OCCUPATIONAL EXPOSURE TO NICKEL SALTS IN ELECTROLYTIC PLATING

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Abstract—An occupational hygiene survey was made in 38 nickel plating shops in Finland and exposure to nickel was studied by means of biological measurements and, in three shops, by using air measurements. The average after-shift urinary nickel concentration of 163 workers was 0.16 μmol l⁻¹ (range 0.001-4.99 μmol l⁻¹). After the 1-5 week vacation the urinary nickel concentration was higher than the upper reference limit of non-exposed Finns indicating that a part of water-soluble nickel salts is accumulated in the body. Urinary nickel concentrations in the shops considered clean in the industrial hygiene walk-through were not different from those observed in the shops considered dirty. The correlation between the concentrations of nickel in the air and in the urine was low, and the amount of nickel excreted in the urine exceeded the calculated inhaled amounts, indicating exposure by other routes such as ingestion. © 1997 British Occupational Hygiene Society. Published by Elsevier Science Ltd.

INTRODUCTION

Two main health effects of nickel are allergic reactions and cancer. The recent reanalysis of the epidemiological studies on the carcinogenicity of nickel and its salts has suggested that the most potent nickel species are water-soluble nickel salts (Doll et al., 1990). No studies have, however, pointed to an elevated cancer risk among nickel platers, who are exposed to soluble nickel compounds. This has been explained (Doll et al., 1990) by the lower exposure to nickel in these industries, by comparison with nickel refining by electrolysis. However, there are few data on exposure to nickel electroplating (Bavazzano et al., 1994; Bernacki et al., 1978, 1980; Grob, 1987; Tandon et al., 1977; Tola et al., 1979; Tossavainen et al., 1980; Warner, 1984). Most of the data are also quite old and reflect exposure to few large facilities.

The purpose of this study was to estimate the current level of occupational exposure to water soluble nickel compounds in nickel plating shops in Finland. An occupational hygiene survey was made in all nickel plating shops and exposure to nickel was studied by the means of biological measurements and, at three workplaces, by using air measurements.

MATERIALS AND METHODS

Plating shops and subjects

The nickel plating shops in Finland were identified from a national directory of enterprises and through contacts with the only nickel producer in Finland (Outokumpu Oy). A survey was made in the 38 identified nickel electroplating
shops by an experienced industrial hygienist. During this survey information on the volume of production, amount of nickel used, number of platers as well as the size, number, temperature, acidity and nickel concentration of the plating baths was collected. Also the type and use of general and local ventilation and measures taken to reduce exposure such as floating plastic balls and covers on the baths was recorded. The hygienist ranked the shops into three classes according to their cleanliness.

A sample was taken from 30 plating baths for the analysis of the nickel concentration and pH of the solutions.

During the survey a questionnaire was administered to the plating workers about the use of protective device, duration of exposure and smoking habits. At the same time an afternoon urine sample was requested for nickel analysis. The number of workers interviewed was 163 (94 men and 69 women) and 145 sent a spot urine sample for analysis.

For the second phase of the study 104 persons from different plating shops were randomly chosen. Their urinary nickel concentrations were followed for one to four consecutive workdays.

Workers (n = 8) who had more than 0.20 μmol Ni l.−1 in morning urine specimens gave an additional morning urine sample after the summer vacation.

Three workshops were chosen for further study. One was classified as clean and another as dirty according to the hygienic survey. Airborne nickel concentrations in these shops were followed for one workday at the same time as the urinary specimens were collected from the platers: air samples were collected from the inside and outside of a protective device (whole mask with filters).

