Cobalt, nickel and chromium release from dental tools and alloys

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Summary

Background. Cobalt–chromium alloys are used as casting alloys by dental technicians when producing dental prostheses and implants. Skin exposure and metal release from alloys and tools used by the dental technicians have not been studied previously.

Objectives. To study the release of cobalt, nickel and chromium from alloys and tools that come into contact with the skin of dental technicians.

Methods. Cobalt and nickel release from tools and alloys was tested with the cobalt spot test and the dimethylglyoxime test for nickel. Also, the release of cobalt, nickel and chromium in artificial sweat (EN1811) at different time-points was assessed. Analysis was performed with inductively coupled plasma-mass spectrometry.

Results. Sixty-one tools were spot tested; 20% released nickel and 23% released cobalt. Twenty-one tools and five dental alloys were immersed in artificial sweat. All tools released cobalt, nickel and chromium. The ranges were 0.0047–820, 0.0051–10 and 0.010–160 μg/cm²/week for cobalt, nickel and chromium, respectively. All dental alloys released cobalt in artificial sweat, with a range of 0.0010–17 μg/cm²/week, and they also released nickel and chromium at low concentrations.

Conclusions. Sensitizing metals are released from tools and alloys used by dental technicians. This may cause contact allergy and hand eczema.

Key words: allergy; alloy; chromium; cobalt; dental technicians; metal release; nickel; occupational.

Cobalt, nickel and chromium are well-known skin sensitizers. Exposure to these metals has resulted in occupational skin disease in vast numbers of workers in a wide range of occupations. Nickel exposure is frequent among cashiers, sales assistants, carpenters, locksmiths, and those working in other occupations (1–4). Chromium exposure and allergy have primarily been associated with construction workers, owing to the presence of chromium VI in cement (5, 6). However, other occupational groups, such as leather workers, cleaners, and metal workers, are also highly exposed to chromium (7). Cobalt is often used in different alloys and hard metals, in orthopaedic and dental prosthetics, as a pigment in pottery, glass, and paints, in detergents, in magnets, in cosmetic products, and in many other applications (8, 9). Occupational contact dermatitis caused by cobalt exposure in hard-metal workers, metal workers and pottery workers is well known among dermatologists, but cobalt allergy often remains unexplained (10–13). To prevent sensitization and dermatitis in workers and consumers, legislation limiting the amount of hexavalent chromium in cement and nickel in items intended for prolonged contact with the skin has been enforced, and now forms part of REACH (14). However, no such legislation exists for cobalt.

Metal exposure can be assessed by measuring how much metal is released from items and how much metal is deposited onto the skin when different tasks
involving metal-containing items are performed. Release studies can be performed with the reference test method for controlling compliance with the nickel limitation, EN1811, by immersing items in artificial sweat (15). The method has also been used to study the release of other metals (16). The dimethylglyoxime (DMG) test is much used in dermatology to show nickel release from items used by nickel-allergic patients. A cobalt spot test is also available, and can be used to indicate the release of cobalt (17). Both tests have been used to study metal release from tools and other items on the market (18–20). Skin doses of metals can now be measured with the acid wipe sampling method (21) or the finger immersion method (22), which have the advantage of relating the dose directly to the level of the metal that may cause allergy.

Dental technicians have a complex pattern of exposure to skin sensitizing chemicals, from plastics to metals. Very little information is available concerning their exposure to metals. Some studies have suggested that dental technicians are not at increased risk of developing contact allergy to metals (23, 24), whereas a study by Lee et al. (25) reported that 12.2% of dental technicians in a health examination in Korea were allergic to cobalt, 18.4% to nickel, and 24.5% to chromium. Cobalt–chromium alloys are increasingly being used as casting alloys in the manufacture and fitting of dental prostheses and implants. Moreover, many tools are used in this occupation for the construction of dentures and dental appliances. To our knowledge, no studies are available on metal release from alloys and tools used by dental technicians.

The aim of this study was to evaluate metal release from alloys and tools handled on a daily basis by dental technicians. The study was performed at the dental technology programme at the Department of Dental Medicine, Karolinska Institutet, Sweden.

