CHAPTER VIII

OCCUPATIONAL EXPOSURE:

EXPOSURE TO TRACE METALS IN GLASS WORK IN CERAMIC INDUSTRIES

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1. General

There is a growing demand for various earthenwares, like household crockery, kitchenware, electrical insulators, sanitaryware and such other ceramic goods. Modern technology has developed many types of glaze materials, and also glaze techniques, to provide the beautiful luster, colour and shades to earthenware. Various metallic salts of zinc, manganese, chromium, lead, mercury, arsenic, nickel, copper, iron, etc. are used widely in various proportions for making glaze solutions.

The way, in which, the glaze materials are handled in the glaze operation, poses the occupational hazards of various kinds. Thakur (1951) had reported the chronic lead poisoning amongst the glaze workers and had made some specific recommendations for eliminating lead poisoning. There are many recent papers attributing glaze materials as the source of metal poisoning (Harris et al., 1967; Hickman, 1970; Klein et al., 1970;
The objective of the study reported in this chapter are:

(i) to evaluate the airborne concentration of chromium, manganese, nickel, copper, zinc, cadmium and lead during the glaze operation;

(ii) to evaluate the degree of absorption of these metals by workers by means of biological monitoring of blood and urine carried out along with the air monitoring programme.

2. Materials and methods

2.1. Working processes in glaze operations

There are two modes of applying the glaze on the earthenware as briefly indicated below.

(A) Dipping: Generally the kitchenware and small pieces are glazed simply by dipping the article in the glaze solution. Such work is done almost continuously, with the result that the glazers' hands remain in the solution with the likely risk of absorption of metallic salts through the skin and ingestion along with food through contaminated hands.
Sanitaryware, toys and big articles like jars on the other hand, are glazed by spraying the glaze solution on the article. During the operation, fine aerosols of the glaze materials in the air environment of the sprayer, may be inhaled and absorbed by the body.

2.2. Analysis of glaze samples

Five glaze samples, collected from three different ceramic industries were analyzed for their metallic concentration. The samples were processed as described below.

The glaze sample (in solution form) was evaporated and the residue was dried at 100°C till moisture was completely removed. A small portion of the dried glaze material was digested in 1 ml Nitric acid (concentrated, Anlar), and evaporated nearly to dryness. The residue was dissolved in 1 ml HCl, and a known volume was made up with triple glass distilled water. This solution was used for the determination of different trace heavy metals by the Atomic absorption spectrophotometer method.

2.3. Air monitoring

Air samples, from the breathing cone of the sprayer,
were collected using the filter cone sampler during actual working hours in the shift. At each spraying booth, two or three samples were collected serially, and were combined for the analysis. At the same time, respirable dust samples were collected using a hemiport sampler.

Details of air sample collection using the filter cone sampler and hemiport, sample preparation and determination by AAS method are discussed in second chapter.

2.6. Biological monitoring

The blood and urine of the 25 exposed workers (17 sprayers and 8 dippers) and 14 matched control groups were used to evaluate the degree of absorption of various metals due to work in glass operation.

Methods for the collection of blood and urine samples, the digestion of these samples by wet oxidation and analysis of samples by using Atomic absorption spectrophotometer are discussed in chapter-2.

3. Results

The results of the analysis of five glass samples are given in Table-34.
Particulates collected on the filter media from air samples were dried along with filter paper at 100°C till the moisture was removed. Total dust, respirable dust and metallic concentrations, after removing the moisture, were worked out. The results are shown in Figure-14.

Relationship between total dust and respirable dust, for the 15 air samples collected during the glass operations, is plotted in Figure-15.

Figures-16 and 17 show the average metal concentrations in blood and urine respectively, of the control, sprayer and dipper groups.

Figures-18 and 19 show the concentrations of various metals in blood and urine respectively in the workers exposed for the various duration.

Table-35 presents the statistical significance for metallic concentrations in blood and urine for exposed workers, sprayer and dipper, compared to control group workers.

Table-36 presents the statistical significance for metallic concentrations in blood and urine of workers exposed to varying duration.
4. Discussion

The concentrations of various metals in the glass solutions are shown in Table-34. The concentration of zinc is comparatively higher (203-2034 μg/gm). Manganese concentration varies from 35-60.2 μg/gm, and that of lead varies from 16-41.4 μg/gm. The concentration of nickel, copper, chromium and calcium varies from 1.2-9.2 μg/gm.

The airborne concentration of these glass material, during glass spraying operation, depends on many factors like specific gravity and size of the droplets. As the glass is being sprayed in the solution form, airborne droplets are formed and settle down. The exhaust provided sucks out the major portion of the airborne particulates away from the breathing zone of the worker. Even then a small amount of particles remain suspended in the air near the breathing zone of the sprayer.

