Long-term urinary platinum, palladium, and gold excretion of patients after insertion of noble-metal dental alloys

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The aim of this study was to investigate to which extent noble-metal dental alloys contribute to the total platinum (Pt), palladium (Pd), and gold (Au) body burden of the general population. The urinary Pt, Pd, and Au excretion was determined in three non-occupationally exposed volunteers before and up to 3 months after insertion of a high-gold dental alloy. The *in-vitro* release of Pt, Pd, and Au from four different types of dental alloys into either artificial saliva or 1% lactic acid solution was additionally investigated. The Pt, Pd, and Au concentrations were determined by sector field inductively coupled plasma mass spectrometry (SF-ICP-MS). Before insertion of the high-gold dental alloy, the Pt excretion of the patients ranged between 1·0 and 7·4 ng l^{-1} (0·6–3·3 ng g^{-1} creatinine). In the immediate post-insertion phase the Pt excretion rose to 10·5–59·6 ng l^{-1} (14·5–33·2 ng g^{-1} creatinine). This is a mean increase by a factor of 12 compared with the average Pt excretion before insertion. Three months after insertion, the Pt excretion was still elevated by a factor of 7. Contrary to Pt, the Au and Pd excretion in urine was not significantly increased after insertion of this type of high-gold dental alloy. Our *in-vitro* investigations confirm the assumption that Pt, Pd, and Au are released from noble metal-containing dental alloys by corrosion. Under the applied conditions, the release was in the lower ng cm^{-2} range. It can be concluded that the Pt release from dental alloys can predominantly contribute to the Pt exposure of non-occupationally exposed persons. It can exceed the exposure from all other environmental sources including the Pt release from automobile exhaust catalysts.

Keywords: Pt, Pd, Au, urine, dental alloys

Introduction

In the past two decades, the safety of amalgam (containing about 50% of mercury) as restorative material in dentistry has been discussed controversially, and this has led to the result that several countries have restricted its usage. As a consequence, alternatives to dental amalgam have been developed and an increasing number of dental casting alloys has appeared on the market. The high price of gold has led to the substitution of high-gold alloys by alloys in which gold is partly replaced by palladium (so-called gold-reduced or high-palladium alloys). In the meantime, many people have had their dental amalgam fillings removed and replaced by such noble metal inlays or bridge work.

Despite the wide use of these dental alloys, data on their corrosion behaviour, bioavailability, and the resulting internal exposure of persons bearing these alloys

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in their mouth, are still lacking. In a few papers, the *in-vitro* release of Pt, Pd, and Au from dental alloys has been reported. Schwickerath and Pfeiffer (1995), for example, found an *in-vitro* release of Au and Pt from high-gold dental alloys and a release of Au and Pd from gold-reduced alloys into artificial corrosion solutions containing lactic acid and sodium chloride, respectively. However, to date it is not known whether noble metals released from dental alloys are bioavailable and if they thus contribute to the internal human background exposure. In past years, the interest in platinum group elements has focused on their release from automobile catalysts and their possible impact on humans, but the exposure from dental restorative materials has been neglected. Though investigations of environmental samples, such as dust, soil, and grass collected near motorways indeed showed increasing Pt and Pd background concentrations (Schierl *et al*. 1996, Wäber *et al*. 1996, Zereini *et al*. 1997), recent studies indicate that Pt and Pd emissions from catalyst-equipped automobiles do not contribute to any great extent, via inhalation, to the internal background exposure of the general population (Schierl *et al*. 1994, Begerow *et al*. submitted).

Information about adverse health effects of Pd, Pt, Au and their compounds comes mainly from the field of occupational exposure and from their application in cancer therapy (Rosner and Merget 1990, Cavellier and Foussereau 1995a, b, c, Wiesmüller *et al*. 1995). Intolerability to dental alloys in the form of allergic reactions has also been reported in individual cases (Aberer *et al*. 1993, Wiesmüller *et al*. 1995, Wirz 1995, Bieger 1996, Begerow *et al*. 1997a, Wirz *et al*. 1997). Thus the possibility that the release of noble metals from dental alloys may cause local or systemic effects cannot be excluded.

