

Snapshot of cobalt, chromium and nickel exposure in dental technicians

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Summary

Background. It is not fully understood where and how people are exposed to sensitizing metals. Much can be learnt from studying occupational settings where metals are handled.

Objectives. To quantify cobalt (Co), chromium (Cr) and nickel (Ni) exposure on the skin and in the air, and urine levels, in dental technicians working with tools and alloys that may result in skin and respiratory exposure.

Methods. The metal skin dose was quantified with acid wipe sampling in dental technicians ($n = 13$). Air exposure was monitored by personal air sampling. Spot urine samples were collected for 24 h. Metals were analysed with inductively coupled plasma mass spectrometry.

Results. Before work, Co was detected on the skin of 10 participants ($0.00025\text{--}0.0039\text{ }\mu\text{g}/\text{cm}^2$), and Cr ($0.00051\text{--}0.011\text{ }\mu\text{g}/\text{cm}^2$) and Ni ($0.0062\text{--}0.15\text{ }\mu\text{g}/\text{cm}^2$) on the skin of all participants. After a 2-h period without hand washing, CoCr-exposed participants had more Co on the skin ($p = 0.004$) than non-CoCr-exposed participants. Co was found in 10 air samples ($0.22\text{--}155\text{ }\mu\text{g}/\text{m}^3$), Cr in nine ($0.43\text{--}71\text{ }\mu\text{g}/\text{m}^3$), and Ni in four ($0.48\text{--}3.7\text{ }\mu\text{g}/\text{m}^3$). Metal urine concentrations were considered to be normal.

Conclusions. Dental technicians were exposed to Co, Cr and Ni on the skin and through the air, which was not reflected in the urine concentrations in this study. Cobalt skin doses may potentially elicit allergic contact dermatitis and cause sensitization.

Key words: acid wipe sampling; air exposure; chromium; cobalt; nickel; skin dose; urine.

Cobalt (Co), chromium (Cr) and nickel (Ni) are frequent skin sensitizers (1), but exposures possibly leading to contact allergy and dermatitis are only partially understood. To increase our knowledge about metal skin exposure, in particular to Co, characterization of exposure in occupational settings where these metals are handled may

provide information that can be extrapolated to general exposure scenarios.

Today, dental technicians in Sweden often work with alloys and tools that release Co, Cr, and Ni (2). CoCr alloys were introduced in dentistry in the United States in the 1920s. Their use has since increased, and varies

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over time and between countries. Variations depend on different factors, including the price of gold, technical developments, and skills among dentists and dental technicians (L Hjalmarsson, pers. comm., Public Dental Health Service, The Mälars Hospital, and Institute of Odontology, Sahlgrenska Academy, University of Gothenburg, Sweden, 30 June 2016). Skin exposure to Co, Cr and/or Ni may occur during handling of alloys or metallic items, or during grinding or polishing of CoCr alloys for the construction of dental implants, but occupational skin exposure to metals has not been quantified for dental technicians. Previous studies of exposure, contact allergy and dermatitis in dental technicians have generally focused on (meth)acrylates, and do not mention CoCr alloys or other Co-containing materials (3, 4).

No restrictions on skin exposure to metals in occupational settings exist, and knowledge about skin exposure levels is scarce, making it difficult to categorize skin exposure as high or low. One way to evaluate metal skin doses in workers would be to compare them with elicitation dose (ED) levels for already sensitized individuals. To support risk assessment and management of allergic contact dermatitis at the workplace, skin doses of Co, Cr and Ni should be measured for comparison with ED₁₀ levels (5, 6).

Occupational respiratory exposure to Co, Cr and Ni is regulated in many countries, as Co is classified by the International Agency for Research on Cancer as possibly carcinogenic (group 2B), and Cr(VI) and Ni are classified as carcinogenic to humans (group 1), mainly owing to airborne exposure. Several countries, including Sweden, have established occupational exposure limits (OELs) for Co, Cr and Ni in workplace air, to prevent lung cancer (7). Air monitoring to evaluate dental technicians' exposure to Co and Cr has shown that workers may be exposed to Co when producing dental prostheses (8, 9). Additionally, workers may develop pneumoconiosis, owing to the dusty environment (10).

The aims of this study were to quantify exposure to Co, Cr and Ni on the skin of dental technicians during a work day, and to concomitantly measure the levels of these metals in air. Metal concentrations in urine were monitored as an additional measure reflecting the exposure. To our knowledge, skin, air and urine levels of Co, Cr and Ni have not been studied simultaneously in order to characterize exposure in an occupational setting.