The mean total (gravimetric) dust concentration was found to be 58 mg/m³ (range 10 mg - 113 mg/m³) during the spraying operation (Figure-14). It was noted that total dust concentration was comparatively very high at the spraying booth when the exhaust fan
was off. The respirable dust concentration was found to be 5.1 mg/m$^3$ (0.91 - 11.03 mg/m$^3$) (Figure-14). The total dust concentration was thus about ten times the respirable dust concentration at the work place. A good regression line was obtained between total dust and respirable dust (Figure-15). The regression equation was:

$$\text{Respirable Dust} = 0.0973 \times (\text{Total Dust}) + 0.019 \quad (r=0.935)$$

It is apropos to mention here that about 20-25% free silica was determined in the ambient air environment of ceramic and pottery units (NICH, 1977) for which TLV is obtained from the following equations (NICH, 1974).

$$\text{TLV for "Total Dust"} = \frac{30 \text{ mg/m}^3}{3 \text{ Free silica} + 3}$$

$$\text{TLV for "Respirable Dust"} = \frac{10 \text{ mg/m}^3}{5 \text{ Free silica} + 2}$$

The results of the present study show that neither total nor respirable particulate concentrations exceeded the TLV. The metallic concentration in the particulates also did not exceed the TLV or MAC values in any of the observed cases.

From Figure-15, it can be seen that sprayer and
dipper show the higher values for metallic concentrations in blood except in case of copper where the values are higher but not significant for the control group compared to the exposed group. No precise explanation for this is possible at this stage.

Table-35, shows that the sprayer group has high value for nickel (P < 0.05), cadmium (P < 0.01) and lead (P < 0.05) in blood, while the dipper group has high values for manganese, nickel, zinc, cadmium and lead (P < 0.05 in all the cases). The metallic concentration in the blood and urine of dipper group of workers was higher than that in the blood of sprayers, but this was significantly so only for zinc (P < 0.05).

Figure-17 shows the urinary metallic concentrations for both the sprayer and dipper groups. The urinary metallic concentrations are comparatively high in both the groups than that in control group for all the metals except copper which is higher in the case of the control group. These increases in the urinary metallic concentration were, however, significant only for nickel (P < 0.01) and cadmium (P < 0.05) in dipper group. The intergroup differences in the metallic concentrations were not statistically significant.
Figure-13 indicates the group mean concentrations of metals in blood of workers with reference to their duration of exposure. The average metal concentrations in blood are higher in exposed group than in the control group, and there is also a relative increase of metal concentration with increase in the exposure duration, except for copper in blood, where the exposed group showed lower concentrations.

These studies indicate (Table-36), that workers having an exposure duration of up to five years show significant increase concentration of manganese, nickel, and cadmium in blood ($P < 0.05$ for all), the group with an exposure duration of from 5-10 years show significant increase for the concentration of cadmium ($P < 0.01$) and lead ($P < 0.05$) in blood, while group exposed for more than 10 years, shows significant increase in the concentration of nickel ($P < 0.01$), cadmium ($P < 0.01$) and lead ($P < 0.01$) in blood.

Broadly, there is no regular pattern for the urinary metallic concentration in the exposed group of glass workers (Figure-19). Only urinary manganese shows significantly lower value ($P < 0.05$) for workers exposed for 1-5 years and for more than 10 years, and
ordinary nickel ($P < 0.05$) shows significantly increased values for the workers exposed for 5–10 years (Table-33).

5. Conclusions and recommendations

The results of this study reveal that:

(1) The use of metallic salts does pose the problem of exposure to metals to various degrees of risk depending on the nature and duration of the work.

(2) The work place air is contaminated with the trace metals.

(3) The results also confirm the good correlation between total and respirable dust concentration ($r = 0.935$). This correlation helps in monitoring the respirable dust concentrations at the work place by determining the total dust concentration only, which is relatively easier.

(4) The dippers show more absorption of metals than sprayers, perhaps because of their almost constant and continuous dipping of hands into the glass solution.

(5) The uncertain pattern of metallic concentrations obtained in urine samples, leave the choice of depending on blood samples as the more reliable
substrate for studying exposure to trace metals in glass work.

The concentration of airborne particulates is higher, and logically so, when the exhaust fan was off during the glass operations. Therefore, the provision for the exhaust device at the spraying booth is recommended and workers should be instructed to keep the fan on during the glass-spray.