Due to difficulties with their determination at ng l^{-1} and sub-ng l^{-1} concentrations in such complex matrices, only few data are available about the internal Pt, Pd, and Au exposure of humans. Only Pt baseline levels in body fluids could be successfully determined using adsorptive voltammetry (Messerschmidt *et al*. 1992). Some information about Au background levels in body fluids could be achieved by neutron activation analysis (NAA) (Minoia *et al*. 1990), a technique restricted to a very few specialized laboratories which have a nuclear reactor accessible. Recently, we presented a powerful analytical method, called sector field inductively coupled plasma mass spectrometry (SF-ICP-MS), for the determination of Pt, Pd, and Au baseline levels in body fluids; this combines rapid multi-element analysis with excellent detection limits. SF-ICP-MS is a new, very promising technique for ultratrace analysis. It enables the determination of Pt, Pd, and Au background concentrations in body fluids within a single run (Begerow *et al*. 1997b, c, d).

The aim of the investigations presented in this paper was to compare the urinary Pt, Pd, and Au excretion of persons before and following insertion of a high-gold dental alloy. For complementary information, the corrosion behaviour of four different types of dental alloys was tested *in-vitro* in two different artificial media (artifical saliva, 1 % lactic acid).

Materials and methods

Instrumentation

The Pt, Pd, and Au determinations in urine, artificial saliva, and lactic acid solution were performed by sector field ICP-MS (ELEMENT by Finnigan MAT, Bremen, Germany), the operating conditions

Table 1.   Instrumental operating conditions.

Instrument	ELEMENT, Fa. Finnigan MAT
Resolution	$m/\Delta m = 300$
R.F. power	$1\cdot30$ kW
Pump speed	$1\cdot4$ ml min^{-1}
Scan type	Magnetic jump with electric scan
Integration time	50 ms
Torch	Fassel Torch
Nebulizer	Meinhard TR-30-A3
Spray chamber	Scott Typ ('double-pass') at 20 °C
Cones	Ni (high performance)
Auxiliary gas	Argon, $0\cdot8$ l min^{-1}
Coolant gas	Argon, $13\cdot3$ l min^{-1}
Nebulizer gas	$0\cdot7$ l min^{-1}
Wash time	3 min
Mass ranges	$104\cdot643$ – $105\cdot167$ (^{105}Pd)
	$105\cdot639$ – $106\cdot168$ (^{106}Pd)
	$193\cdot6$ – $194\cdot286$ (^{194}Pt)
	$194\cdot6$ – $195\cdot291$ (^{195}Pt)
	$195\cdot6$ – $196\cdot292$ (^{196}Pt)
	$196\cdot6$ – $197\cdot295$ (^{197}Au)
Passes	5
Runs	2
Sample time[a]	$0\cdot025$ s
Scan time[b]	8 s
Total number of samples[c]	480

[a] Dwell time (in s) per measuring point. A sample is described as a data pair made up of a mass and its intensity.
[b] Made up of the individual sample times, time for one run.
[c] Quotient of the scan duration and the sample time of all segments of a measuring programme.

are summarized in table 1. The instrument was operated in an air-conditioned laboratory (18–22 °C) equipped with a filter to remove dust particles ($\geq$99·997 % for particles of 0·3 μm).

Reagents and standard solutions

To reduce the risk of contamination from ambient air and dust all work was performed on a clean bench. Before use, all materials (pipettes, vials) and chemicals were randomly checked for contamination which means that the blanks were determined regularly on a statistical basis. Polyethylene vials were effectively cleaned by soaking in HNO_3 (1 + 2 diluted with ultrapure water, 50 °C, 30 min). The vials were then rinsed with ultrapure water and dried at 50 °C.

Commercially available ultrapure HNO_3 (> 69·5 % 'TraceSelect', by Fluka, Neu-Ulm, Germany) was purified by sub-boiling distillation in a quartz device (Hans Kürner Analysentechnik, Rosenheim, Germany). By this purification step, a significant decrease of the very low Pt, Pd, and Au background levels was achieved (Begerow *et al.* 1997d).

