Dermal Exposure to Chromium in the Grinding of Stainless and Acid-proof Steel

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Received 3 February 2003; in final form 24 April 2003

Objectives: The aim of the study was to measure the dermal exposure levels of chromium dust during grinding of stainless and acid-proof steel parts.

Methods: The potential dermal exposure of the body was measured with a patch sampling method and the actual exposure of hands with a hand-wash method. Simultaneously, personal air samples were also collected.

Results: The range of body and hand exposure to chromium dust was 4.04–3406 and 0.72–79.7 mg/h, respectively. Dust was distributed quite evenly to different body parts.

Conclusions: Workers using hand-held grinding tools were more exposed than those using band grinders. It was judged that the sampling methods applied in this study gave a realistic estimation of exposure levels, because of the uniform distribution of contamination during grinding. Respiratory exposure was high compared to Finnish occupational exposure limit values.

Keywords: chromium; dermal exposure; grinding; worker exposure

INTRODUCTION

Stainless and acid-proof steels contain allergenic metals like chromium, nickel and in some cases molybdenum to prevent corrosion. For example, the stainless steel used in cookware production contains 18% chromium and 10% nickel. Both nickel and chromium are known to be highly important causes of occupational allergic contact dermatitis (Kanerva et al., 2000). Even though nickel may for that case be even more important than chromium, we concentrated on assessing the metal dust and chromium exposure in this study.

When ground, stainless and acid-proof steel dust contains metallic, and di- and trivalent chromium in a wide range of particle sizes. It has been noticed that grinding of steel also produces so-called ultrafine particles, <100 nm in diameter (Zimmer and Maynard, 2002). Grinding dust contains undetectable amounts of hexavalent chromium (Karlsen et al., 1992). However, most health risks are associated with carcinogenic and allergenic hexavalent chromium; di- and trivalent chromium are considered to be mostly irritants. Divalent chromium is unstable, and therefore trivalent chromium is more important to human health. Regardless of the exposure route, trivalent chromium absorbs poorly (Hostýnek et al., 1993; Dayan and Paine, 2001). Eczematous skin may, however, take up more chromium than intact skin (Hostýnek et al., 1993).

Trivalent chromium is able to sensitize and elicit allergic contact dermatitis, but much higher concentrations are needed than for hexavalent chromium (Barré Hansen et al., 2002). It has been suggested that the induction of clinical skin sensitization is dose dependent. Therefore, there are threshold concentrations below which sensitization or clinical symptoms do not exist. The concentration of the chemical encountered per unit area of skin has been identified as a critical determinant (Kimber et al., 1999). It is probable that more of these threshold values are going to be introduced in the future. The results of actual occupational hygiene measurements may prove valuable in the assessment of sensitization risk.

In order to collect data for solid substances emitted in grinding, and to assess occupational exposure to chromium dust, dermal and respiratory exposure to chromium were measured. Processes and tasks were observed and the working conditions documented with a structured questionnaire (Hebisch and Auffarth, 2001; RISKOFDERM, 2001, 2002). The...
need for studies of dermal exposure has been recognizes for assessing the exposure levels and constructing exposure models (Marquart et al., 2001). The study described in this article was a part of an EU-funded Risk Assessment for Occupational Dermal Exposure to Chemicals (RISKOFDERM, QLK4-CT-1999-01107), which will increase the understanding of dermal exposure and give tools to exposure assessors (van Hemmen, 1997). An introductory article describing the aims of the project in more detail is published in this issue.

MATERIALS AND METHODS

Description of workplaces and work practices

The study was conducted in four companies, which produced kitchen furniture, acid-proof pipes and pipe parts, boiling kiers used in pulp production, and cookware. The number of workers in the companies varied between 28 and 50. The total number of workers participating the study was 15 and the number of measurements was 29. Consequently, the exposure of most of the workers was measured twice. All workers were skilled, and 13 out of 14 had a formal vocational training for their jobs. The average sampling time was 138 min (range 47–214 min). The study protocol was approved by the Ethical Committee of the Finnish Institute of Occupational Health and the workers participating in the study gave their informed consent.

Grinding and finishing of steel parts were done with a hand-held grinding machine or a band-grinder. The size of the handled pieces varied from cookware slabs (diameter ~30 cm) to large pulp-processing tanks, which the worker had to enter. Figure 1 shows an example of grinding with a hand-held tool.

A structured questionnaire was developed in the RISKOFDERM project (Hebisch and Auffarth, 2001; RISKOFDERM, 2001, 2002). This questionnaire was used also to gather information during the occupational hygiene measurements. Trained occupational hygienists interviewed and observed the workers during the measurements and filled up the questionnaire forms.

