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AMBIENTAL AND BIOLOGICAL MONITORING OF ELECTROPLATING WORKERS

Brigitte Scutaru, Doina Popa, V Cazuc, Irina Popescu, Iulia Roman, Valeria Hurduc, Iliana Palamaru

Institute of Public Health Iaşi, România

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, χ^2-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

Rezumat. Legislaţia română cu privire la sănătatea şi securitatea în muncă obligă angajatorii să monitorizeze expunerea printr-un procedeu adecvat, în orice situaţie în care se impune controlul expunerii lucrătorilor la substanţe periculoase. **Obiectiv.** Scopul acestui studiu a fost evaluarea riscului ocupaţional al lucrătorilor din sectorul de acoperiri metalice. **Materiale şi metode.** Calitatea aerului din zona ocupaţională a fost evaluată prin măsurători ale agenţilor chimici în două unităţi de acoperiri metalice cu cadmiu-nichel-crom şi zinc. Pentru determinarea dozei interne de expunere, 69 de angajați (vârsta medie: 42,7±6,.3; vechime medie: 20,0±7,4), dintre care 28 femei şi un lot martor adecvat (72 de subiecți) au fost examinați în cadrul unui studiu transversal. S-au analizat cadmiul în probe de sânge total şi *beta* 2-microglobulina în probe de urină, recoltate la sfârşitul schimbului. Nivelurile de expunere tegumentară la metale grele au fost determinate prin prelevare cu fâşii de bumbac, combinată cu metode analitice adecvate. Rezultatele au fost prelucrate statistic utilizând metode uzuale (testul-t Student, testul χ^2, coeficientul de corelație Pearson). **Rezultate şi discuții.** Concentrațiile din aer au depăşit valorile limită (TLV-TWA) pentru cadmiu, crom, nichel, cianuri, hidroxid de sodiu, acid sulfuric şi tricloretilenă. Concentrațiile medii de cadmiu în sânge total, de cadmiu, crom, şi nichel tegumentar precum şi de *beta* 2-microglobulină urinară au fost semnificativ statistic mai crescute la galvanizatori față de martori. S-a constatat o corelație pozitivă între *beta* 2-microglobulina urinară şi cadmiul sanguin. Prevalența aberațiilor cromozomice şi a micronucleilor în limfocite periferice a fost semnificativ mai crescută la expuşi în comparație cu martorii. **Concluzii.** Studiul evidențiază un risc crescut în unitățile de acoperiri metalice. Concentrațiile unui mare număr de agenți chimici, unii din aceştia fiind cancerigeni, depăşesc valorile limită admise. Rezultatele confirmă că *beta* 2-microglobulina este un indicator suficient de sensibil de monitorizare a expunerii la metale grele, în special la cadmiu. Monitorizarea depunerilor de aerosoli pe pielea lucrătorilor, ca o completare a evaluărilor de risc tradiționale, ar putea fi o metodă simplă şi rapidă de *screening* a depunerilor de metale.

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

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

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 χ^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.

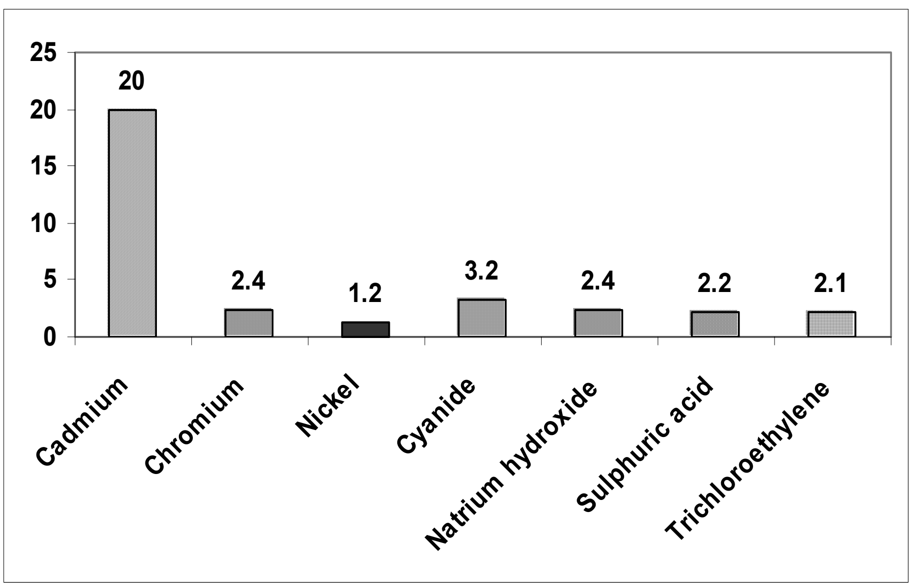

Fig. 1. Air pollutants concentration / TLV-TWA

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 2. Mean values ± SD of biomarkers in exposed compared with controls