Sample collection and storage

Urine: The study group consisted of three volunteers (two women and one man, aged between 20 and 34 years) with no known exposure to noble metals, having no inlays or bridge work made of noble metal-containing alloys in their mouths. Morning urine samples were collected in acid-washed polypropylene bottles on at least two different days before insertion of a high-gold dental alloy (Degunorm™, by Degussa) and at day 1–14, 21, and 1–3 months after insertion. The noble metal inlays or bridge work were placed in between eight and ten teeth. The insertion was carried out in one single treatment.

For stabilization purposes, the samples were acidified with concentrated HNO_3 ('TraceSelect', by Fluka 69·5 %, purified by sub-boiling distillation, 1 ml per 100 ml of urine) and stored at –20 °C until analysis.

Artificial saliva : Cubes (edge length 0·5 cm, surface area: 1·5 cm^2) of four different types of dental alloys (Degunorm™, Degulor M™, Degupal G™, Deva 4™, all available from Degussa, Frankfurt am Main, Germany) were incubated for 7 days in artificial saliva (Glandosane by Fresenius, Taunusstein,

Table 2.   Alloy composition (weight %).

	Au	Pd	Pt	Type of alloy
Degunorm™	73·8	< 0·5	9·0	High-gold
Degupal G™	4·4	77·3	< 0·5	High-palladium
Degulor M™	70·0	2·0	4·4	High-gold
Deva 4™	51·1	38·5	< 0·5	Gold-reduced

Germany, pH 5·1) at 37 °C in a drying cupboard. In a second series of *in-vitro* tests, 1 % lactic acid solution (made from DL-lactic acid purum (90 %, by Fluka, Neu-Ulm, Germany, pH 2·6) was used instead of artificial saliva.

The Pt, Pd, and Au content of the four different dental alloys (as given by the manufacturer) is summarized in table 2.

Sample preparation

Urine: UV photolysis was carried out with a digester UV–1000 (Hans Kürner Analysentechnik, Rosenheim, Germany) using a 1000-W medium-pressure Hg lamp. Before dividing into aliquots, the sediment of the urine samples was distributed as homogeneously as possible by rigorous shaking to get a representative portion of the specimen. Then, 5-ml aliquots of the acidified urine samples were mixed with 200 µl of H_2O_2 ('Suprapur' by Merck, Darmstadt, Germany) and digested for 15 min at a water cooling flow of $0·9$ ml min^{-1}, resulting in a sample temperature of about 70 °C. Then a second 200 µl portion of H_2O_2 was added and photolysis was continued for another 15 min. After addition of a third 200 ml portion of H_2O_2 and further irradiation for another 15 min, photolysis was complete, resulting in clear colourless solutions. Afterwards, the digested sample solutions were transferred to 10-ml quartz vials and made up to 10 ml with 0·5 % nitric acid. Two analytical blanks containing the same concentration of HNO_3 and H_2O_2 as the digested urine samples were analysed within each analytical series.

Artificial saliva and lactic acid solution: The Pt, Pd, and Au content of these solutions before and after incubation of the dental alloys was measured directly after dilution with ultrapure water to a defined volume.

Calibration

Calibration was performed by the standard addition procedure adding diluted single-element standard solutions ('for AAS' by Aldrich, Heidenheim, Germany) in 0·5 % HNO_3 (made from 'TraceSelect' by Fluka, Neu-Ulm, Germany) containing 5, 10, and 50 ng l^{-1} Pt and 50, 100, and 500 ng l^{-1} Pd and Au. These standard solutions were prepared freshly every day. The samples were analysed without spiking and spiked with the three different standard solutions.

Urine: Aliquots of 500 µl of these standard solutions were added to 500 µl of the digested urine sample and diluted with 2 ml of ultrapure water. For the unspiked samples 500 µl 0·5 % HNO_3 was added instead of the standard solutions.

Saliva: Aliquots of 100 µl of standard solution were added to 500 µl of saliva and diluted with 5400 µl of ultrapure water. For the determination of the analytical blank, 100 µl of ultrapure water was added instead of the standard solution.