Work areas were usually equipped with local exhaust systems (21 measurements done when local exhaust system was available), but according to smoke tube tests they were not always working properly (11 classified as adequate and 10 inadequate).

Different kinds of powered breathing apparatus or powered visor respirators were used by 12 of 15 workers. In 26 measurements gloves were worn all the time and in three cases part of the time. All 15 grinders used overalls and nine of them had their heads covered with the hood of the respirator or a separate cap. Two workers changed their work clothes more than once per week. Six workers changed them weekly, and six less often. One worker changed clothes irregularly. Seven workers wore gloves made of leather and cotton, and seven had leather gloves. One worker wore rubber-coated cotton gloves. Gloves were changed daily by four workers, weekly by six workers and less often than weekly by five workers. One of the workers studied was complaining of work-related dryness of skin.

Sampling

Potential dermal exposure, or in other words contamination of the outer clothing contaminant layer of the body, was studied with a method modified from the OECD sampling protocol for pesticides using 10 α-cellulose patches (Schleicher & Shüll, technical filter paper 0860, 74 g/m²) attached to the chest, back, left and right forearm, left and right upper arm, left and right upper leg, and left and right lower leg (OECD, 1997). The size of each of the patches was 100 cm². The exposure of the head was included in the upper torso measurements and a separate patch for forehead or back of the head was not used. Actual exposure and the penetration through the protective clothing were assessed with a patch attached to the chest under the work clothing. To prevent contamination of the inner side of the patches, they were taped onto a piece of polyethylene (PE) plastic, which was then attached to clothes with safety pins. After the sampling, all 11 patches were removed hygienically from the clothes of the worker, detached from the plastic background and folded carefully to prevent the dust falling off. The patches were transferred to PE bags (Minigrip®) for transport and storage.

Fig. 1. Manual grinding of stainless steel kitchen table with a hand-held tool.
Hand exposure was studied by hand washing. The washing was done according to the procedure described in EN 1499 to equalize the washing efficiency as much as possible (CEN, 1997). Washing solution was poured onto workers’ hands held above a beaker for 30 s, and during that time the worker rubbed his/her hands in a specific way described in the standard. Deionized water (200 ml) containing 1.0 ml/l hypoallergenic liquid soap was used for hand-wash sampling. The beaker was rinsed with 2 × 25 ml of unused washing solution. The solutions were combined and poured into PE bottles for transportation and storage.

Inhalable dust was collected simultaneously with dermal exposure measurements on Millipore® cellulose-acetate filters (0.8 μm) with IOM® samplers attached to portable, pre-calibrated SKC 224® pumps (SKC Inc., Eighty Four, PA) at a flow rate of 2.0 l/min.

Analysis

The patch samples were burned to ash in porcelain pots at 500°C overnight or for at least 6 h. Samples were digested with nitric acid (65%, 2.5 ml, Merck 411 Suprapur®) and hydrochloric acid (30%, 2.5 ml, Merck 318 Suprapur®), and dried on a warming plate. The residues were dissolved with 2 × 5 ml of acid solution containing 5.5% HNO₃ and 2.1% HCl. The solutions were filtered through Macherey-Nagel 640μm filter paper® to a 25 ml volumetric flasks and filled with the acid solution.

Hand-wash samples were transferred into 250 ml glass beakers in the laboratory. Acid solution containing 5 ml of 65% HNO₃ and 5 ml of 30% HCl was added. PE bottles were rinsed with the acid solution and 5 ml of deionized water, which were combined to the samples. The samples were evaporated to dryness in a water bath. The residues were diluted and the solutions filtered as for those of the patch samples.

The limit of detection (LOD) and the limit of quantification (LOQ) were determined on Millipore® cellulose-acetate filters (0.8 μm) with IOM® samplers attached to portable, pre-calibrated SKC 224® pumps (SKC Inc., Eighty Four, PA) at a flow rate of 2.0 l/min.

RESULTS

Dermal exposure

Dermal exposure to chromium dust is presented in Table 1. It was also seen that the exposure varied widely between workers and that the dust was distributed evenly to different body parts (Fig. 2). The results in Table 1 have been calculated from the concentrations analysed from patches or hand-washing solutions, taking into account the representative body area, sampling time, chromium concentration and ‘formulation’ the amount of metal dust calculated backwards from
analyte results. The body region areas published by EPA Exposure Factors Handbook (US EPA, 1997) and then adapted to the OECD measuring protocol were used (OECD, 1997). The estimated total area of body (excluding hands) was 18720 cm². In all calculations, values below LOQ are presented as a half of LOQ and values below LOD (not detected) as a half of LOD.

An exceptionally high concentration (3410 mg/h) was found on the body of a worker who was grinding the inside seams of a pulp-processing tank. High contamination of the back explained 68% of the total body contamination in this case. As the work scenario differed significantly from others, this result was treated as an outlier and omitted from further calculations.