**Analyses**

All air samples were collected as whole shift samples. Cellulose ester membrane filters (Millipore AAWP, Ø37 mm for stationary locations and Ø25 mm for breathing zone specimens, pore size 0.8 μm) were used for the collection of air samples (stationary pumps, flow rate 20 l. min⁻¹; personal sampling pumps, flow rate 2 l.min⁻¹). The soluble nickel compounds were dissolved into hot water (1 h at 70°C) from the filters, which were rinsed thoroughly thereafter. For the analysis of acid soluble nickel, the filters were dried at 100°C overnight and thereafter dissolved in 5 ml concentrated nitric acid and thereafter 5 ml hydrochloric acid was added to the solution, which was evaporated to dryness. The residue was dissolved in 5% nitric acid, the solution was filtered quantitatively into a glass bottle and water was added to give a final nitric acid concentration of 0.5%. From this solution nickel was analysed by electrothermal atomic absorption spectrophotometer (Varian SpectrAA 400 Zeeman) calibrating against AAS-nickel standards (Merck) diluted in 0.5% nitric acid. A spiked control was run in every series (Tossavainen, 1976).

In addition, 150–200 l. air samples were collected for particle size and composition analyses on polycarbonate filters (Nuclepore, pore size 0.2 μm). These samples were studied by scanning electron microscopy (JEOL 6400) and microanalysis (Tracor Northern TN5500). The membranes were covered with a gold layer (about 20 nm in thickness) in an ion-sputtering device (JEOL JFC 1100). The magnifications used were from 1000 to 100 000×. The smallest detectable particles
were about 0.1 μm in size. X-Ray peaks of nickel, sulphur and chloride were used to identify the composition.

The schedule for urine collection is presented in Table 1. The samples were analysed with electrothermal atomic absorption with a dilution method using nitric acid and oxalic acid as matrix modifiers (Kiilunen et al., in press). Commercial urine standards (Lyphochek 1 and 2, Bio-Rad, U.S.A. and Seronorm trace metal Nycomed, Norway), a spiked control and two natural pooled urine controls (low and high nickel concentration) were used for internal quality assurance. The recovery of commercial urine standard was 103.1±2.4% and the day to day variation 4–7%.

The nickel analysis from plating bath samples was performed by flame atomic absorption against standards made in 5% nitric acid solution (Pye Unicam 9400) and the pH was measured with pH-meter (Orion Research digital ionmeter 501).

**RESULTS**

The plating shops

The number of workers in the plating shops varied between one and 16; in eight shops there was only one worker, in seven there were two, in eight three. In 11 shops, the number of employees was between four and eight, and in only four were they more than 10. The surface area of the plating shops varied between 50 and 300 m², and the size of the baths, depending on the items plated, between 0.04 and 13.5 m³. The maximal number of baths in a shop was eight. The products varied from small electric components, zippers, medals, parts for plumbing fittings to parts of motors, bicycles, baby prams and pushchairs, and furniture. A rough estimate was made that in 15 shops the consumption of nickel sulphate in a month was below 10 kg, in 14 shops 10–100 kg and in three shops more than 100 kg. The consumption of nickel chloride was below 10 kg in 20 shops, 10–100 kg in 12 and more than 100 kg per month in two. The consumption of nickel anode varied from 10 kg to 10 tons in a year. The nickel concentrations measured (n = 30) in the plating solutions were 23.4–92.3 g l⁻¹ (mean 62.6 g l⁻¹). In a sample from a NiF-bath the nickel concentration was 1.65 g Ni l⁻¹.

The electroplating was mainly of decorative and technical quality. The thickness of the nickel layer was 10–25 μm in decoration plating, 1–50 μm in technical plating and in some special cases it reached 10 mm. In the process either the current (10–1000 A), current density (0.5–100 A dm⁻²) or voltage (1–30 V) was constant. The temperature of the baths was 25–70°C and the pH between 4.7 and 6.1. Fat removal
was achieved with organic solvents \(n = 8\), alkali solutions \(n = 35\) or by electricity \(n = 30\). Chemical pickling was performed in 31 plating shops.

The nickel baths were covered during use in 20 shops, in 13 they were covered only after work, in five there were no lids over the baths. In one shop plastic balls were used on the surface of the bath and another shop used both the balls and a cover, in almost all shops a surface-active agent was used.