1 % lactic acid solution: Aliqouts of 500 µl of standard were added to 50 µl of the lactic acid solution and diluted with 4450 µl of ultrapure water. The analytical blank was determined by adding 500 µl of ultrapure water instead of the standard solution.

After subtraction of the blank of the analytical procedure, the results of the urinary Pt, Pd, and Au determinations were adjusted according to the creatinine concentration to correct with regard to the varying degree of dilution. Creatinine levels in urine were determined using a test kit (Boehringer, Ingelheim, Germany) based on the Jaffe-reaction.

Detection limits and quality control assessment

The detection limits were calculated as the three-fold standard deviation of replicated measurements of blank values containing the same reagent concentrations as the samples. All analyses were carried out under internal quality control conditions: an internal control sample was analysed within each analytical series. As control samples with known or certified Pt, Pd, and Au concentrations are not commercially available, they were prepared in our laboratory by pooling real samples which were stored in portions in a deep-freezer at –18 to –20 °C. The day-to-day precision was calculated from this native urine sample containing 2·2 ng l^{-1} Pt, 22·4 ng l^{-1} Pd, and 23·3 ng l^{-1} Au. The average of 12 determinations of the day-to-day precision was found to be 4·9 % for Pd, 9·8 for Pt and 11·6 % for Au.

Table 3.   Blank values (mean, standard deviation, range) and detection limits of the analytical procedures.

	Blank values			Detection limits		
	Urine (*n* = 10) ng l^{-1}	Saliva (*n* = 3) ng l^{-1}	Lactic acid (*n* = 8) ng l^{-1}	Urine (*n* =10) ng l^{-1}	Saliva (*n* = 3) ng l^{-1} (ng cm^{-2})	Lactic acid (*n* = 8) ng l^{-1} (ng cm^{-2})
Pt	0·4 ± 0·08 (0·22–0·53)	12 ± 3 (10–16)	17 ± 5 (10–20)	0·2	10 (0·013)	12 (0·016)
Pd	0·4 ± 0·06 (0·36–0·54)	56 ± 6 (50–60)	36 ±3 (30–39)	0·2	17 (0·022)	90 (0·12)
Au	0·3 ± 0·06 (0·23–0·4)	143 ± 12 (130–150)	101 ± 24 (81–119)	0·2	35 (0·046)	51 (0·063)

In the case of Pt in urine, external quality control was achieved by participation in an interlaboratory comparison programme (Deutsche Gesellschaft für Arbeits- und Umweltmedizin, DGAUM, Erlangen, Germany) including urine samples for the analysis of environmental Pt concentrations. The designated Pt concentration of the circulating urine sample was 22·72 ng l^{-1}, our result was 23·05 ng l^{-1}.

Results

The SF-ICP-MS instrument in combination with appropriate sample preparation steps allows the extremely sensitive and precise determination of Pt, Pd, and Au in human urine samples (before and following insertion of noble-metal dental alloys) as well as in artificial saliva and lactic acid solutions (before and after incubation of noble-metal dental-alloy test specimen). Though all work was done under ultraclean conditions using ultrapure reagents, Pt, Pd, and Au blank values of the applied analytical procedures exceeded the instrumental background. The blank values for the determination for the Pt, Pd, and Au determination in urine, artificial saliva, and 1% lactic acid solution as well as the resulting detection limits are listed in table 3. Nevertheless, the blank values and detection limits for Pt, Pd, and Au are distinctly below the concentrations which were found in saliva and lactic acid samples following incubation with the dental-alloy test specimen and in the urine samples before and after insertion of the dental alloy.