Materials and Methods

Appendix S1 describes chemicals, instruments, sample preparation and inductively coupled plasma mass spectrometry (ICP-MS) analysis of metals, measured metal concentrations of quality control reference materials,

individual values for Co, Cr and Ni measured on the skin and in air and urine samples, and the questionnaire used.

Study participants

A dental laboratory with 21 employees was contacted for participation in this study, and 13 dental technicians gave their informed consent. This study was approved by Stockholm's regional ethical review board (ethical permit no. 2012/1802-31/1).

Measurements were performed on 2 days in the same week. Acid wipe samples from skin and personal air samples were collected during a work day, and spot urine samples for 24 h from the start of that work day. All participants answered a questionnaire regarding work tasks, protective equipment, smoking, dietary habits and the 1-year prevalence of eczema.

Participants were divided in two groups for analysis of data: CoCr-exposed and non-CoCr-exposed participants, based on work tasks during the sampling day according to self-reports (Table 1). The CoCr-exposed participants ($n = 8$) had performed work tasks including grinding, sandblasting and polishing of the material, but had not worked exclusively with CoCr alloys during the work day (Fig. 1a). It was not feasible to register the duration of contact with CoCr alloys or other metal-releasing materials in this study. Participants categorized as non-CoCr-exposed had worked with plastics, gypsum or porcelain during the sampling day ($n = 5$).

Work benches for 8 participants (6 CoCr-exposed and 2 non-CoCr-exposed) were placed in one room and supplied with tools and other equipment, such as local process ventilation. Participants were not confined to working at the same bench every day, although most of them did. Two CoCr-exposed and 3 non-CoCr-exposed participants performed their work in individual rooms with their own equipment.

Acid wipe sampling from skin

An area of 2 cm² on the volar aspect of the fingertip of the non-dominant index finger was sampled before participants started work in the morning, after a 2-h period during which they performed normal work tasks but without hand washing, and at the end of the work day. Before the 2-h period, both hands of the participants were cleaned with 1% HNO₃, rinsed with deionized water, and dried with Kimtech Science precision wipes (Kimberly-Clark Professional, Roswell, GA, USA), to remove all metals from the hands. The top of the non-dominant little finger was covered with an OPSITE Post-Op bandage (Smith & Nephew, London, UK), to act as a reference surface for the cleaning procedure.

Table 1. Characteristics of 13 dental technicians working at a laboratory in Stockholm

ID	Work task on study day	CoCr-exposed on study day ^a	Sex	Age (years)	Work as dental technician (years) ^b
1	Preparing prostheses	Yes	Male	34	7
2	Preparing metal constructions for dental crowns	Yes	Female	42	10
3	Preparing metal constructions for dental crowns	Yes	Female	56	28
4	Preparing metal constructions for dental crowns	Yes	Female	40	12
5	Preparing porcelain part of dental crown	Yes	Female	55	12
6	Preparing metal constructions for dental crowns	Yes	Female	37	4
7	Preparing metal constructions for dental crowns	Yes	Male	37	7
8	Preparing porcelain part of dental crown	Yes	Female	44	10
9	Administrative work	No	Male	55	37
10	Preparing porcelain part of dental crown	No	Male	43	13
11	Preparing porcelain part of dental crown	No	Male	49	8
12	Mixed work tasks, internship	No	Female	22	0.04
13	Rebasing of prostheses, other work with plastics	No	Male	25	0.5

^aBased on self-reported work tasks during the sampling day.^bYears of employment at the studied dental laboratory.

The acid wipe sampling method has been described in detail elsewhere (11–13). In brief, marked skin areas for sampling were wiped with three consecutive wipes (injection swab; Attends Healthcare, Aneby, Sweden), each moistened with 0.5 ml of 1% HNO₃ (65% HNO₃ analysis grade; Merck, Darmstadt, Germany). The wipes were pooled in a 50-ml polyethylene test tube (series 303; Kautex, Bonn, Germany), and 23.5 ml of 1% HNO₃ was added before extraction of metals. Each extract was poured into a 40-ml polypropylene test tube (Sarstedt, Nümbrecht, Germany), and stored at room temperature until analysis. Participants washed their hands after each sampling occasion to remove excess acid.