No general mechanical ventilation was installed in three shops, no local exhausts existed above the baths in 14 shops. In one shop the general ventilation did not function properly.

According to the industrial hygiene survey 12 shops were classified as clean (group 1), 15 were classified in the middle (2) group and eleven were considered dirty (group 3). The mean values of urinary nickel were calculated according to the apparent cleanliness of the shops.

**Urinary nickel concentrations**

The average working time of the 163 workers in the nickel plating shops was 12 years; 14 years for men and 10 years for women. The newest worker had been employed in a shop less than 1 year and the longest working time was 35 years. More than half the workers were non-smokers \(n = 95\), 58%.

During the hygienic survey an individual interview was conducted with all the platers. Most workers (91% from women and 87% from men) used gloves in their work, about half used protective overalls and shoes but less than a third used protective masks (Table 2).

Urine specimens from 89% of the interviewed workers were sent for nickel analysis. The nickel concentration in urine was on average 0.16 \(\mu\)mol l.\(^{-1}\) \((0.001-4.99 \mu\text{mol l.}^{-1}, n = 145)\), 0.14 \(\mu\text{mol l.}^{-1}\) \((0.005-2.84 \mu\text{mol l.}^{-1}, n = 63)\) for women and 0.18 \(\mu\text{mol l.}^{-1}\) \((0.001-4.99 \mu\text{mol l.}^{-1}, n = 82)\) for men. The mean values for different workplaces varied greatly \((0.01-0.89 \mu\text{mol l.}^{-1})\) while the median values were more uniform \((0.02-0.05 \mu\text{mol l.}^{-1})\).

During the second stage of the study, the urinary nickel concentrations of 97 workers were followed for one working week. As expected, there was an exposure-related fluctuation of urinary nickel concentrations (Fig. 1); the mean nickel concentration in morning specimens was 0.10-0.11 \(\mu\)mol l.\(^{-1}\) and in the afternoon specimens, 0.12-0.16 \(\mu\text{mol l.}^{-1}\) (Table 3).

<table>
<thead>
<tr>
<th>Question</th>
<th>All</th>
<th>Men</th>
<th>Women</th>
</tr>
</thead>
<tbody>
<tr>
<td>Do you use protective equipment in your work?</td>
<td>Total number*</td>
<td>Number of users</td>
<td>% from all†</td>
</tr>
<tr>
<td>protective mask</td>
<td>159</td>
<td>53</td>
<td>32.7</td>
</tr>
<tr>
<td>gloves</td>
<td>163</td>
<td>105</td>
<td>64.4</td>
</tr>
<tr>
<td>overall</td>
<td>162</td>
<td>79</td>
<td>48.8</td>
</tr>
<tr>
<td>shoes</td>
<td>162</td>
<td>68</td>
<td>42.0</td>
</tr>
</tbody>
</table>

*Number of workers, who answered the question.
†Percentage from all/men/women interviewed.
Nine workers had urinary nickel concentration over 0.20 μmol l.−1 in the morning samples. They were asked to send a spot urine specimen on the first morning after the summer vacation (1–4 weeks) when the mean nickel concentration was 0.16 μmol l.−1 (0.03–0.40 μmol l.−1).
Table 3. Urinary nickel concentrations in plating workers (μmol l.⁻¹)