The dippers' hands remain in the glass solution, and also, during the spraying operation, glass solution falls on the body and sticks there for a longer time. It was also observed that glaziers, being illiterate and unaware of the trade hazards, do not take proper care for washing the hands before taking food. It is, therefore, recommended that glaziers should be provided suitable hand gloves, and face masks. Washing facilities at the place of work, should be provided and supervisors must check their use routinely.
Table 34
Concentration of trace metals in close samples

<table>
<thead>
<tr>
<th>Close sample</th>
<th>Cr (µg/g)</th>
<th>Hg (µg/g)</th>
<th>Mn (µg/g)</th>
<th>Fe (µg/g)</th>
<th>Cu (µg/g)</th>
<th>Zn (µg/g)</th>
<th>Cd (µg/g)</th>
<th>Pb (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.2</td>
<td>47.0</td>
<td>7.2</td>
<td>3.5</td>
<td>1950.0</td>
<td>3.6</td>
<td>21.2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.1</td>
<td>39.8</td>
<td>5.4</td>
<td>2.6</td>
<td>1330.0</td>
<td>2.7</td>
<td>16.9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.6</td>
<td>35.0</td>
<td>5.4</td>
<td>2.6</td>
<td>803.0</td>
<td>1.9</td>
<td>31.3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5.2</td>
<td>60.2</td>
<td>6.0</td>
<td>3.9</td>
<td>2334.0</td>
<td>1.2</td>
<td>41.4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.5</td>
<td>45.0</td>
<td>6.2</td>
<td>4.2</td>
<td>1345.0</td>
<td>3.0</td>
<td>22.5</td>
<td></td>
</tr>
</tbody>
</table>
### Table 35

**Statistical significance (t-test) for metallic concentrations in blood and urine of ciliates (sporozoan and dinoflagellate)**

<table>
<thead>
<tr>
<th>Subject and no.</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Control (14)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Spore</strong> (17)</td>
<td>P &lt; .05</td>
<td>.5</td>
<td>.05</td>
<td>.005</td>
<td>.005</td>
<td>.01</td>
<td>.005</td>
</tr>
<tr>
<td><strong>Tiger</strong> (3)</td>
<td>P &lt; .05</td>
<td>.5</td>
<td>.05</td>
<td>.005</td>
<td>.005</td>
<td>.01</td>
<td>.005</td>
</tr>
</tbody>
</table>

*P < .05 significant.*

*Mean ±S.E. values for the concentration of metals in blood and urine are shown in Fig.10*
Table 36

Statistical significance (t-test) for metallic concentrations in blood and urine of the workers (with respect to their exposure duration).

<table>
<thead>
<tr>
<th>Exposure duration</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Hg</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Zn</th>
<th>Cd</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-5 yrs. (13)</td>
<td>*</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
</tr>
<tr>
<td>5-10 yrs. (13)</td>
<td>*</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
</tr>
<tr>
<td>10 yrs. (4)</td>
<td>*</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
<td>&lt;</td>
</tr>
</tbody>
</table>

* = Not significant.

(Can be *3.5* values for the concentrations of metals in blood and urine are shown in Fig.17)
Figure 14: Airborne particulate matters in the ceramic glaze spraying operation.

<table>
<thead>
<tr>
<th></th>
<th>CONCENTRATION</th>
<th>mg/m³</th>
<th>ug/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOTAL DUST</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RESPIRABLE</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHROMIUM</td>
<td>8</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>MANGANESE</td>
<td>8</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>NICKEL</td>
<td>8</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>COPPER</td>
<td>8</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>ZINC*</td>
<td>8</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>CADMIUM</td>
<td>8</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>LEAD</td>
<td>8</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

* READ THIS VALUE IN mg/m³
Figure 15. Relationship between total and respirable dust concentrations.

\[ C_{\text{resp}} = 0.0978 \times C_{\text{total}} + 0.019 \]

\[ r = 0.985 \]

\[ P < 0.01 \]
Figure 16: Concentrations of trace metals in blood in glaziers (sprayers & dippers) & control workers.
Concentrations of trace metals in Urine in glassers (C sprayers & dippers) & control workers.

Figure 17
Figure: 18 Concentrations of trace metals in blood of glaziers (with respect to exposure duration) & control workers.

EXPOSURE DURATION (in Years)

Control 1-5 6-10 >10

Metallic Concentration in Blood (µg/100ml)
Figure 19: Concentrations of trace metals in urine of glaziers (with respect to exposure duration) & control workers.

*EXPOSURE DURATION [In Years]*

- CONTROL
- 1-5
- 6-10
- >10

Metallic Concentration in Urine [ug/100ml]