Collection of urine samples

At the beginning of the work day, all participants received high-density polyethylene bottles (250 ml; Emballator Mellerud Plast, Mellerud, Sweden) to collect a midstream spot urine sample of each void during the following 24 h. Up to 35 ml of each urine sample was transferred to a 40-ml test tube (Sarstedt, Nümbrecht, Germany) before being frozen at –18°C until metal analysis. The specific gravity of all urine samples was measured with a refractometer (RD 712; Euromex, Arnhem, The Netherlands) prior to freezing. To correct for dilution variations of urine, all measured metal concentrations in urine were adjusted to the mean specific gravity in this population (1.015).

Air monitoring

Personal air monitoring was performed according to EN 481 (14) in the breathing zone of 10 participants (owing to limited equipment, it was not possible to monitor all 13

participants) (Fig. 1b). After changing into work clothes at the start of the work day, they were equipped with an Institute of Occupational Medicine (IOM) inhalable fraction sampler (SKC, Blandford Forum, UK) connected to a portable pump (AirChek XR5000; SKC, Eighty Four, PA, USA). Air sampling was performed during a complete work day. The pumps were precalibrated with the filter attached before the start of sampling. During the day, the flow over the filter was monitored every 2 h with a calibrated flow meter, and adjusted, if needed, to maintain a flow of 2 l/min. At the end of the work day, the IOM samplers were collected, closed, and stored at room temperature until filter analysis.

Metal analysis

All plastic materials used for acid wipe sampling, collection of urine samples and laboratory preparation and analysis were washed in 10% HNO₃ (analysis grade) for 4 h, and rinsed four times in deionized water.

Metal analysis of all samples was performed with ICP-MS (iCAP™ Q; Thermo Fisher Scientific, Waltham, MA, USA). For a full description of the preparation of samples, internal standards, reference materials, and calibration curves, see Appendix S1. The isotopes ⁵²Cr, ⁵⁹Co, and ⁶⁰Ni were used for quantification of metals. The method limit of detection (LOD) was set at three times the standard deviation of the blank sample matrix. For acid wipe samples, the LODs in µg/cm² were 0.00016 for Co, 0.00021 for Cr, and 0.00018 for Ni; for the urine samples, the LODs in µg/l were 0.092 for Co, 0.094 for Cr, and 0.24 for Ni; and for the air samples, the LODs in µg/l were 0.007 for Co, 0.11 for Cr, and 0.3 for Ni. The proportions of acid wipe samples below the LOD were 15% for Co and 6% for Cr, and the proportions of urine

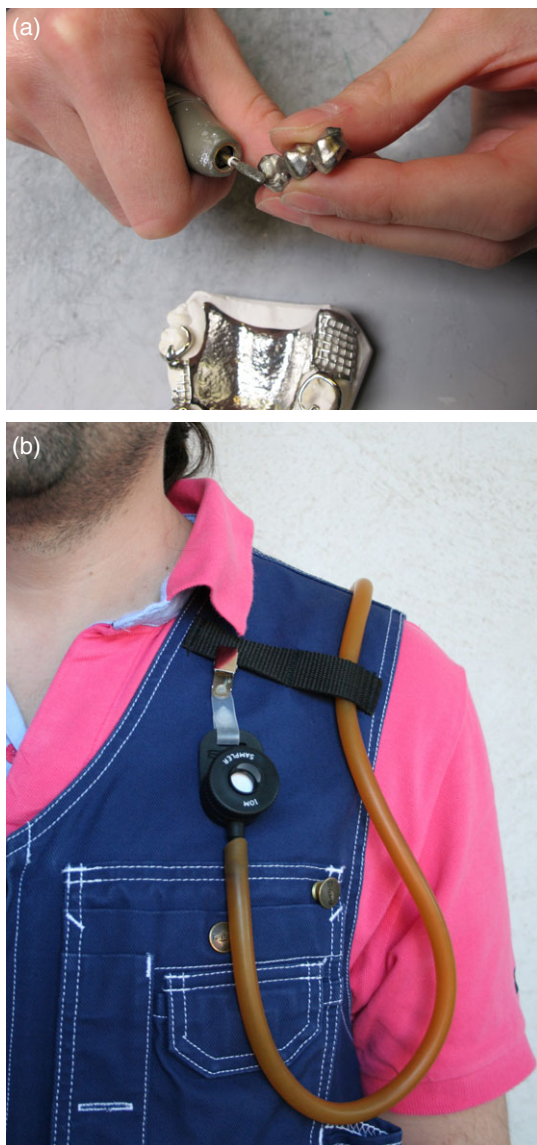


Fig. 1. Illustrations of dental technician work and air sampling. (a) Example of how a CoCr material is held when it is ground or polished. The same procedure is used for working with gypsum or porcelain, except that a different head is placed on the tool. (b) Placement of the Institute of Occupational Medicine inhalable fraction sampler within the breathing zone of the participant.

samples below the LOD were 30% for Co and 51% for Cr. No acid wipe and urine samples were below the LOD for Ni. All air samples were above the LOD for Co, whereas one sample was below the LOD for Cr, and six of 10 air samples were below the LOD for Ni.

