AMBIENTAL AND BIOLOGICAL MONITORING OF ELECTROPLATING WORKERS

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Abstract. Romanian health and safety regulations require employers to monitor the exposure by a suitable procedure in any case where it is necessary for ensuring the maintenance of adequate control of exposure of employees to hazardous substances. Objectives. The aim of this study was to estimate the occupational exposure risk of electroplating plant’s workers. Materials and methods. Indoor air quality was evaluated by workplace measurements of chemicals in two cadmium-nickel-chrome electroplating and zinc coating units. For the determination of internal exposure 69 workers (mean age: 42.7±6.3 years, mean exposure length: 20±7.4), including 28 women, and a matched control group (72 subjects) were examined in a cross-sectional study. Whole blood samples were analyzed for cadmium and post-shift urine samples for beta 2-microglobulin. The dermal exposure levels of heavy metals were measured by wipe sampling in combination with adequate analytical techniques. 23 electroplaters belonging to workplaces with major risk were analyzed for chromosomal aberrations and micronuclei in peripheral lymphocytes. The results were statistically analyzed through usual methods (Student’s t-test, χ²-test, Pearson’s correlation coefficient). Results and discussion. Airborne concentrations exceeded threshold limit values (TLV-TWA) for cadmium, chromium, nickel, cyanide, sodium hydroxide, sulphuric acid and trichloroethylene. Mean concentrations of cadmium in whole blood, of dermal chrome, cadmium and nickel and of urinary beta 2-microglobulin were significantly higher among electroplaters than in controls. A positive correlation was found between urinary beta 2-microglobulin and blood cadmium levels. The prevalence of chromosomal aberrations and micronuclei in peripheral lymphocytes was significantly higher in exposed as compared with controls. Conclusions. The study revealed the presence of a high occupational risk in metal plating shops. The concentrations of a great number of chemicals, some of them inducing cancer, exceeded the allowed exposure limits. The results confirm that beta 2-microglobulin is a sufficiently sensitive indicator for use in monitoring heavy metal occupational exposure, especially for cadmium. As a complement to traditional exposure assessment, monitoring deposition of aerosols on employees’ skin can be a simple and quick screening method for identifying deposited metals.

Key words: electroplaters, biological monitoring, exposure/effects biomarkers

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determinarea dozei interne de expunere, 69 de angajați (vârsta medie: 42,7 ± 6,3; vechime medie: 20,0 ± 7,4), dintre care 28 femei și un lot martor adecvat (72 de subiecți) au fost examinați în cadrul unui studiu transversal. S-au analizat cadmiul în probe de sânge total și beta 2-microglobulina în probe de urină, recoltate la sfârșitul schimbului. Nivelurile de expunere tegumentară la metale grele au fost determinate prin prelevare cu fâșii de bumbac, combinată cu metode analitice adecvate. Rezultatele au fost prelucrate statistic utilizând metode uzuale (testul-t Student, testul $\chi^2$, coeficientul de corelare Pearson).


Cuvinte cheie: galvanizatori, monitorizare biologică, biomarkeri de expunere/efect

INTRODUCTION
Electroplating involves the coating of an electrically conductive object with a layer of metal to achieve decorative or engineering requirements (e.g., abrasion and wear resistance, corrosion protection, lubricity, improvement of aesthetic qualities etc.) (1).

Most metal surface treatment and plating operations have three basic steps:
• Surface cleaning or preparation
• Deposition process
• Rinsing or other work-piece finishing operations.

The surfaces are processed using mechanical methods (grinding and polishing), chemical and electrochemical methods (degreasing and scaling). These operations involve employing of solvents, alkaline and/or acid cleaners, abrasive materials and/or water.

After surface preparation, the object that is to be plated is submerged into the electrolyte (plating bath). The bath is a specially designed chemical solution that contains the desired metal dissolved in a form of submicroscopic metallic particles. In addition, various substances (additives) are introduced in the bath to obtain smooth and bright deposits. Cadmium, chromium, copper, gold, nickel, and silver are the metals most commonly used to plate different objects.