<table>
<thead>
<tr>
<th>Day/time</th>
<th>number</th>
<th>mean</th>
<th>median</th>
<th>minimum</th>
<th>maximum</th>
<th>95th percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/morning</td>
<td>104</td>
<td>0.10</td>
<td>0.05</td>
<td>0.006</td>
<td>0.71</td>
<td>0.40</td>
</tr>
<tr>
<td>1/afternoon</td>
<td>103</td>
<td>0.12</td>
<td>0.06</td>
<td>0.005</td>
<td>1.32</td>
<td>0.51</td>
</tr>
<tr>
<td>2/morning</td>
<td>98</td>
<td>0.10</td>
<td>0.05</td>
<td>0.01</td>
<td>0.85</td>
<td>0.38</td>
</tr>
<tr>
<td>2/afternoon</td>
<td>97</td>
<td>0.14</td>
<td>0.07</td>
<td>0.01</td>
<td>2.15</td>
<td>0.44</td>
</tr>
<tr>
<td>3/morning</td>
<td>97</td>
<td>0.11</td>
<td>0.07</td>
<td>0.01</td>
<td>0.93</td>
<td>0.58</td>
</tr>
<tr>
<td>3/afternoon</td>
<td>97</td>
<td>0.13</td>
<td>0.07</td>
<td>0.01</td>
<td>1.31</td>
<td>0.38</td>
</tr>
<tr>
<td>4/morning</td>
<td>96</td>
<td>0.11</td>
<td>0.07</td>
<td>0.02</td>
<td>1.06</td>
<td>0.28</td>
</tr>
<tr>
<td>4/afternoon</td>
<td>93</td>
<td>0.16</td>
<td>0.07</td>
<td>0.01</td>
<td>3.19</td>
<td>0.51</td>
</tr>
<tr>
<td>after vacation</td>
<td>8</td>
<td>0.16</td>
<td>0.07</td>
<td>0.03</td>
<td>0.40</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Table 4. Urinary nickel concentration of platers from shops in the different categories of cleanliness

<table>
<thead>
<tr>
<th>Cleanliness category</th>
<th>N</th>
<th>n</th>
<th>Mean μmol l.⁻¹</th>
<th>Minimum μmol l.⁻¹</th>
<th>Median μmol l.⁻¹</th>
<th>Maximum μmol l.⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean</td>
<td>12</td>
<td>72</td>
<td>0.161</td>
<td>0.008</td>
<td>0.044</td>
<td>4.99</td>
</tr>
<tr>
<td>Intermediate</td>
<td>15</td>
<td>41</td>
<td>0.166</td>
<td>0.001</td>
<td>0.047</td>
<td>2.84</td>
</tr>
<tr>
<td>Dirty</td>
<td>11</td>
<td>27</td>
<td>0.161</td>
<td>0.007</td>
<td>0.084</td>
<td>0.647</td>
</tr>
</tbody>
</table>

N = number of workshops, n = number of workers studied. The differences were not statistically significant (Analysis of variance, Wilcoxon rank score test).

The urinary concentrations of nickel among workers of the shops considered clean, intermediate or dirty were not different (Table 4).

Air measurements

In the shop selected to represent low-level exposure, the nickel content was 0.5 μg m⁻³ in the breathing zone of hanger workers; one sample was mostly water-soluble nickel but in the other the amount of water soluble nickel was only 30%. In stationary locations close to the hangers the nickel concentrations were 0.05 and 0.2 μg m⁻³ and the proportion of water-soluble nickel was 60 and 25%, respectively. Higher nickel concentrations in the air were found near the nickel bath: 26 μg m⁻³, out of which almost 100% was water-soluble. The worker responsible for maintenance of the bath had a nickel concentration of 0.7 μg m⁻³ (80% water-soluble) in his breathing zone.

In the work shop, where the exposure was expected to be high, the nickel concentrations in the breathing zone of the workers were between 5.6 and 78.3 μg m⁻³ (n = 6). Highest concentrations were measured in the breathing zone of the worker who worked beside the nickel bath. In half the samples 80–90% of nickel was water-soluble nickel, but in one it was only 18%. In stationary samples, the highest concentration was observed beside the nickel bath (73.3 μg m⁻³) and lowest in the hanging area (11.9–17.8 μg m⁻³). In all samples taken from stationary locations the proportion of water-soluble nickel was about 90%.