The results of the Pt analyses in the urine samples of the three volunteers are illustrated in figure 1. Before insertion of the high-gold dental alloy, the mean Pt excretion of the patients on three different days ranged between 1·0 and 7·4 ng l^{-1} (0·6–3·3 ng g^{-1} creatinine). In the immediate post-insertion phase (up to 7 days after insertion), the mean Pt excretion (mean of days 1–7 after insertion) rose significantly to concentrations between 10·5 and 59·6 ng l^{-1} (14·5–33·2 ng g^{-1} creatinine). During the first 7 days after insertion, an increase by a factor of 12 on average was observed compared with the mean Pt excretion before insertion. Three months after insertion, the Pt excretion was still elevated by a factor of 7. Although Au was the main component of this type of high-gold dental alloy (see table 2), its urinary excretion did not significantly rise after insertion of this alloy. The urinary Au excretion of the three patients ranged between 6·1 and 184·3 ng l^{-1} (10·4–110·1 ng g^{-1} creatinine) before insertion and between 19·9 and 187·7 ng l^{-1} (10·4 and 335·8 ng g^{-1} creatinine) in the first 7 days after insertion. The Pd excretion was also not increased after insertion of the dental alloy, but this was expected due to the composition of the dental alloy having a Pd content of < 0·5 %. The urinary Pd excretion was found to range between 12·4 and 121·4 ng l^{-1} (4·7–110·5 ng g^{-1} creatinine) before insertion, and between 20·2 and 143·2 ng l^{-1} (19·3–72·3 ng g^{-1} creatinine) after insertion of this type of dental alloy.
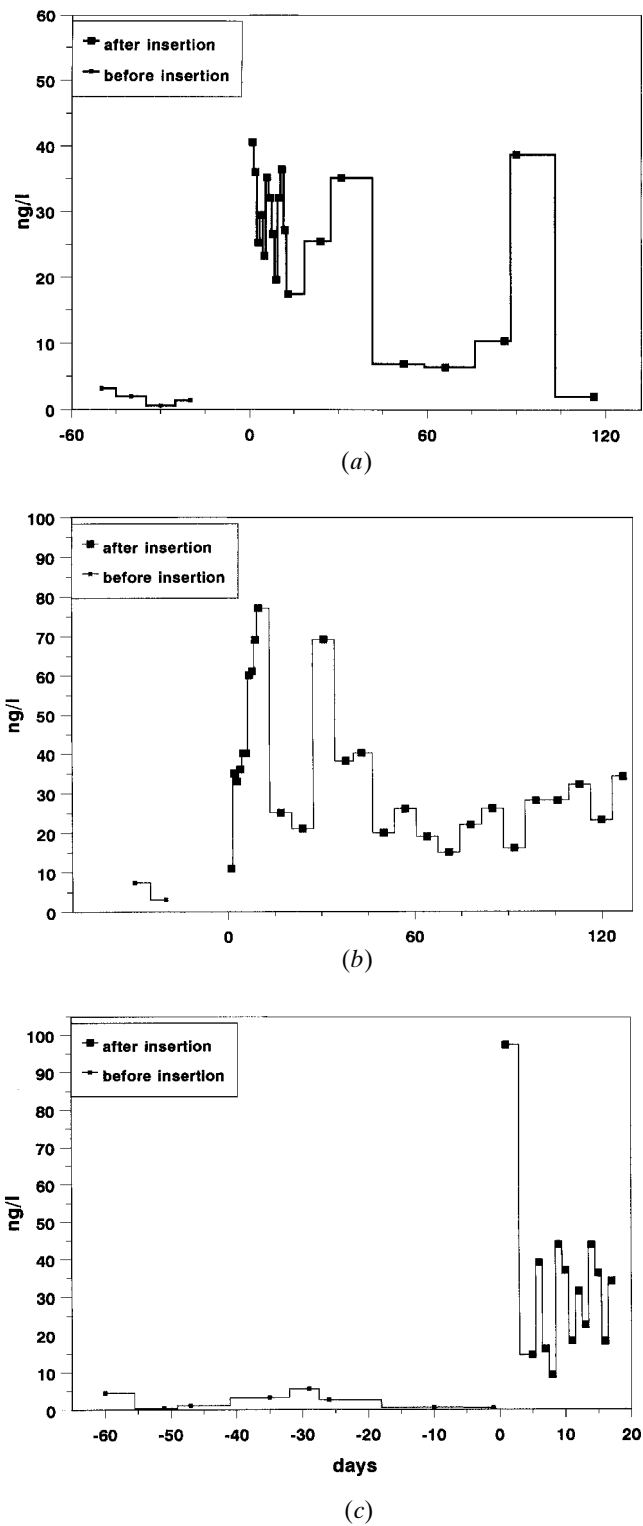
Figure 1.   Platinum excretion of three patients before and after insertion of a high-gold dental alloy.