Material and Methods

Study design

A selection of metal tools (n = 61) and one alloy, Remanium® wire (Table 1), considered to come into contact with the skin of dental technicians, were obtained from the stockroom of the Department of Dental Medicine. In addition, four commonly used dental alloys (Table 1) were bought from K.A. Rasmussen AS (Solna, Sweden). Solibond C plus, Wirobond C and Wirobond 280 are used by students and dental technicians, and have a similar size, shape, and composition. Phantom Metal NF is an alloy that is used by dental technology students for training purposes only, instead of gold alloys.

The selected tools were categorized as grinding tools (e.g. drill bits and grinding discs), hand-held tools (e.g. brushes, scissors, forceps, and pliers), or other tools [e.g. articulators (mechanical devices to fix casts of teeth), measuring tools, and matrix band (thin metal strip to fit around a tooth)]. Spot tests for nickel and cobalt release were performed on the tools in the stockroom, without cleaning, because students and dental technicians handle the tools unwashed. Spot testing of the dental alloys and all testing of metal release in artificial sweat were carried out in our laboratory.

Spot tests for cobalt and nickel

The cobalt spot test was prepared with 0.1% oxalic acid (purified, 99.999% metals basis; Aldrich Chemistry, St. Louis, MO, USA), 0.02% disodium-1-nitroso-2-naphthol-3,6-disulphonate (nitroso R salt; Fluka Analytical, Bangalore, India) and 5.0% sodium acetate (minimum 99.0%; Merck KGaA, Darmstadt, Germany) in deionized water (17). The dimethylglyoxime (DMG) test (Chemo-Nickel Test™; Chemotechnique Diagnostics, Vellinge, Sweden), containing DMG (1%), ammonia (9.9%), and ethanol, was bought. Both tests were stored in a refrigerator at 6°C.

The two spot tests were performed on metal parts of items, on separate areas of similar appearance on one item, or on another item of the same type if the object was too small for two tests to be performed. If an item consisted of parts with different appearances, each part was tested. For large items, only parts that come into contact with skin were tested. For both spot tests, 50 μl of test reagent was pipetted on the tip of a cotton wool stick, which was then rubbed against an item for 30 seconds. The spot test reactions were scored as positive, negative, or doubtful. A positive test is orange/clearly dark yellow for the cobalt spot test, whereas a pink colour indicates a positive DMG test. A negative test has no colour change. A doubtful test result was defined as discoulouration other than orange/clearly dark yellow for the cobalt spot test and other than pink for the DMG test. Tools were scored as positive (at least one positive spot), doubtful (no positive spots and at least one doubtful spot), or negative (only negative spots).

Metal release

The release of cobalt, nickel and chromium was studied quantitatively by immersing items in artificial sweat according to the reference test method for the EU nickel regulation (EN 1811: 2011) (15). Before immersion, items were degreased in a 0.5% [mass per mass (m/m)]
Table 1. Composition (% by weight) of dental alloys obtained from K.A. Rasmussen, Solna, Sweden, and the Department of Dental Medicine, Karolinska Institutet, Huddinge, Sweden

<table>
<thead>
<tr>
<th>Alloy, producer</th>
<th>Co</th>
<th>Cr</th>
<th>Ni</th>
<th>W</th>
<th>Mo</th>
<th>Si</th>
<th>Mn</th>
<th>Nb</th>
<th>Ga</th>
<th>Cu</th>
<th>Sn</th>
<th>Zn</th>
<th>Other elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solibond C plus</td>
<td>63.3</td>
<td>24</td>
<td>–</td>
<td>8.1</td>
<td>2.9</td>
<td>1.1</td>
<td>–</td>
<td>0.9</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Wirobond® Cb</td>
<td>61</td>
<td>26</td>
<td>–</td>
<td>5</td>
<td>6</td>
<td>1.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Fe, Ce</td>
</tr>
<tr>
<td>Wirobond® 280</td>
<td>60.2</td>
<td>25</td>
<td>–</td>
<td>6.2</td>
<td>4.8</td>
<td>4</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.9</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Phantom Metal NF</td>
<td>2.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>87.5</td>
<td>9</td>
</tr>
<tr>
<td>Remanium® wire</td>
<td>–</td>
<td>16–18</td>
<td>6–8</td>
<td>–</td>
<td>–</td>
<td>1</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>C, P, S</td>
</tr>
</tbody>
</table>

a YETI Dental-produkte GmbH, Engen, Germany.
b BEGO, Bremen, Germany.
c DeguDent GmbH, Hanau-Wolfgang, Germany.
d Dentaurum, Ispringen, Germany, Product Ref. 513-070-00.
e Trace elements.
f Used for training purposes only, instead of using gold alloys.