Within- and between-worker variances, referring to day-to-day variability and variability between measured individuals, were estimated with analysis of variance (ANOVA) from log-transformed exposure data. The procedure has been described in detail elsewhere (e.g. Kromhout et al., 1993). The total variances of body and hand exposure (\(S^2\)) were 1.83 and 1.66, respectively. Between-worker exposure highly dominated in both cases. The proportion of the between-worker component of variance (\(S^2\)) was 82% for body exposure and 87% for hand exposure (\(P < 0.01\)).

The workers studied used two different types of tools. Nineteen measurements (outlier excluded) were done while the grinders used hand-held machines and nine when the band grinder was used. The total body exposure differed significantly between these two groups (\(P = 0.0004\), Kruskall–Wallis test). Manual grinders were exposed to 228 mg/h and band grinders to 39.8 mg/h. These differences in the work practices were not picked up accurately by the questionnaire. The tools used were all classified as manual, powered tools, even though there were considerable differences.

The level of exposure of the body was 282 mg/h in workplaces with only general ventilation. In workplaces that were equipped with local ventilation systems classified as adequate in the questionnaire, the average exposure was about at the same level (307 mg/h). Surprisingly, the exposure was lowest when the local ventilation was classified as inadequate (116 mg/h). These findings were not, however, statistically significant.

The hands of the workers wearing leather gloves were significantly less exposed than the ones using leather and cotton mixture gloves (\(P = 0.04\), Kruskall–Wallis test). The average actual exposures were 6.7 and 23 mg/h, respectively.

Some chromium was found from the inner patch of 21 workers. The maximum concentration was

Table 1. Dermal exposure of grinders (mg/h)

<table>
<thead>
<tr>
<th></th>
<th>Total body</th>
<th>Hands</th>
<th>Hands</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Formulation</td>
<td>Analyte</td>
<td></td>
</tr>
<tr>
<td>Arithmetic mean</td>
<td>343</td>
<td>61.7</td>
<td>15.2</td>
</tr>
<tr>
<td>Range</td>
<td>4.04–3410</td>
<td>0.73–613</td>
<td>0.72–79.7</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>632</td>
<td>114</td>
<td>19.2</td>
</tr>
<tr>
<td>Median</td>
<td>181</td>
<td>32.6</td>
<td>7.68</td>
</tr>
<tr>
<td>Geometric mean</td>
<td>150</td>
<td>27.1</td>
<td>7.33</td>
</tr>
<tr>
<td>Geometric standard deviation</td>
<td>3.87</td>
<td>3.87</td>
<td>3.62</td>
</tr>
</tbody>
</table>

Fig. 2. Dermal exposure distribution of different body parts (mg/cm²/h). Error bars indicate one standard deviation.
Table 2. Concentrations (mg/m³) of inhalable dust and chromium during grinding (n = 28)

<table>
<thead>
<tr>
<th></th>
<th>Inorganic dust</th>
<th>Chromium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arithmetic mean (range)</td>
<td>27.4 (0.50–300)</td>
<td>1.39 (0.01–6.75)</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>55.9</td>
<td>1.80</td>
</tr>
<tr>
<td>Median</td>
<td>10.9</td>
<td>0.72</td>
</tr>
</tbody>
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10 µg/cm². The median actual exposure of the chest was 0.8 µg/cm².

Respiratory exposure

The results of the breathing zone measurements are presented in Table 2. The Finnish occupational exposure limits for inorganic dust, and for metallic chromium and di- and trivalent chromium compounds are 10 and 0.5 mg/m³, respectively.

The results of the dermal exposure measurements were also compared with the breathing zone concentrations taken simultaneously (analyte versus inhalable chromium). No significant correlation was found.

DISCUSSION

When observed visually, the chromium dust seemed to distribute quite evenly on the front side of workers’ clothes, especially when hand-held grinding tools were used and the workers were standing. This could also be concluded from the patch sample concentrations. A major drawback in patch sampling is that it requires extrapolation from a small area to the total body area. The exposure estimates may be incorrect if the deposition is not uniform and the number of observed workers is small (Fenske, 1993). In the present case, patches were judged to give realistic estimations of the body exposure.

The exposure varied widely, especially between workers. Within-worker variability was, however, estimated on the basis of only two repeated samples. Personal working habits, the conditions at the workplaces and the shape of the piece ground are the probable causes of this variability.