Table 4.   Results (mean ± standard deviation) of the incubation tests ($n = 4$) given in ng cm^{-2}.

Type of alloy		Au	Pd	Pt
(a) Artificial saliva				
Degunorm™	High-gold	1·2 ± 0·1	0·3 ± 0·1	3·4 ± 0·4
Degupal G™	High-palladium	1·1 ± 0·2	71·7 ± 8·1	0·1 ± 0·02
Degulor M™	High-gold	1·3 ± 0·2	0·5 ± 0·07	8·2 ±1·6
Deva 4™	Gold-reduced	1·5 ± 0·4	15·4 ± 1·1	0·1 ± 0·03
(b) 1 % lactic acid solution				
Degunorm™	High-gold	1·3 ± 0·5	0·9 ± 0·07	0·3 ± 0·04
Degupal G™	High-palladium	1·5 ± 0·4	25·5 ± 6·1	0·1 ± 0·02
Degulor M™	High-gold	1·8 ± 0·5	0·6 ± 0·17	0·2 ± 0·03
Deva 4™	Gold-reduced	1·9 ± 0·6	2·3 ± 0·6	0·1 ± 0·08

Our *in-vitro* investigations confirm that a corrosion and dissolution of Pt, Pd, and Au occurs which depends on the type of the alloy and the composition of the incubation solution. The results (means of four parallel experiments) of the *in-vitro* tests are summarized in table 4. Regarding Pt and Pd, the solubility was higher in artificial saliva than in 1 % lactic acid. The release of alloy elements from the four different cubes of the same alloy was reproducible, the coefficient of variation was generally below 20 %.

The dental alloys Degunorm™ and Degulor M™ (both high-gold alloys) containing 9·0 and 4·4 % Pt, respectively, release distinctly higher amounts of Pt (3·4 and 8·2 ng cm^{-2}) into the artificial saliva test solution than the other dental alloys (Degupal G™, Deva 4™), the Pt share of which is lower than 0·5 %. Nevertheless, Pt is also released from these types of dental alloys, but at distinctly lower rates (0·1 ng cm^{-2}). Using 1 % lactic acid (pH 2·6) instead of artificial saliva (pH 5·1), the release was lower, indicating differences in the corrosion behaviour between the test solutions.

Degupal G™, a high-palladium alloy containing 73·8 % Pd, released more Pd into the articificial saliva than the gold-reduced alloy (Deva 4™) containing 51·1 % Pd and both high-gold alloys containing < 0·5 % and 2·0 % Pd, respectively. Similar to Pt, the Pd solubility was also higher in artificial saliva than in 1 % lactic acid.

Contrary to Pd and Pt, Au did not dissolve to such an extent into the test media. Au release was not related to its content in the test alloys and ranged between 1 and 2 ng cm^{-2} in both test media.

Discussion

The mean urinary Pt, Pd, and Au excretion of the three volunteers before insertion of the high-gold dental alloy corresponded well to the background levels reported in former papers (Minoia *et al.* 1990, Messerschmidt *et al.* 1992, Begerow *et al.* 1996b). In a previous study (Begerow *et al.* 1997b) in which we determined the urinary Pt and Pd excretion in 21 unexposed volunteers (adults), we found Pd levels between 32·7 and 219·7 ng l^{-1} and Pt levels between 0·5 and 7·7 ng l^{-1} for Pt. The urinary Au excretion in these 21 persons ranged between 10·3 and 312 ng l^{-1} (Begerow *et al.* in press). Regarding Pt, our results are also in complete accordance with those of Messerschmidt *et al.* (1992). These authors, who used adsorptive voltammetry for the determination of urinary Pt background levels in 14 unexposed persons, reported Pt concentrations between 0·5 and 14·3 ng l^{-1}. Data on

physiological Au levels in blood have been published by Minoia *et al*. (1990) who applied neutron activation analysis. In healthy subjects with no known exposure, they found urinary Au concentrations from 30 to 850 ng l^{-1} ($n = 43$).

