Use of Inhalable Cr\textsuperscript{+6} Exposures to Characterize Urinary Chromium Concentrations in Plating Industry Workers

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Abstract: Use of Inhalable Cr\textsuperscript{+6} Exposures to Characterize Urinary Chromium Concentrations in Plating Industry Workers: Jyh-Larng Chen, et al.

In this study, both personal sampling and biological monitoring were conducted on 27 and 30 workers selected from decorative plating and hard-surface plating operations, respectively. For personal sampling, the inhalable aerosol sampling technique was adopted in order to measure worker's soluble Cr\textsuperscript{+6} exposure level ($C_{\text{INH}}$) on the last day of the workweek. For biological monitoring, a urine specimen was collected at the end of the shift on the last day of the workweek in order to determine a worker's urinary chromium concentration ($C_{\text{URINE}}$).

Results show that hard-surface plating workers had higher $C_{\text{INH}}$ (arithmetic mean $\approx 25.2 \mu g/m^3$) than decorative plating workers (arithmetic mean $\approx 1.91 \mu g/m^3$). The above results could be due to the longer plating time involved in the former plating operation than in the latter. The relationship between $C_{\text{INH}}$ and $C_{\text{URINE}}$ was found as $C_{\text{URINE}} = 1.86 C_{\text{INH}} - 0.21$ ($R^2 = 0.87, n=57$), which suggests that the inhalable aerosol sampling results were able to explain the variation in workers' urinary chromium concentrations up to 87%. Assuming the level of $C_{\text{INH}}$ was equivalent to the current TLV-TWA of 50 $\mu g/m^3$, the above regression model yielded a level of $C_{\text{URINE}}$ as approximately 93 $\mu g/g\cdot$creatinine. The above value is clearly different from the current present biological exposure index BEI of 30 $\mu g/g\cdot$creatinine which is known to be applicable only to welding workers. The above discrepancy could be due to the intrinsic difference in particle size distribution between the Cr\textsuperscript{+6} droplets generated during the plating process and Cr\textsuperscript{+6} fumes generated during the welding process. Considering that no BEI has been suggested for chromium plating industries, the result obtained in this study will be helpful in introducing a new BEI in the future.

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Long term exposure to soluble hexavalent chromium (Cr\textsuperscript{+6}) has been known to cause ulceration and perforation of the nasal septum, bronchitis, asthma and liver and kidney damage in exposed workers\textsuperscript{1–3).} In order to protect workers from irritation of the respiratory tract and possible liver and kidney damage, the American Conference of Governmental Industrial Hygienists (ACGIH) has suggested a TLV-TWA of 50 $\mu g/m^3$ for soluble Cr\textsuperscript{+6} exposure for both plating and welding workers\textsuperscript{4).} In addition, the ACGIH has also suggested another two biological exposure indices (BEIs) for worker's urinary chromium concentration measured at the end of the shift on the last day of the workweek (= 30 $\mu g/g\cdot$creatinine) and the increase in a worker's urinary chromium concentration during one work shift (= 10 $\mu g/g\cdot$creatinine), respectively\textsuperscript{5).} Nevertheless, it should be noted that the above BEIs were developed based on the results of tests conducted on manual metal arc (MMA) welding workers on the condition that their soluble Cr\textsuperscript{+6} fume exposure levels were at 50 $\mu g/m^3$\textsuperscript{6–8).} Therefore, the ACGIH has clearly indicated that the above BEIs were applicable only for MMA welding workers, but not for plating workers. Although a number of studies have set out to relate workers’ urinary chromium concentrations to their corresponding soluble Cr\textsuperscript{+6} droplet exposures, no relationship could be established\textsuperscript{9–11).} The ACGIH has concluded that the above results might be due to difficulty in characterizing workers’ soluble Cr\textsuperscript{+6} exposure levels to justify their corresponding urinary excretions\textsuperscript{9),} but it should be noted that the exposure levels estimated in the above studies were based on the so-called ‘total’ aerosol sampling technique. But according to several wind tunnel studies, the above sampling technique was found to not only fail to accurately collect the ‘true total’ aerosols,
but also poorly reflected the fraction of aerosols that would actually be inhaled by workers (i.e., inhalable aerosol exposure)\(^{12-14}\). A number of studies in particular have shown that the inhalable aerosol sampling results were consistently greater than ‘total’ aerosol sampling results in various industries\(^ {15-21}\). Therefore, it is reasonable to suspect that no relationship could be established between workers’ soluble Cr\(^{6+}\) droplet exposure and their corresponding urinary chromium concentration was the limitation of the ‘total’ aerosol sampling technique in characterizing workers’ exposure levels.

For aerosol measurement to be meaningful in relation to human health, theoretically it must be carried out in a way that properly reflects the nature of exposure. This leads to the idea of the ‘inhalability’ of the human head, and has been developed as a quantitative definition for health-related aerosol sampling since the 1970s. In particular, the above idea has also been agreed on between the International Standards Organization (ISO), the Comité Européen Normalization (CEN), and the American Conference of Governmental Industrial Hygienists (ACGIH) for aerosol sampling\(^ {22-24}\). To date a number of inhalable aerosol samplers have been developed for health-related sampling\(^ {25}\). In addition, the use of inhalable aerosol sampling results has also been demonstrated to have a better correlation with workers’ urinary excretions than the use of the so-called ‘total’ sampling results\(^ {26}\). Based on these, it is expected that the inhalable aerosol sampling technique would be more feasible for measuring workers’ Cr\(^{6+}\) droplet exposure than the traditional ‘total’ aerosol sampling technique.