sodium dodecyl benzene sulfate solution (technical-grade dodecylbenzenesulfonic acid sodium salt; Sigma Aldrich, Lyon, France), and then thoroughly rinsed in deionized water (16.7 MΩ/cm). The artificial sweat solution consisted of deionized water and 0.5% (m/m) sodium chloride (≥ 99.8%; Sigma Aldrich, Copenhagen, Denmark), 0.1% (m/m) lactic acid (AnalaR®; BDH, Poole, UK), and 0.1% (m/m) urea (puriss. p.a., ACS reagent, ≥ 99.5% (T); Sigma Aldrich, Munich, Germany). Sodium hydroxide (1 m and 0.1 m (ACS reagent, Munich, ≥ 97% pellets; Sigma Aldrich, Munich, Germany) solutions were used to adjust the pH to 6.5. The solution was used within 5 hr after preparation.

All plastic materials used in the release study were acid washed for 4 hr in 10% HNO₃ (65%; Merck KGaA) and rinsed four times with deionized water prior to use, to remove possible metal contamination on the surfaces.

Twenty-one tools were selected for release studies on the basis of the outcome of the spot tests (positive, doubtful and negative items for both tests) and size of the tools (no need to disassemble, and should easily fit into a 60-ml plastic container). Therefore, grinding tools were mostly used for the release study. Each tool was measured with a calliper, and the surface area was calculated. Some tools were placed on glass beads (Ø 5 mm; Glaswarenfabrik Karl Hecht GmbH & Co. KG, Sondheim, Germany) in the container to avoid reduction of the surface area exposed to artificial sweat. The amount of artificial sweat added to each container was at least 1 ml per cm² surface area of the tool, or enough to cover the entire tool. The containers (60 ml PP plastic; Sarstedt, Nümbrecht, Germany) were closed with a lid and stored in an oven at 30°C for 1 week.

Surface area calculations were performed, and each alloy was put in a separate container. The amount of artificial sweat was approximately 2 ml/cm² for Solibond C plus, Wirobond® C, and Wirobond® 280, and 1 ml/cm² for Phantom Metal NF. Phantom Metal NF was placed on glass beads. The Remanium® wire (Ø 0.7 mm) was cut into pieces of 7 ± 0.1 cm, which were immersed in 3 ml/cm². Durations of immersion were 2 min, 30 min, 1 hr, 24 hr and 1 week at 30°C, and triplicates were made with every alloy for each time-point. For the shortest durations (2 min, 30 min, and 1 hr), the artificial sweat was preheated to 30°C before immersion of the items.

After the release period, items were taken out of the containers, and the test solution was transferred to a different plastic container (25-ml tube, PP plastic; Sarstedt) and acidified with HNO₃ (65%) to obtain a concentration of approximately 1% HNO₃ (pH < 2). The eluates were stored in a refrigerator at 6°C until analysis.

Analysis

Chemical analysis of the samples was performed with inductively coupled plasma-mass spectrometry with a hexapole collision cell (X Series II; Thermo Scientific, Waltham, MA, USA). Argon was used as carrier gas, and rhodium was used as an internal standard at a concentration of 10 ppb. Recovery for internal standards was 95–105%. Metals were monitored at mass/charge ratios (m/z) of 60 for nickel, 59 for cobalt, and 52 for chromium. No distinction was made between different oxidation states of chromium. The limit of detection (LOD) was set to 0.05 μg/l for cobalt, 0.10 μg/l for nickel, and 0.04 μg/l for chromium, calculated as three standard deviations in the blank samples.

Results

Spot tests

A total of 61 tools were tested with the DMG test and the cobalt spot test. In total, 20 (33%) of the tools were
Table 2. Results of the dimethylglyoxime (DMG) test and the cobalt spot test for 61 tools at the Department of Dental Medicine, Karolinska Institutet, Huddinge, Sweden, categorized according to type of tool.