Table 1 summarizes the process material inputs and the emissions of generated substances.
Table 1. Materials inputs and pollutant emissions for electroplating process

<table>
<thead>
<tr>
<th>Process</th>
<th>Material input</th>
<th>Emissions to air</th>
<th>Emissions to water</th>
<th>Discharge to land</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface preparation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent degreasing and emulsion, alkaline and acid cleaning</td>
<td>Solvents, acids emulsifying agents, alkalis</td>
<td>Solvents from degreasing and emulsion cleaning only</td>
<td>Solvent, alkaline and acid wastes</td>
<td>Solvent wastes and still bottoms</td>
</tr>
<tr>
<td>Surface finishing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electroplating</td>
<td>Acid solutions, metal and cyanide solutions</td>
<td>Metal-ion-bearing mists, acid mists</td>
<td>Acid/alkaline, cyanide, metal wastes</td>
<td>Metal and reactive wastes</td>
</tr>
<tr>
<td>Other finishing methods</td>
<td>Metals and acids</td>
<td>Metal and acid fumes</td>
<td>Metal and acid wastes</td>
<td>Polishing and etching sludges</td>
</tr>
</tbody>
</table>

Adapted from (2)

The main source of exposure is to tank contents (for example, mists, gases, vapors) that become airborne due to tank agitation, tank temperature, dipping of parts, parts moving along on hanging conveyors as well as bath changing activities and tank recharging. The toxic gases hydrogen cyanide and hydrogen sulfide can be released if acids come in contact with cyanides or sulfides. Nitrogen oxides can be released from baths containing nitric acid. Other plating processes can generate mists of chromic acid, sulfuric acid, hydrofluoric acid, ammonia, and zinc chloride (3).

As shown in table 1, the employees of the electroplating shop are simultaneously exposed to multiple hazards (heavy metals, acids, bases, solvents, cyanides, nitrogen oxides, sulfur dioxide, metallic oxides, glittering agents), whose effects can cumulate or even potentate, affecting the health status of the exposed workers. Electroplaters can develop:

- short term throat, lung, sinus, skin and eye irritation and burns;
- long term health problems such as asthma, heart, lung and nerve disorders and, in some cases, cancer.

In previous study, Roberti S et al evidenced an increased mortality from lung cancer among workers of a bright electroplating factory which correlates with the increase of chromosomal aberrations observed in the past among these workers (4).

Dermal exposure to electroplating fluids was measured at three sites on 27 subjects who were dipping objects into tanks of chromic acid, nickel sulphate, copper sulphate, copper cyanide or zinc hydroxide. Contamination was assessed using the method of Dirichlet tessellation. Almost all of the electroplating samples were below the limit of quantification.
More than one species of metal atoms was found on some of the samples afterwards, indicating cross-contamination from other baths during the sampling period (5). Bright et al. mentioned that chrome used in electroplating is a potential cause of occupational asthma (6). Sensitivity to chrome in electroplaters may occur in situations where exposure levels are likely to be within the current exposure standards.

Makinen and Linnainmaa measured the dermal and respiratory exposure levels of hexavalent chromium during electroplating work (7). The results of breathing zone samples and dermal exposure did not correlate with each other. In manual electroplating processes, dermal exposure was higher than in semi-automatic and automatic processes. The amount of hexavalent chromium the workers were exposed to is probably high enough to cause a risk of skin sensitization.

A biomonitoring study of chromium for residents of areas with a high density of electroplating factories revealed that these subjects had significantly higher levels of chromium in whole blood, compared to residents of the low-density areas and to the general population (8).

Baldasseroni et al assesses the time trend in exposure to nickel especially among electroplaters and underlines the usefulness for occupational risk evaluation of a biological monitoring data-base of routinely collected data (9).

The aim of this study was to estimate the occupational exposure risk of electroplating plant’s workers by ambient and biological monitoring.