Contrary to Pt, the urinary Au concentrations did not significantly increase after insertion of this type of dental alloy. This finding may, on one hand, be explained by the, in comparison to Pt, relatively high, urinary background levels originating from other environmental sources and, on the other hand, by the relatively low dissolution rate of Au which we found in our *in-vitro* experiments. The Pd excretion did also not increase following insertion of this type of dental alloy, but this can be explained by the very low Pd content of this type of alloy (< 0·5 % according to the manufacturer).

In spite of the small number of volunteers, the results clearly show that the Pt release from dental alloys can predominantly contribute to the Pt exposure of non-occupationally exposed persons. This exposure from dental alloys can exceed the exposure from all other environmental sources including the Pt exposure from traffic exhaust caused by the Pt release from automobile exhaust catalysts. In a former study we were able to show the Pt excretion of heavily traffic-exposed road construction workers was comparable with that of the general population indicating that emissions from catalyst-equipped automobiles do not contribute to any great extent via the inhalative path to the internal Pt and Pd exposure. (Begerow *et al*. submitted).

Our *in-vitro* experiments confirm the results of former papers (Schwickerath 1988, Watanabe *et al*. 1991, Schwickerath and Pfeiffer 1995,) that noble metals are released from noble-metal dental alloys into *in-vitro* test media. They also show that Pt, Pd, and Au were released at different rates from these dental alloys and that these rates depend upon the composition of the test medium and the type of dental alloy, but primarily not on the abundance of the element in the alloy. Our findings that the Pt and Pd solubility from noble-metal dental alloys is higher in the artificial saliva than in the lactic acid test medium confirms the results of a former study by Schwickerath (1988) who found a higher solubility of noble-metal dental alloys at pH 4·2 than at pH 2·0. Schwickerath reported that the Pd release of high-Pd alloys at pH 4·2 ranged between 10 and 80 ng cm^{-2} per day. This is in good accordance with the results of this study in which we found a Pd release of 71·2 ng cm^{-2} per 7 days for a high-Pd alloy (Degupal G™). Regarding the gold-reduced alloy Deva 4™, a Pd release of 130 ng cm^{-2} for the first day of incubation was reported in a paper by Kappert *et al*. (1995). As test medium they used a 0·1 mol l^{-1} sodium chloride/lactic acid solution at pH 2·3. The same authors were able to show that the solubility per cm^2 and day decreases during the first 10 days of incubation. According to table 4, we found a Pd release of 15·4 ng cm^{-2} after an incubation time of 7 days with artificial saliva, and of 2·3 ng cm^{-2} per 7 days with 1 % lactic acid solution as test medium. The differences between the release rate presented by Kappert *et al*. (1995) and our results may be explained by the longer incubation time used in our experiments and by the addition of chloride ions in their experiments, which have a high affinity to form chloro-complexes with Pd. These chloro complexes may dissolve into the test medium and oppose the formation of a passivation layer.

The commercially available noble-metal dental alloys exhibited a complex release behaviour which cannot be predicted from their nominal composition. This result is in principle in agreement with the findings of Watanabe *et al*. (1991) who

tested commercial dental alloys for their element release into a cell-culture medium. According to Bessing *et al*. (1987) and Kappert *et al*.(1995), the pre-treatment of the alloys (annealing, polishing, etc.) has also a decisive influence on their corrosion resistance.

Our *in-vivo* and *in-vitro* experiments support the assumption that noble-metal dental alloys can contribute to a great extent to the internal platinum background exposure of the general population. Thus, *in-vivo* investigations are urgently needed to study the behaviour and biocompatibility of different commercially available dental alloys under real-life conditions. *In-vivo* studies with noble-metal dental alloys other than Degunorm™ and a greater number of patients are in progress.

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