When solid dust is measured, it is usually not possible to prevent the dust from falling off the sampling matrix without using an adhesive method, which might overestimate the exposure. It was assumed that, as a porous material, the α-cellulose would behave similarly to clothing or skin where the contamination of the material is concerned, and therefore provide a reasonable estimate of the potential exposure (OECD, 1997; Soutar et al., 2000). In hand washing, problems could arise with the removal efficiency of the washing. The field tests made earlier with cobalt dust in hard metal manufacturing and handling showed, however, that hand washing efficiently removes the dust (unpublished results). In that test the hands of the workers (n = 5) were washed twice, and after that the residues were stripped with Fixomull® tape cut into 2.5 × 4 cm pieces (Surakka et al., 1999). On average, 84% of the total cobalt dust was found from the first washing solution (78–92%). All the tape stripping results were under the limit of detection (<11 µg).

Grinding with hand-held tools caused higher exposure levels than grinding with band grinders. This supports the assumption that increasing levels of automation should decrease exposure. However, the questionnaire used in the study did not recognize this, as both types of tools were categorized as ‘manual’. The accuracy of the scaling of the questionnaire was inadequate in this case. It would have been advantageous to find these kinds of possible determinants of exposure with the questionnaire. In further studies, structured data-gathering, by sets of questions on particular types of processes or exposure patterns, might be useful, or at least the level of automation should be better distinguished, separating the different types of tools.

The negative correlation between exposure levels and ventilation efficiency may be due to the fact that the hand-held tools caused higher concentrations. Also the band grinding machines were more easily equipped with effective exhaust devices than the hand-held tools. In all, both the results of the dermal exposure measurements and the measured respiratory exposure levels show that the effect of the ventilation systems is not in many cases sufficient.

It was also shown in this study that air concentration cannot be a reliable estimate of dermal exposure even when it was measured in the breathing zones of the worker. It might be thought that air concentrations would represent dermal exposure, as the route is via airborne dust, but in this case it proved to be a faulty assumption. This might be due to the fact that the size distribution of particles on the patch and on the filter of the IOM sampler may be different.

Hand exposure was in this case measured by rinsing the hands with soapy water. The workers wore leather or some other kind of sturdy gloves, at least part of the time, and therefore this method measured actual exposure. However, the main intention of these gloves is to protect hands from wounding and the abrasive effects of sharp edges and small metal pieces. They cannot be considered as chemical protective gloves and at least the ultrafine particles emitted from grinding process would definitely penetrate the glove material and seams. It would have been unethical to ask the workers not to wear any gloves or to wear cotton liners on the top of the leather gloves as they could have increased the risk of injury by catching in the moving parts of the tools used.

Assessing the relative risk of dermal uptake of chromium, local skin effects or sensitization during
grinding could be possible with the actual hand exposure data presented here. According to the theory of thresholds in contact sensitization, the amount reaching the skin could be meaningful in assessing the risk of sensitization and clinical skin effects (Kimber et al., 1999). For trivalent chromium, no threshold concentrations have been proposed.

A conceptual model describing the processes of dermal exposure and uptake with consistent terminology has been introduced by Schneider et al. (1999). They point out the fact that most of the current methods used to assess dermal exposure determine the mass of contaminant depositing on the skin (e.g. patch sampling) or remaining on the skin at the end of the exposure period (e.g. hand washing). However, the risk of dermal uptake can only be estimated if the time-dependent concentration is measured on the skin (Schneider et al., 1999). This is an especially difficult task for particles, as the uptake is due both to dissolution and diffusion through the stratum corneum (Schneider et al., 2000). Potential exposure measurements do not in any case give enough information on the amount of contaminant reaching the skin, not to mention doses of target organs. Biological monitoring should be included when systemic risks to individuals are estimated. It could be seen that some metal dust penetrates the work clothing, which is not surprising as grinding dust contains ultrafine particles (Zimmer and Maynard, 2002). From the viewpoint of practical occupational hygiene at workplaces, information on the effectiveness of protective equipment and personal hygiene should be made available and the workers should be educated about the importance of hygienic behaviour, e.g. changing clothes and gloves regularly, which was not always the case in this study. Based on these results, it is also recommended that workers use leather gloves instead of cotton gloves while grinding.

Acknowledgements—The authors wish to thank all plating shops and their employees for their participation in the study. We are especially grateful to Professor Juhani Kangas, FIOH, Dr Joop van Hemmen, TNO, Dr Bob Rajan, HSE, and Professor Hans Kromhout, University of Utrecht, for their constructive comments. Mrs Sirkka Rosvainen, laboratory technician, for her skilful assistance in field surveys and analysis of the samples, and Maria Hirvonen, MSc, for the statistical analyses. This study was part of the RISKOFDERM project (Risk Assessment for Occupational Dermal Exposure to Chemicals, QLK4-1999-01107). We want to thank European Commission (DG Research) and Finnish Work Environment Fund for financial support.

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