<table>
<thead>
<tr>
<th>Test result</th>
<th>Grinding toolsa (n = 21)</th>
<th>Hand-held toolsb (n = 30)</th>
<th>Other tools (n = 10)</th>
<th>Total (n = 61)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMG test, no. of items (% of total in this category)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Positive</td>
<td>7 (33)</td>
<td>8 (27)</td>
<td>5 (50)</td>
<td>20 (33)</td>
</tr>
<tr>
<td>Negative</td>
<td>9 (43)</td>
<td>10 (33)</td>
<td>3 (30)</td>
<td>22 (36)</td>
</tr>
<tr>
<td>Doubtful</td>
<td>5 (24)</td>
<td>12 (40)</td>
<td>2 (20)</td>
<td>19 (31)</td>
</tr>
<tr>
<td>Cobalt spot test, no. of items (% of total in this category)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Positive</td>
<td>10 (48)</td>
<td>7 (23)</td>
<td>6 (60)</td>
<td>23 (38)</td>
</tr>
<tr>
<td>Negative</td>
<td>7 (33)</td>
<td>11 (37)</td>
<td>2 (20)</td>
<td>20 (33)</td>
</tr>
<tr>
<td>Doubtful</td>
<td>4 (19)</td>
<td>12 (40)</td>
<td>2 (20)</td>
<td>18 (29)</td>
</tr>
<tr>
<td>DMG test and cobalt spot test, no. of items (% of total in this category)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Negative</td>
<td>2 (10)</td>
<td>9 (30)</td>
<td>2 (20)</td>
<td>13 (21)</td>
</tr>
</tbody>
</table>

a Examples: drill bit and grinding disc.
b Examples: brush, scissors, and forceps.
c Examples: articulator [mechanical device to fix casts of teeth], measuring tools, and matrix band (thin metal strip to fit around a tooth).

scored as DMG test-positive, and 23 (38%) as cobalt spot test-positive (Table 2). Thirteen (21%) of the tools were both DMG test-negative and cobalt spot test-negative. The largest proportion of DMG test-positive tools was found in the ‘other tools’ category, whereas the largest proportion of DMG test-negative tools was found among the grinding tools, and the largest proportion of doubtful tools was found among the hand-held tools. Ten (48%) of the grinding tools were cobalt spot test-positive. Among the other two categories, 13 cobalt-positive test results were found, and most of the hand-held tools were scored as cobalt spot test-negative or doubtful. Of all 61 tools, 13 (21%) were scored negative for both the cobalt spot test and the DMG test. These were mainly hand-held tools (Table 2).

Phantom Metal NF and the cobalt–chromium alloys Solibond C plus, Wirobond® C, and Wirobond® 280 were cobalt spot test-positive (Table 4). The Remanium® wire was cobalt spot test-negative. None of the alloys was DMG test-positive, but Wirobond® C, Wirobond® 280 and Phantom Metal NF gave doubtful results.

**Metal release**

Immersion of 21 tools in artificial sweat for 1 week showed release of cobalt, nickel and chromium from all tools, except for one (no cobalt release). The ranges of release were 0.0047–820 μg/cm² for cobalt, 0.0051–10 μg/cm² for nickel, and 0.010–160 μg/cm² for chromium (Table 3).

Release of cobalt, nickel and chromium in artificial sweat was detected for all dental alloys after 1 week, with the exception of release of chromium from Phantom Metal NF, which was below the LOD (Table 4). The cobalt–chromium alloys released cobalt in the range of 0.82–2.7 μg/cm²/week, whereas the Remanium® wire released only 0.0010 μg/cm²/week. High levels of cobalt were released from Phantom Metal NF (17 μg/cm²/week). Release of nickel and chromium from all dental alloys was much lower, and ranged between 0.0046 and 0.024 μg/cm²/week for nickel, and between 0.0054 and 0.066 μg/cm²/week for chromium.