MATERIAL AND METHODS
The risk assessment was performed in two cadmium-nickel-chrome electroplating and zinc coating units. The technological process was manual or semi-automatic. The measuring strategy in case of workplace characterization was carried out following the Romanian regulations for safety and health at work (10). The cadmium (Cd), hexavalent (VI) chromium (Cr), nickel (Ni), trichloro-ethylene, cyanide, sulfuric acid, zinc oxide, sulfur dioxide, and sodium hydroxide concentrations in the air of work areas were measured using Casella sampling equipment. Metals were analyzed in a flame atomic absorption spectrophotometer, the volatiles by gas chromatography and spectrophotometrically, respectively. For the determination of internal exposure 69 workers (mean age: 42.7±6.3 years, mean exposure length: 20±7.4), including 28 women, and a control group (72 subjects), matched for age, sex and socioeconomic status, were examined in a cross-sectional study. Whole blood samples were analyzed for cadmium (Cds) by atomic absorption spectroscopy and post-shift urine samples for beta 2-microglobulin (B2MG) using a commercial ELISA diagnostic kit purchased from RANDOX Laboratories (11). The dermal exposure levels of heavy metals were measured by wipe sampling in combination with adequate analytical techniques.
The potential dermal contamination of face and hands was estimated according to NIOSH method 9100 (12). These 69 workers were further categorized in a subgroup (23 subjects) according to their Cds levels, representing the high exposed group, and analyzed cytogenetically for possible chromosome aberration and micronuclei abnormalities in peripheral blood lymphocytes (13, 14). The results were statistically analyzed through usual methods: Student's t-test and $\chi^2$-test were used to compare the mean levels and frequencies, respectively, of biomarkers between exposed workers and control group. Pearson's correlation coefficient was used to find out the association between urine B2MG levels and Cds.

RESULTS AND DISCUSSION
Data of workplace air quality showed 8-hourly average concentrations (TWA) of hazardous chemical substances (Cd: 1.0 mg/m$^3$; Cr (VI): 0.12 mg/m$^3$, Ni: 0.12 mg/m$^3$, cyanide: 1.6 mg/m$^3$, sodium hydroxide: 2.4 mg/m$^3$, sulphuric acid: 1.1 mg/m$^3$, trichloroethylene: mg/m$^3$), which exceeded the threshold limit values (TLV) of occupational environment as shown in figure 1. Airborne cadmium concentrations were highest in the plating area, especially during bath changing activities.

![Fig. 1. Air pollutants concentration / TLV-TWA](image-url)
These high exposure levels are reflected in increased Cds concentrations, as direct indices of Cd exposure, and in increased urinary B2MG values, as markers of renal tubular function.

Mean concentrations of cadmium in whole blood, of dermal chrome, cadmium and nickel and of urinary B2MG was significantly higher among electroplaters than in controls (table 2).

<table>
<thead>
<tr>
<th></th>
<th>Cds [µg/l]</th>
<th>B2MG [mg/gC]</th>
<th>Cd dermal [µg/cm²]</th>
<th>Cr dermal [µg/cm²]</th>
<th>Ni dermal [µg/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposed</td>
<td>8.95±11.45</td>
<td>1.39±2.19</td>
<td>0.35±0.63</td>
<td>0.31±0.39</td>
<td>0.19±0.32</td>
</tr>
<tr>
<td>Controls</td>
<td>3.13±6.80</td>
<td>0.28±0.20</td>
<td>0.003±0.01</td>
<td>0.0076±0.009</td>
<td>0.006±0.01</td>
</tr>
<tr>
<td>Statistically</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Significance</td>
<td>P &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.0001</td>
<td>p &lt; 0.0001</td>
<td>p &lt; 0.0001</td>
</tr>
</tbody>
</table>

It is known, that the dermal uptake of metals is a relevant route of exposure. However, there are no occupational hygienic limit values for dermal exposure. Wass and Wahlberg proposed a ‘threshold value’ for safe exposure of 0.3 µg/cm² in the study of the chromium-sensitized patients (15). With the results of dermal exposure measurements it is possible to evaluate the sites and sources of exposure, the effect of personal behavior, and to give instructions on personal protective equipment and other exposure reduction techniques (16). The data obtained after dermal exposure measurements varied widely between workers, as presented in table 2. The investigated electroplaters wore protective equipment, but the gloves only part time. In previous study Mäkinen et al observed the importance of personal hygienic behavior in dermal uptake (7).