The nickel concentration inside the protective device was 1.6 μg m⁻³ while it was 11.4 μg m⁻³ outside the mask of the worker who made plating solutions from nickel sulphate and chloride. Accordingly, the effectiveness of the mask was about seven during this half-hour period. At the side of the repairing bath the...
Fig. 2. Electromicroscopic appearance of the nickel sulphate aerosol during the production of nickel plating solution (magnification 2000×).
concentrations were 4–6 μg m$^{-3}$. Inside the mask almost half the nickel was watersoluble but outside the proportion was only 10%. In the stationary locations the share of water-soluble nickel was 60–75%. The aerosol consisted mostly of particles 5–10 μm in size that were dry salt or liquid droplets (Fig. 2).

The relationship between air and nickel concentrations was studied using the measured concentrations as such, as well as the values corrected to a common relative density or creatinine. The number of data points was only seven, though, and no consistent correlation was observed between the breathing zone nickel concentrations and the urinary nickel concentrations ($r=0.22–0.46$) (Table 5). Higher correlation coefficients were observed for nickel concentrations from the stationary samples and urinary nickel concentrations (0.84 for total air nickel) but the uncertainty of the slope of the regression lines was very large. The mean airborne total nickel concentration among these workers was 12.8 μg m$^{-3}$, and the mean urinary nickel concentration was 0.29 μmol l$^{-1}$.

**DISCUSSION**

In the Finnish nickel plating shops the air nickel concentrations were low, of the order of a few micrograms per cubic metre. Similar results have been reported in Canada (Warner, 1984) and in the U.S.A. (Bernacki et al., 1980). A large range (0.10–42.00 μg m$^{-3}$) with a low median value (2.3 μg m$^{-3}$) was observed recently in 25 different plating shops in Italy (Bavazzano et al., 1994). In Germany a mean nickel concentration of 10 μg m$^{-3}$ has been reported when a soluble nickel anode and 110 μg m$^{-3}$ when an insoluble anode was used (Groß, 1987). A clear decrease to 7 μg m$^{-3}$ was observed when surface active agent was added to the solution. Earlier in Finland 10–100 times higher concentrations of nickel have been measured in the air (20–170 μg m$^{-3}$) (Tola et al., 1979; Tossavainen et al., 1980).

The nickel concentration in urine of the plating workers was low in most platers, although the average levels were clearly higher than those observed in non-exposed Finns (95th percentile, 0.06 μmol l$^{-1}$) (Kiilunen et al., in press). Higher concentrations of nickel in urine were observed in platers during the first survey. This may be a consequence of contamination during specimen collection although very detailed instructions on how to avoid contamination were given to the workers. In several cases the platers had no earlier experience in urine sample collection for nickel analysis. As they learned to avoid contamination through practice, values over 3 μmol l$^{-1}$ were no longer observed in the second phase of the study.

During nickel plating the mean value for urinary nickel reported from India in 1977 (Tandon et al., 1977) was only a little higher (0.21 μmol l$^{-1}$) than that we observed among Finnish platers, but the highest concentration they found was only 0.40 μmol l$^{-1}$; on the other hand, Bernacki and coworkers (Bernacki et al., 1980) found values almost twice as high (about 6 μmol l$^{-1}$). Recently Bavazzano and coworkers (Bavazzano et al., 1994) reported that the median value of nickel in urine of electroplating workers from 25 Italian plating shops was 0.07 μmol l$^{-1}$ with a maximum value of 0.85 μmol l$^{-1}$.

The hygiene walk-through survey seemed to give an inaccurate estimation of the exposure, because the urinary concentrations of nickel among the workers did not differ between the clean and dirty shops.
Table 5. The relationships between air and urine nickel.