For all five alloys, the release of cobalt, nickel and chromium per hour (release rate) was calculated for each release time-point (Fig. 1). The rate of release of metals from Solibond C plus, Wirobond® C and Wirobond® 280 was highest after a short exposure time, and decreased over time. Similarly, the rate of release of cobalt from Phantom Metal NF decreased over time; however, the release after 1 week was high as compared with the other alloys. The rate of release of nickel and chromium from Phantom Metal NF and of all three metals from Remanium® wire was low, and showed no clear change over time.

**Discussion**

**Metal release**

Dental technicians are, on a daily basis, exposed to alloys and tools that contain skin sensitizing metals. Most studies concerning dentistry and metals have considered the effect of metal release from dental restorations on the health of patients (20, 26, 27). Several studies, reviewed by Leggat et al., have been concerned with the health of dental workers (28). Studies related to occupational skin disease in dental workers have mostly looked at irritant contact dermatitis resulting from wet work, contact allergy to acrylates and rubber chemicals, and latex allergy (29). Some studies have recognized dental
Table 3. Comparison of the results of the dimethylglyoxime (DMG) test and the cobalt spot test for metal release from dental tools (n = 21) immersed for 1 week in artificial sweat (tools from the Department of Dental Medicine, Karolinska Institutet, Huddinge, Sweden)

<table>
<thead>
<tr>
<th>Tool number</th>
<th>Tool category</th>
<th>DMG test</th>
<th>Cobalt spot test</th>
<th>Nickel (μg/cm²/week)</th>
<th>Cobalt (μg/cm²/week)</th>
<th>Chromium (μg/cm²/week)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>+</td>
<td>–</td>
<td>0.19</td>
<td>0.0047</td>
<td>0.010</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>?</td>
<td>?</td>
<td>2.2</td>
<td>0.33</td>
<td>160</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>+</td>
<td>+</td>
<td>1.5</td>
<td>0.049</td>
<td>0.017</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>+</td>
<td>+</td>
<td>2.0</td>
<td>0.19</td>
<td>150</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>?</td>
<td>+</td>
<td>1.3</td>
<td>0.24</td>
<td>140</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>?</td>
<td>+</td>
<td>1.2</td>
<td>0.18</td>
<td>120</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>?</td>
<td>+</td>
<td>0.96</td>
<td>260</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>–</td>
<td>+</td>
<td>0.16</td>
<td>760</td>
<td>11</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>?</td>
<td>+</td>
<td>1.5</td>
<td>58</td>
<td>83</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>–</td>
<td>+</td>
<td>0.60</td>
<td>590</td>
<td>0.050</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>–</td>
<td>+</td>
<td>0.91</td>
<td>820</td>
<td>0.24</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>+</td>
<td>–</td>
<td>10</td>
<td>0.090</td>
<td>0.49</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>+</td>
<td>–</td>
<td>1.6</td>
<td>0.12</td>
<td>91</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>–</td>
<td>+</td>
<td>0.27</td>
<td>310</td>
<td>0.015</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>+</td>
<td>–</td>
<td>7.1</td>
<td>0.47</td>
<td>0.064</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>–</td>
<td>+</td>
<td>0.43</td>
<td>720</td>
<td>0.14</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>?</td>
<td>?</td>
<td>0.043</td>
<td>0.082</td>
<td>0.14</td>
</tr>
<tr>
<td>18</td>
<td>3</td>
<td>?</td>
<td>?</td>
<td>0.0051</td>
<td>&lt; LOD&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.011</td>
</tr>
<tr>
<td>19</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>0.030</td>
<td>0.013</td>
<td>0.063</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>+</td>
<td>+</td>
<td>0.27</td>
<td>0.010</td>
<td>0.11</td>
</tr>
<tr>
<td>21</td>
<td>1</td>
<td>+</td>
<td>–</td>
<td>10</td>
<td>0.010</td>
<td>0.019</td>
</tr>
</tbody>
</table>

<sup>a</sup> Scoring: positive (+), doubtful (?), or negative (–).
<sup>b</sup> Tools are categorized as grinding tools (1), hand-held tools (2), or other tools (3).
<sup>c</sup> Total chromium.
<sup>d</sup> The value is below the limit of detection (LOD). The LOD is 0.05 μg/l for cobalt, 0.1 μg/l for nickel, and 0.04 μg/l for chromium.