Group	***Cds [µg/l]***	***B2MG [mg/gC]***	***Cd dermal [µg/cm²]***	***Cr dermal [µg/cm²]***	***Ni dermal [µg/cm²]***
Exposed	8.95±11.45	1.39±2.19	0.35±0.63	0.31±0.39	0.19±0.32
Controls	3.13±6.80	0.28±0.20	0.003±0.01	0.0076±0.009	0.006±0.01
Statistically Significance	P < 0.001	p < 0.001	p < 0.0001	p < 0.0001	p < 0.0001

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/cm^2 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.

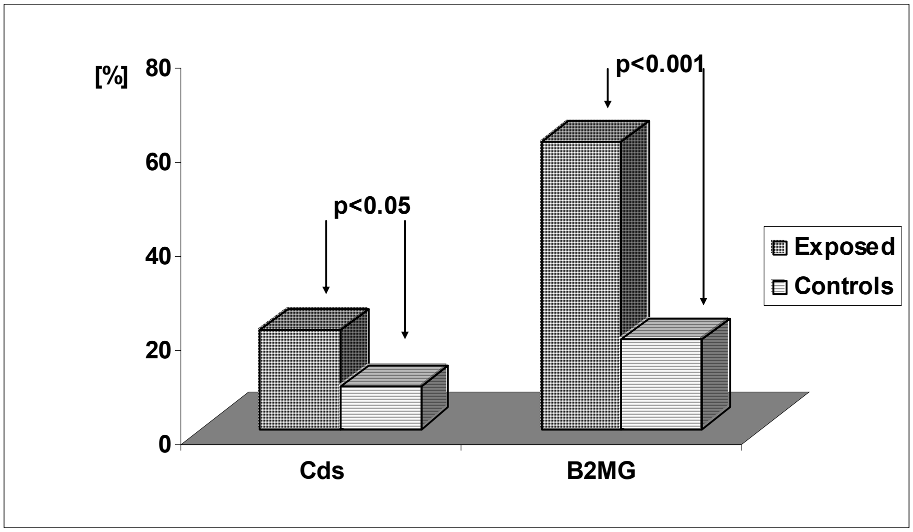

Fig.2. Frequency of abnormal Cds and B2MG levels in electroplaters versus controls

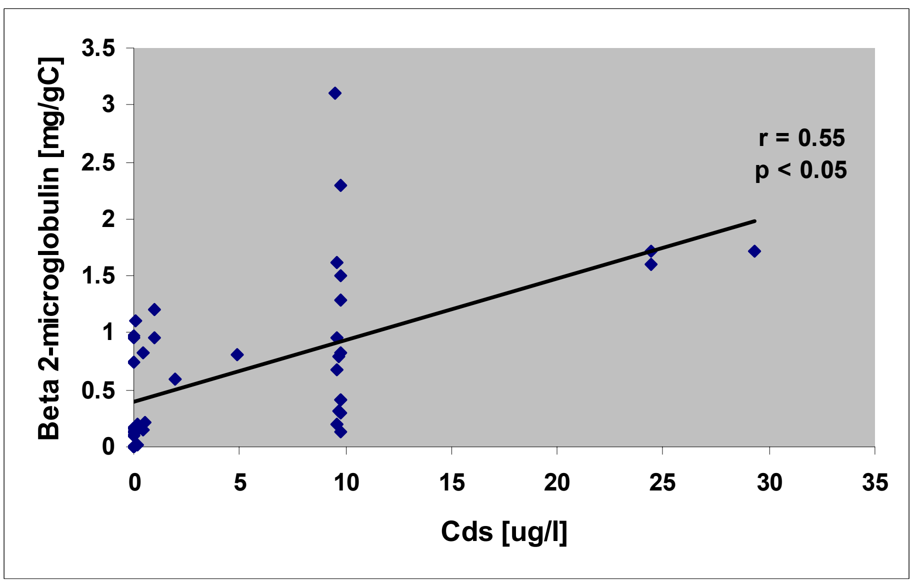

Fig. 3. Correlation between urinary beta 2-microglobulin and blood cadmium levels

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

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

* 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 according 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