The prevalence of increased blood cadmium (> 5 µg/l) and urinary B2MG (> 2 mg/l) was significantly higher in exposed as compared with controls (fig. 2). A positive correlation was found between urinary B2MG and blood cadmium levels (fig. 3). Possible genotoxic effects were evaluated by analyzing numeric and structural chromosomal aberration and micronuclei frequencies in peripheral lymphocytes of only 23 subjects belonging to workplaces with major risk.
Fig. 2. Frequency of abnormal Cds and B2MG levels in electroplaters versus controls

Fig. 3. Correlation between urinary beta 2-microglobulin and blood cadmium levels
Table 3 summarizes the mean age and length of exposure as well as the mean frequencies of cells with chromosomal aberration and micro-nuclei.

Table 3. Average percentage of cells with chromosomal aberration and micronuclei in exposed and controls

<table>
<thead>
<tr>
<th>Investigated subgroup</th>
<th>Mean age ±SD [years]</th>
<th>Mean length of work ±SD [years]</th>
<th>Mean Cds level ±SD [µg/l]</th>
<th>Frequencies of numeric aberration [%]</th>
<th>Frequencies of total structural aberration [%]</th>
<th>Frequencies of micronuclei [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposed n = 23</td>
<td>40.04±6.49</td>
<td>19.86±6.30</td>
<td>10.18±12.70*</td>
<td>1.57±1.35*</td>
<td>3.60±2.30*</td>
<td>8.9±3.5</td>
</tr>
<tr>
<td>Controls n = 20</td>
<td>45.1±6.9</td>
<td>-</td>
<td>2.35±5.23</td>
<td>0.50±0.22</td>
<td>1.60±0.80</td>
<td>0.7±0.4</td>
</tr>
</tbody>
</table>

* Statistically significant value (p < 0.001) compared to the value of the control group

The remarkable structural chromosomal aberrations recorded in the present investigation included chromatid breaks, acentric fragments, chromatid and chromosome gaps. The observed numerical aberrations were polyploidy and endoreduplication. A significant increase in the frequency of the total number of micronuclei was detected too.

There are very few studies on the possible clastogenic effects of hazardous chemicals from electroplating shops (17, 18, 19, 20). Other studies of cultured mammalian cells have shown that cadmium compounds cause genetic damage, including gene mutations, DNA strand breaks, chromosomal damage, cell transformation (a step in tumor formation), and disrupted DNA repair. The accumulated information supports the conclusion that ionic cadmium is the active, genotoxic form of cadmium and its compounds (21).

CONCLUSIONS

- The study revealed the presence of a high occupational risk in metal plating shops.
- The concentrations of a great number of chemicals, some of them inducing cancer, exceeded the allowed exposure limits.
- The used biomarkers proved to be valuable biomonitoring tests. The results confirm that beta 2-microglobulin is a sufficiently sensitive indicator for use in monitoring heavy metal occupational exposure, especially for cadmium.
- Even the prevalence of chromosomal damage in the lymphocyte pool is reversible and the aberration frequencies may revert to control levels in two to three years after reduction of exposure, it is recognized that chromosomal damage may be a sign of possible health risks.
As a complement to traditional exposure assessment, monitoring deposition of aerosols can be a simple and quick screening method for identifying deposited metals. Even if there are no occupational hygienic limit values for dermal exposure, the obtained results are relevant when compared with those of a reference group.

In agreement with other studies (22, 23), electroplating appeared to understand the short term adverse effects of the chemicals to which they are exposed, although their understanding of long term, or chronic effects appeared to be incomplete. They knew about personal protective equipment, but did not always use it, or used gloveware that was deficient or contaminated. The great variability of findings with respect of dermal exposure seems to be caused due to personal working habits.

There is an urgent need for better training and more attention to skin care in electroplating workshops.

REFERENCES

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