Table 4. Comparison of results of the dimethylglyoxime (DMG) test and the cobalt spot test for metal release during immersion in artificial sweat for 1 week for five dental alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Spot test result&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Metal release in artificial sweat (μg/cm²/week)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMG test Cobalt spot test</td>
<td>Nickel Cobalt Chromium&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Solibond C plus</td>
<td>–+</td>
<td>0.024 2.7 0.066</td>
</tr>
<tr>
<td>Wirobond® C</td>
<td>?+</td>
<td>0.017 0.82 0.053</td>
</tr>
<tr>
<td>Wirobond® 280</td>
<td>?+</td>
<td>0.0058 1.2 0.062</td>
</tr>
<tr>
<td>Phantom Metal NF</td>
<td>?+</td>
<td>0.0046 17 &lt; LOD&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Remanium® wire</td>
<td>–</td>
<td>0.0058 0.0010 0.0054</td>
</tr>
</tbody>
</table>

<sup>a</sup> Composition in Table 1.
<sup>b</sup> Scoring: positive (+), negative (–), or doubtful (?).
<sup>c</sup> Total chromium.
<sup>d</sup> The value is below the limit of detection (LOD). The LOD is 0.05 μg/l for cobalt, 0.1 μg/l for nickel, and 0.04 μg/l for chromium.

workers, mainly dentists and dental technicians, as being at risk of sensitization to certain metals, including cobalt, nickel and chromium (25, 30), whereas some authors have suggested that their contribution to the development of allergic contact dermatitis is low (23, 24). The frequency of contact allergy to cobalt, nickel and chromium in dental technicians may be comparable to that in people working in occupations known to have a high prevalence of these allergies, such as workers in the electronics industry and construction workers (9). Furthermore, exposure of dental technicians to these metals through the handling of dental alloys has not been studied before. Nearly all alloys and tools in the present study released cobalt, nickel and chromium in artificial sweat.

The release of high levels of metals from items in this study is considered to cause a high risk of allergy for dental technicians and students. All cobalt spot test-positive tools that were immersed in artificial sweat released cobalt at between 0.010 and 820 μg/cm²/week. Seven tools released high amounts of chromium (30–160 μg/cm²/week). All DMG test-positive tools that were immersed released nickel at between 0.19 and...
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Fig. 1. The average release of cobalt, nickel and chromium per hour from dental alloys immersed in artificial sweat (according to EN 1811:2011). Chemical analysis was performed with inductively coupled plasma-mass spectrometry. Alloy compositions are shown in Table 1.

10 μg/cm²/week. Two previous tool studies have shown release of nickel from several hand-held non-powered tools, as shown by the DMG test and in artificial sweat, although dental tools were not specifically included in these studies (18, 19). The release of cobalt from the four positive spot tested dental alloys was in the range of 0.82–17 μg/cm²/week. It could also be mentioned that surface area measurement of dental tools was quite difficult to perform, as most of the tools were irregularly shaped. Nevertheless, the surface area calculations were the closest approximation possible.

The minimum amount of cobalt, nickel or chromium that is needed to induce sensitization and elicit allergic contact dermatitis is unknown. To reduce nickel allergy and nickel dermatitis, the European Commission has established a migration limit for nickel of 0.5 μg/cm²/week for articles that come into direct and prolonged contact with the skin (14). No migration limit has been established for cobalt or chromium, and there is no limit for metal release from hand-held tools. The nickel migration limit of 0.5 μg nickel/cm²/week in artificial sweat was exceeded by 13 of 21 assessed tools. Amounts of cobalt as low as 1.2 μg/cm² have elicited positive patch test reactions in cobalt-sensitive patients (16). Cobalt release at 1 week from seven of the 21 tools in the present study was approximately 50–700 times higher than this value (range 58–820 μg/cm²). Also, positive patch test reactions in chromium-sensitive patients were seen when they were tested with amounts of chromium as low as 1.04 μg/cm² (31). Seven of 21 tools in the present study released chromium in amounts well above that level (range 30–160 μg/cm²/week). Dental technicians come into short and repeated contact with most of the tested tools (approximately 1–2 min per contact), whereas contact with dental alloys can be prolonged and intensive (from 10 min to 1 hr per contact), but not on a daily basis. Moreover, for practical reasons, gloves are mostly not used by students and dental technicians. It has been previously shown that large amounts of nickel are deposited on skin after short and repeated contact with items with high nickel release, and that these deposited amounts can elicit allergic contact dermatitis (2, 32, 33). The high nickel and cobalt release from tools in the present study is therefore considered to pose an allergy risk to dental technicians, and this might also be true for chromium. However, the clinical significance of the high chromium release needs further consideration.

