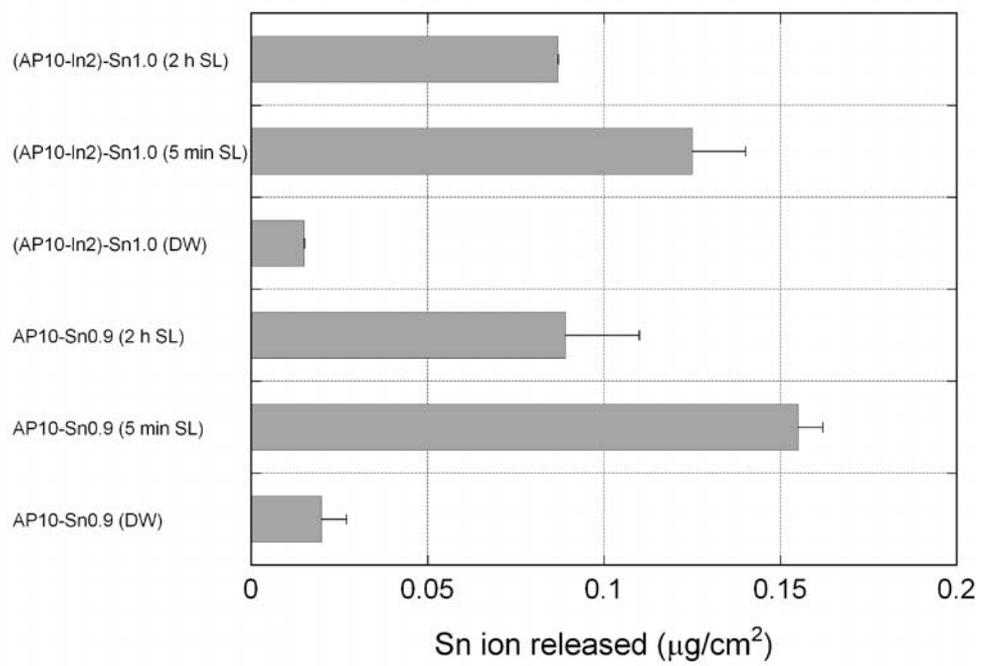


Table 1

Alloys	Au	Pt	In	Fe	Zn	Sn	Rh & Ta
AP10	90.1	9.9	0	0	0	0	0
AP10-In1.0	89.1	9.9	1.0	0	0	0	0
AP10-In1.7	88.4	9.9	1.7	0	0	0	0
AP10-Fe0.8	89.2	10.0	0	0.8	0	0	0
AP10-Fe1.9	88.3	9.8	0	1.9	0	0	0
AP10-Zn1.7	88.5	9.8	0	0	1.7	0	0
AP10-Sn0.9	89.2	9.9	0	0	0	0.9	0
(AP10-In2)- Fe1.0	87.3	9.7	2.0	1.0	0	0	0
(AP10-In2)- Fe1.7	86.6	9.7	2.0	1.7	0	0	0
(AP10-In2)- Zn2.1	86.3	9.6	2.0	0	2.1	0	0
(AP10-In2)- Sn1.0	87.3	9.8	1.9	0	0	1.0	0
BiOcclus 4	83.3	10.8	2.8	0	1.5	0	1.6

Table 2

Elements	Detection limits (ng L ⁻¹)
Pt, Zn, Sn, Rh, Ta	1
In	3
Fe	5
Au	6

Table 3

Element	Ion Release ($\mu\text{g}/\text{cm}^2$)		
	Deionised Water	Sprite Light [®] 5 min	Sprite Light [®] 2 hrs
Au	0.019 (a)	0.017 (b)	0.136 (c)
Pt	0.108 (d)	0.038 (e)	0.116 (f)
In	0.291 (g)	0.341 (h)	0.467 (i)
Fe	43.6 (j)	117.5 (k)	128.7 (l)
Zn	0.733 (m)	2.46 (n)	4 (o)
Sn	0.017 (p)	0.14 (q)	0.088 (r)
Rh	0.005 (s)	0.004 (t)	0.008 (u)
Ta	0.02 (v)	0.02 (w)	0.028 (x)