The mean concentrations of Co, Cr and Ni in reference materials for quality control of the urine and air filter analysis are shown in Table S1 in Appendix S1.

Statistical analysis

Statistical analyses were performed with IBM SPSS STATISTICS version 22. The exact version of the non-parametric Mann–Whitney *U*-test was used to assess differences in skin doses between CoCr-exposed participants and non-CoCr-exposed participants. Concentrations below the LOD were replaced by $\text{LOD}/\sqrt{2}$ for statistical analysis (15).

Results

Table 1 shows the characteristics of the 13 participants. Six males and 7 females participated; their average age was 41 years (range 22–56 years), and their years of employment as a dental technician at the studied laboratory ranged from 2 weeks (internship) to 37 years. In general, participants only used gloves when they worked with gypsum, composites, or glue, or when they were in contact with patients. Local process ventilation was used by participants when considered appropriate. No participant reported current hand eczema or hand eczema at any time during the last 12 months. A graphical presentation of individual results for acid wipe, air and urine sampling on a log scale is shown in Fig. 2.

Metals on skin

Median metal skin doses measured before work, after a 2-h period without hand washing and at the end of the work day are shown in Table 2. Before work, Cr and Ni could be detected on the skin of all participants, whereas Co was detected on the skin of only 10 participants. At the end of the work day, Co, Cr and Ni were detected on the skin of all participants. The 2-h period actually varied between 1:45 h and 2:48 h. For individual skin doses, see Table S2 in Appendix S1. Co was detected on the skin of all but 1 non-CoCr-exposed participant, and Cr on the skin of all but 1 CoCr-exposed participant. Ni was detected on the skin of all participants. Co and Cr skin doses of CoCr-exposed participants were statistically significantly higher than those of non-CoCr-exposed participants ($p = 0.004$ and $p = 0.003$, respectively) (Fig. 2). At the end of the work day, all participants had detectable skin doses of the three metals, but only the skin dose of Co was significantly higher in CoCr-exposed participants than in non-CoCr-exposed participants ($p = 0.045$) (Table 2).

Metals in air and urine

Co was found in all air samples ($0.22\text{--}155\text{ }\mu\text{g}/\text{m}^3$), whereas Cr was detected in nine samples