1. Dufour Jim: *An Introduction to Metallurgy,* 5th ed. Cameron, 2006, IX: 1.
2. National Pollutant Inventory: *Emission Estimation, Technique Manual for Electroplating and Anodising*, Queensland Department of Environment and Heritage, 1997, 4-8.
3. Burgess WA: *Recognition of Health Hazards in Industry - A Review of Materials & Processes,* 2nd ed. John Wiley & Sons Inc, 1995, 227-40.
4. Roberti S, Mabilia T, Stocco CF, Sarto F, Merler E: *An increased mortality from lung cancer among workers of a bright electroplating factory*, Epidemiol Prev. 2006, 30:(4-5): 232-6.
5. Roff M, Bagon DA, Chambers H, Dilworth EM, Warren N: *Dermal exposure to electroplating fluids and metalworking fluids in the UK,* Ann Occup Hyg. 2004, 48(3): 209-17.
6. Bright P, Burge PS, O'Hickey SP, Gannon PF, Robertson AS, Boran A: *Occupational asthma due to chrome and nickel electroplating,* Thorax. 1997, 52(1): 28-32.
7. Makinen M, Linnainmaa M: *Dermal exposure to chromium in electroplating,* Ann Occup Hyg. 2004, 48(3): 277-83.
8. Chang FH, Wang SL, Huang YL, Tsai MH, Yu ST, Chang LW: *Biomonitoring of chromium for residents of areas with a high density of electroplating factories,* J Expo Sci Environ Epidemiol. 2006, 16(2): 138-46.
9. Baldasseroni A, Gasparrini A, Locatelli F, Lorini C, Lanciotti E, Bavazzano P: *Occupational exposure to nickel in Tuscany: analysis of a biological monitoring register for the period 1991-1998,* Med Lav. 2005, 96(5): 409-18.
10. xxx: *Hotărârea nr. 1218 din 06/09/ 2006 privind stabilirea cerințelor minime de securitate şi sănătate în muncă pentru asigurarea protecției lucrătorilor împotriva riscurilor legate de prezența agenților chimici*, Monitorul Oficial, Partea I, 2006, nr. 845.
11. xxx: *NIOSH Manual of Analytical Methods*, Fourth Edition, 8/15/94, Method 8003.
12. xxx: *NIOSH Manual of Analytical Methods*, Fourth Edition, 8/15/94, Method 9100.
13. Evans HJ, O'Riordan ML: *Human peripheral blood lymphocytes for the analysis of chromosome aberrations*

in mutagen tests, Mutat. Res. 1975, 31: 135.

14. Schmid W: *The micronucleus test for cytogenetic analysis*. In: Chemical Mutagens, Vol. 4, ed. A. Hollaender, Plenum Press, New York, 1976, 31-53.
15. Wass U, Wahlberg JE: *Chromated steel and contact allergy. Recommendation concerning a 'threshold limit value' for the release of hexavalent chromium,* Contact Dermatitis, 1991, 24: 114–8.
16. Fenske RA: *Dermal exposure assessment techniques,* Ann Occup Hyg, 1993, 37: 687–706.
17. Sarto F, Cominato I, Bianchi V, Levis AG: *Increased incidence of chromosomal aberrations and sister chromatid exchanges in workers exposed to chromic acid (CrO3) in electroplating factories*, Carcinogenesis, 1982, 3(9):1011-6.
18. Kiilunen M, Utela J, Rantanen T, Norppa H, Tossavainen A, Koponen M, Paakkulainen H, Aitio A: *Exposure to soluble nickel in electrolytic nickel refining*, Ann Occup Hyg. 1997, 41(2):167-88.
19. Sarto F, Tomanin R, Giacomelli L, Iannini G, Cupiraggi AR: *The micronucleus assay in human exfoliated cells of the nose and mouth: application to occupational exposures to chromic acid and ethylene oxide,* Mutat Res. 1990, 244(4):345-51.
20. Vaglenov A, Nosko M, Georgieva R, Carbonell E, Creus A, Marcos R: *Genotoxicity and radioresistance in electroplating workers exposed to chromium*, Mutat Res. 1999, 446(1):23-34.
21. IARC: *Beryllium, Cadmium, Mercury and Exposures in the Glass Manufacturing Industry*, IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, Lyon, France, 1993, vol. 58: 444
22. Sadhra S, Petts J, McAlpine S, Pattison H, MacRae S: *Workers' understanding of chemical risks: electroplating case study*, Occup Environ Med 2002, 59:689–695.
23. Halliday-Bell J**,** Palmer K**,** Crane G**:** *Health and safety behavior and compliance in electroplating workshops,* Occup Med (Lond), 1997, 47(4):237-40.