<table>
<thead>
<tr>
<th>Dependent variable</th>
<th>Independent variable Stationary</th>
<th>Independent variable Breathing</th>
<th>n</th>
<th>r</th>
<th>Slope</th>
<th>Intercept</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-Ni rd*</td>
<td>Air-Ni(total)</td>
<td></td>
<td>7</td>
<td>0.841</td>
<td>0.017</td>
<td>0.061</td>
<td>0.018</td>
</tr>
<tr>
<td>U-Ni rd*</td>
<td>Air-Ni(soluble)</td>
<td></td>
<td>7</td>
<td>0.750</td>
<td>0.016</td>
<td>0.082</td>
<td>0.052</td>
</tr>
<tr>
<td>U-Ni rd*</td>
<td>Air-Ni(a.soluble)</td>
<td></td>
<td>7</td>
<td>0.789</td>
<td>0.116</td>
<td>0.069</td>
<td>0.035</td>
</tr>
<tr>
<td>U-Ni cr†</td>
<td>Air-Ni(total)</td>
<td></td>
<td>7</td>
<td>0.849</td>
<td>0.856</td>
<td>5.207</td>
<td>0.016</td>
</tr>
<tr>
<td>U-Ni cr†</td>
<td>Air-Ni(soluble)</td>
<td></td>
<td>7</td>
<td>0.810</td>
<td>0.863</td>
<td>6.169</td>
<td>0.027</td>
</tr>
<tr>
<td>U-Ni cr†</td>
<td>Air-Ni(a.soluble)</td>
<td></td>
<td>7</td>
<td>0.660</td>
<td>5.250</td>
<td>6.508</td>
<td>0.106</td>
</tr>
</tbody>
</table>

*Corrected to relative density; †corrected to creatinine; soluble = water soluble; a.soluble = acid soluble.
In early studies at relatively high exposure levels, good and consistent correlations between air-borne and post-shift urinary concentrations of nickel have been observed among nickel platers: Eight-hour time-weighted exposure to 100 μg m⁻³ nickel has been reported to lead to a post-shift urine nickel concentration of 0.7–1.3 μmol l⁻¹ (Nieboer et al., 1984; Norseth, 1984; Tola et al., 1979; Ulrich et al., 1991). In studies where the exposure has been low, the correlations have not been equally good, and urinary nickel concentrations have been higher, by comparison with the air levels (Ghezzi et al., 1989; White and Boran, 1992). In this study a limited number of simultaneous measurements of concentrations of nickel in the air, and urine, were made. However, the tendency is similar to the earlier studies: the correlations between breathing zone nickel and urine nickel were weak, not statistically significant (although there was a positive correlation between stationary air sampling and urine nickel concentrations), and the urine concentrations of nickel were much higher than those predicted by the studies performed at high air nickel concentrations. These findings are in line with those of Bavazzano and colleagues (Bavazzano et al., 1994) in electroplaters and of our own among nickel electrolysis workers (Kiilunen et al., in press), and indicate that nickel is absorbed via routes other than inhalation, most likely via ingestion—probably because of hand contamination. Bavazzano and coworkers (Bavazzano et al., 1994) proposed that the nickel deposited on the facial skin is the main contributor to an increase in urinary nickel levels and hands a minor one, but concluded that the contamination is based mainly on personal habits.

The effectiveness of the protective mask was estimated from the difference between the nickel concentrations inside the protective mask and in stationary locations during the preparation of plating solution. It was seven for the worker during this a half hour process. During electrorefining the effectiveness was estimated to be 150–250 during a whole day (Kiilunen et al., in press).

After inhalation exposure to soluble compounds, nickel is excreted in urine with a half time ranging from 17 to 39 h (Tossavainen et al., 1980). After the 1–5 week vacation the median value in urine of the eight persons studied was still higher than the upper reference limit of non-exposed Finns (0.06 μmol l⁻¹) and the highest concentration was as high as 0.40 μmol l⁻¹. This clearly indicates that a part of water-soluble nickel salts is accumulated in the body with a long half time. This phenomenon is similar to that we have observed earlier in the nickel refining workers (Kiilunen et al., in press).

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