The release of cobalt from Phantom Metal NF at 1 week in artificial sweat was much higher than from the other four dental alloys, although the cobalt content in Phantom Metal NF, a copper–cobalt alloy, is much lower than in the cobalt–chromium alloys Solibond C plus, Wirobond® C, and Wirobond® 280. It should be kept in mind that Phantom Metal NF is used by dental technology students for training only, as a substitute for gold alloys. This may result in a high level of exposure to cobalt and an increased risk of developing cobalt allergy during their training. Solibond C plus, Wirobond® C and Wirobond® 280 are used by both students and dental technicians. The shape, size and cobalt and chromium contents (Table 1) of these three alloys were quite similar. However, Solibond C plus released the highest amount of cobalt for all release periods, followed by Wirobond® 280 and Wirobond® C.
respective. For chromium, this pattern of release differences was seen only for the longest release period (1 week). This could be explained by the observed differences in surface irregularity of the alloys, whereby more irregularity means a larger surface area and therefore a higher release rate. Moreover, the alloys used in this study were crude materials that will be melted, shaped and ground by the dental technician. It is considered likely that the release of metals will be different in the occupational setting, as these modifications change the surface area and give rise to the formation of small particles that may increase the release rate. No study of skin doses of these metals on the hands of dental technicians has been published.

**Spot tests**

The DMG test and cobalt spot test are useful as quick and inexpensive semi-quantitative tests to screen for nickel and cobalt release. However, it is difficult to set a distinct LOD for the tests. The DMG test is able to detect levels of nickel lower than 0.5 μg/cm²/week, but it can also miss items that release more than this limit value (18, 34). The sensitivity (proportion of correctly identified positive results) and specificity (proportion of correctly identified negative results) of the DMG test in the present study were 75% and 67%, respectively. This is in the same range as found in previous studies (34). The number of DMG test-positive tools in the present study (33%) could therefore be an underestimation. The cobalt spot test is able to identify cobalt at a concentration of 8 ppm in solution (17), but no limit level for cobalt release from surfaces has been determined.

The interpretation of the cobalt spot test result was sometimes difficult. If a distinction is made between a weakly positive (clear colour change from light to darker yellow) and a strongly positive (colour change to orange/red) cobalt spot test result, it can be shown that strongly positive items all released high amounts of cobalt (58–820 μg/cm²/week), whereas weakly positive items released much lower amounts (0.010–0.24 μg/cm²/week). This distinction was not used in the present study, as we consider that a number of factors may influence the assessment of the test result, and these need to be further explored. One such factor is a green discolouration that was observed frequently, most likely resulting from a reaction with iron salts, as described by Van Klooster (35).

The scoring of a spot test result was also subject to some difficulties. A doubtful test result was defined as a discolouration other than an orange or clearly dark yellow colour for the cobalt spot test and a discolouration other than pink for the DMG test, which could mask the orange for cobalt or pink for nickel. Most tools that had a doubtful spot test result in the present study released high amounts of cobalt and nickel (Table 3). A doubtful reaction should therefore not be interpreted as a negative reaction, as discolorations may mask positive reactions.

**Conclusion**

Tools and alloys used by dental technicians have been shown to release high amounts of sensitizing metals. Students have an increased risk of developing contact dermatitis during their studies, owing to the use of alloys that release high amounts of cobalt. Dental technicians and students mostly have short and repeated contact with tools and alloys, which may result in the deposition of large amounts of metal on their skin. Further research is needed to study the actual skin exposure to cobalt, nickel and chromium, to assess the metal allergy risk among dental technicians. It is recommended that dental technicians should only use tools that are both DMG test-negative and cobalt spot test-negative.

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