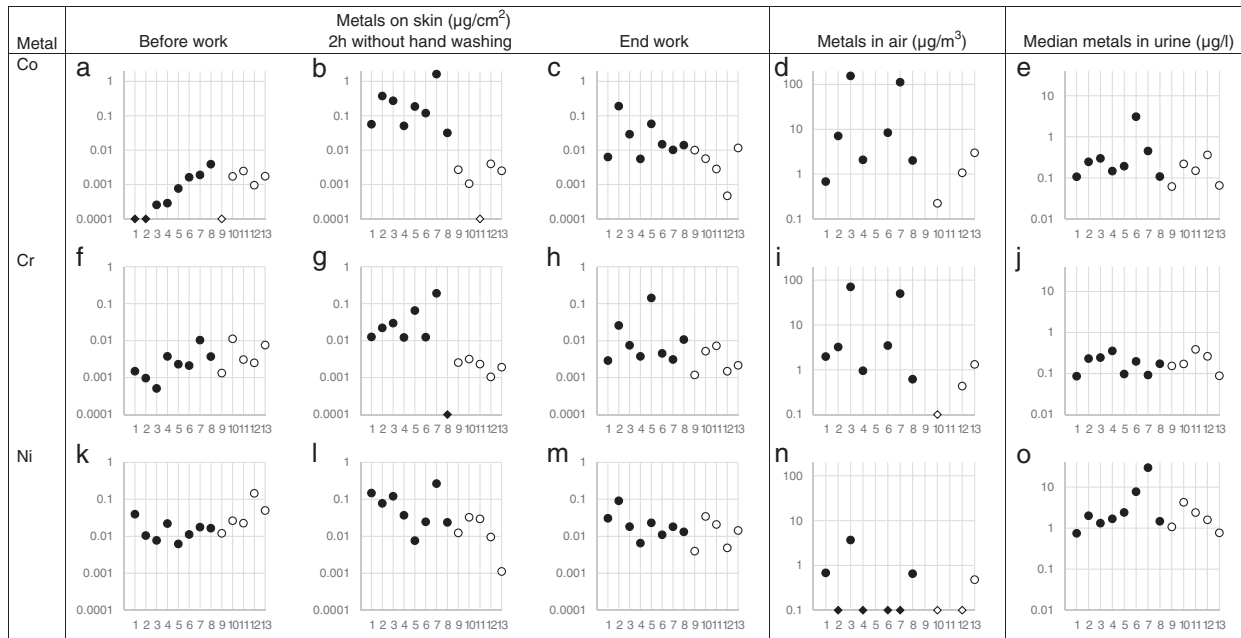


Fig. 2. Individual concentrations of Co (a–c), Cr (f–h) and Ni (k–m) on the skin before work, after a 2-h period without hand washing, and at the end of the work day, and individual concentrations in air and median concentrations in urine of Co (d–e), Cr (i–j), and Ni (n–o). The x-axis shows participants 1–13: filled black circles, CoCr-exposed (1–8); open circles, non-CoCr-exposed (9–14); diamonds, value below the limit of detection. Note that all y-axes are on a logarithmic scale.

Table 2. Metal skin dose ($\mu\text{g}/\text{cm}^2$) before work, after 2 h without hand washing, and at the end of the work day for Co, Cr and Ni

Metal	Sample	CoCr-exposed (n = 8)		Non-CoCr-exposed (n = 5)		All (n = 13)	
		n ^a	Median in $\mu\text{g}/\text{cm}^2$ (range)	n ^a	Median in $\mu\text{g}/\text{cm}^2$ (range)	n ^a	Median in $\mu\text{g}/\text{cm}^2$ (range)
Co	Before work	6	0.0012 (0.00025–0.0039)	4	0.0017 (0.00096–0.0025)	10	0.0017 (0.00025–0.0039)
	Two hours without hand washing	8	0.15 (0.032–1.6)**	4	0.0026 (0.0011–0.0040)	12	0.054 (0.0011–1.6)
	End of work day	8	0.014 (0.0055–0.19)*	5	0.0057 (0.00047–0.012)	13	0.010 (0.00047–0.19)
Cr	Before work	8	0.0022 (0.00051–0.010)	5	0.0031 (0.0013–0.011)	13	0.0025 (0.00051–0.011)
	Two hours without hand washing	7	0.022 (0.012–0.19)**	5	0.0023 (0.0010–0.0032)	12	0.012 (0.0010–0.19)
	End of work day	8	0.0060 (0.0029–0.14)	5	0.0022 (0.0012–0.0072)	13	0.0045 (0.0012–0.14)
Ni	Before work	8	0.014 (0.0062–0.039)	5	0.026 (0.012–0.15)	13	0.018 (0.0062–0.15)
	Two hours without hand washing	8	0.057 (0.0076–0.27)	5	0.012 (0.0011–0.033)	13	0.030 (0.0011–0.27)
	End of work day	8	0.018 (0.0065–0.091)	5	0.014 (0.0040–0.035)	13	0.018 (0.0040–0.091)

The results for two different exposure groups (CoCr-exposed and non-CoCr-exposed) and for all participants are shown. CoCr-exposed participants (n = 8) are participants working with CoCr alloys during the study day; non-CoCr-exposed participants (n = 5) worked with plastics, gypsum, or porcelain.

Statistically significant difference between CoCr-exposed and non-CoCr-exposed participants (exact Mann–Whitney *U*-test) at * $p < 0.05$ and ** $p < 0.01$.

^aMissing data are due to concentrations below the limit of detection (LOD). Measured concentrations below the LOD were replaced by $\text{LOD}/\sqrt{2}$ for statistical analysis.

(0.43–71 $\mu\text{g}/\text{m}^3$) and Ni in four samples (0.48–3.7 $\mu\text{g}/\text{m}^3$). For the full dataset, see Table S2 in Appendix S1. The median levels of Co, Cr and Ni in urine samples of dental technicians are shown in Fig. 2 and Table S2 in Appendix S1. Some participants had two or fewer samples with Co or Cr concentrations above the

LOD, in which case only the concentrations above the LOD are reported.

Discussion

With the aim of increasing our knowledge regarding metal skin exposure, in particular to Co, we characterized

occupational exposure in a workplace where Co, Cr and Ni were handled. We quantified the doses of Co, Cr and Ni on the skin of 13 dental technicians during a work day, and monitored these metals in air. Metal concentrations in urine served as an additional measure reflecting the exposure.

Dental technicians working with CoCr on the sampling day were more exposed to Co and Cr on the skin and through air than those who had other tasks on that day. However, this higher exposure was not reflected in urine in this study. The levels of skin exposure to Co are considered to be high enough to elicit allergic contact dermatitis in Co-allergic individuals, and possibly to induce sensitization to Co.

Metals on skin

All dental technicians in this study had Co, Cr and Ni on their skin. The measured dose range of Co overlapped with the ED range for Co (ED_{10} 0.066–2.0 $\mu\text{g}/\text{cm}^2$) (5). Hence, individuals who are sensitized to Co may develop allergic contact dermatitis when performing work tasks similar to those assessed in this study, emphasizing the need for protective measures (use of disposable gloves). The skin doses of Cr and Ni in our study did not exceed ED_{10} for Cr (1.04 $\mu\text{g}/\text{cm}^2$) or Ni (0.78 $\mu\text{g}/\text{cm}^2$) (6, 16). We could detect Co, Cr and Ni on the skin of non-CoCr-exposed participants before work, after 2 h without hand washing, and at the end of the work day. However, the skin doses of Co and Cr in the CoCr-exposed participants were statistically significantly higher after the 2-h period without hand washing, and for Co there was a statistically significant difference even at the end of the work day. This shows that working with CoCr alloys was a main source of skin exposure to these metals, under the conditions in this study. Ni was found on the skin of all participants after 2 h without hand washing and at the end of the work day, suggesting that Ni exposure might be related to Ni-releasing tools and materials (2, 17, 18). The metal skin doses of Co, Cr and Ni in the 13 dental technicians were slightly lower than for metal workers in a previous study (11). In general, the results from this study agree with observations from previous studies of occupational skin exposure to metals showing large variations in measured skin doses because of the different work tasks performed (13).

Metals in air

The dental technicians in the present study were exposed to airborne metals. Co was found in air samples of all participants, and Cr and Ni in most of them (nine and six

out of 10 samples, respectively). The air levels of Co and Cr in dental laboratories reported in a study from 1994 were comparable to the levels found in the present study (9). For Co, 2 participants were exposed to levels above the Swedish OEL (20 $\mu\text{g}/\text{m}^3$). The OEL for Ni (500 $\mu\text{g}/\text{m}^3$) was not exceeded. As the ICP-MS method only gives the total Cr content, it is not possible to evaluate whether Cr concentrations exceeded the OELs for Cr(VI) and Cr(II/III), respectively. Grinding of CoCr alloys may generate particles that are too large to be inhaled but still might be caught on the air filter. Some of the air filters used for sampling in this study were glistening with metal particles when collected after the work day. It is therefore possible that the high values for Co and Cr in air in this study do not completely reflect the inhalable fraction. Improved use of local process ventilation would probably reduce or eliminate the air exposure.

Metals in urine

The measured urine concentrations reflected neither exposure to Co, Cr and Ni on the skin nor exposure via air on the work day. These results are similar to findings in previous studies monitoring urine levels in dental technicians (9), but the concentrations also correspond to the levels reported for a normal population (19). The limited study sample size and the fact that dental technicians were not highly exposed and did not work with CoCr alloys on a daily basis are probable reasons for the lack of a clear association between exposure to metals and metals in urine. A larger study would be required in order to evaluate whether a correlation exists between metal levels in urine, on the skin, or in the air.

Conclusions

To the best of our knowledge, this is the first study to characterize occupational exposure to Co, Cr and Ni in dental technicians by concurrent measurement of the metals on the skin, in the air, and in urine. The results show that dental technicians are exposed to these metals from their daily occupational activities. Measured Co skin doses were found in the dose range known to elicit allergic contact dermatitis in sensitized individuals. Co levels in air were above the Swedish OEL for 2 participants. Urine levels of the metals were considered to be normal for all participants. Generalization of the results is difficult, owing to the small sample size. However, the results provide an indicative 'snapshot' example of occupational skin exposure to sensitizing metals that contributes to a better understanding of general exposure

scenarios leading to contact allergy and dermatitis in the population.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Appendix S1. Description of chemicals, instruments, sample preparation and ICP-MS analysis of metals; measured metal concentrations of quality control reference materials (Table S1); individual values for Co, Cr and Ni measured in skin, air and urine samples (Table S2).

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