To the best of our knowledge, the inhalable aerosol sampling technique has never been adopted by the chromium-plating industry for assessing workers’ Cr\(^{6+}\) droplet exposure. Therefore, the objective of this study was to assess workers’ Cr\(^{6+}\) droplet exposure in the chromium plating industry, and particular interest was focussed on whether the inhalable aerosol sampling results could fully explain the corresponding urinary chromium concentrations. In addition, if a relationship between the inhalable aerosol sampling results and their corresponding urinary chromium concentrations could be established, a new BEI would be suggested for the chromium plating industry.

**Methods and Materials**

1. **Selection of plating operations and plating workers**

   In this study, two types of chromium plating operations, one in the decorative plating process (i.e., nickel-chromium plating) and the other in the hard-surface plating process (chromium plating) were selected. In order to ensure each selected plating operation had similar operating conditions, two selecting criteria, plating duration and the thickness of the chromium film on the plated object were set prior to the selection of plating plants. In this study, the above two selecting criteria for decorative and hard-surface plating operations were <10 sec/batch and <0.75 μm, and >50 min/batch and >5.0 μm, respectively. As a result, two decorative plants and two hard-surface plating plants were selected in this study.

   All non-smoking workers who performed their tasks near plating tanks were selected from each selected plant. A total of 57 workers were selected, which included 27 selected from two decorative plating plants and 30 workers selected from two hard-surface plating plants. During the sampling work week, all selected workers were requested to wear an apron and gloves to minimize the effect of skin contact.

2. **Field sampling and sample analysis**

   In this study, both personal sampling and biological monitoring were conducted on all selected workers. To properly assess workers’ exposure, the inhalable aerosol sampling technique was adopted in this study for personal sampling. Because the IOM personal sampler (manufactured by SKC Inc.) was developed for sampling the fraction of aerosols inhaled via the inhalation route\(^ {12}\), the sampler was adopted for this study. During sampling, the sampler was mounted randomly on the left or right side of the chest of each selected worker with the sampling flow rate adjusted to approximately 2.0 l/min for approximately 7 h on the last day of the work week. After sampling, all samples collected were analyzed by a modification of NIOSH Method 7600\(^ {27}\) to determine soluble Cr\(^{6+}\) content. The above analytical method has been compared with the NIOSH Method 7600\(^ {28}\) in field sampling of Cr\(^{6+}\)-bearing aerosols, and the results showed the former had a much lower limit of detection (=1.0 ng/m\(^3\)) than the latter (=500 ng/m\(^3\))\(^ {29}\). Analysis modified NIOSH Method 7600 samples involved extracting the PVC filter in a 0.02 N sodium bicarbonate solution and filtering the extract. The extract was then injected into an IC separation column (packed with IonPac AS7: Dionex, Sunnyvale, Calif.). The eluted chromate ion was mixed with 0.002 M diphenylcarbazide to form a red chromium complex, then quantified by visible absorption spectrometry (HP7 8452 Diode Array UV/VIS). A calibration curve was established with seven standard solutions at concentrations of 0.005, 0.010, 0.020, 0.050, 0.100 and 0.400 μg/ml, and a straight linear correlation of r=0.999 was detected. The present study yielded a limit of detection of approximately 2.4 ng/m\(^3\). Analysis of duplicate experiments yielded differences in Cr\(^{6+}\) concentrations ranging from 3.5% to 7.7% and averaging 5.8% for air samples. The blank tests were accomplished by using the same procedure without adding the known standard solution, and no significant contamination was detected (<detection limit).

   Because of worker’s unwillingness, only one urine
specimen was collected from each selected worker at the end of the shift on the last day of the work week by using a PVC bottle. All selected workers were required to wash their hands before sample collection. Before collection of the urine sample, the PVC bottle was pretreated with 10% HNO₃ to ensure that it was free of chromium contamination. After sampling, all urine specimens were stored at a -70°C in a refrigerator before analysis. The urinary chromium was analyzed by atomic absorption spectrometry (AAS) with a graphite furnace (GF HGA 600; Perkin Elmer Model 5500PC). The method of analysis followed the NIOSH Method 720439). This method yielded a limit of detection for urinary chromium of approximately 0.19 ng/l. To minimize the effect of the various hydration states of workers, the urinary chromium concentrations were further calibrated by their creatinine concentrations and thus were expressed in terms of µg/g creatinine. In this study, the creatinine concentration was analyzed by an accredited laboratory in Taiwan.

3. Data analysis
a. Assessing workers’ Cr⁺⁶ exposure levels and urinary chromium concentrations

In this study, the range, log-normality (by using the W-test that suggested by Gilbert50) and arithmetic mean (AM) were calculated for both personal inhalable aerosol sampling and biological monitoring results. In this study, the AM was used because it provided a more effective basis for characterizing both a worker’s average and cumulative doses rather than the use of the geometric mean (GM)31,32. The method of the minimum variance unbiased estimate (MVUE)33 was adopted for estimating the AM, including the point of estimate (AM MVUE), and the upper and lower 95% confidence limits (AM UCL-1, 95% and AM LCL-1, 95%, respectively) were calculated. Detailed calculating procedures were described in a study conducted by Attfield and Hewet34. The fraction of personal exposures that exceeded the level of current TLV-TWA (50 µg/m³) was estimated according to the method suggested by Hewett and Ganser35. Based on the above method, including the point of estimate (F), the upper and lower 95% confidence limits (F UCL-1, 95% and F LCL-1, 95%, respectively) were calculated.

b. Establishing the relationship between Cr⁺⁶ exposure levels and their corresponding urinary chromium concentrations

In this study, the regression model used to relate to workers’ soluble Cr⁺⁶ exposure levels to their corresponding urinary chromium concentrations was taken in the form of:

\[ C_{URINE} = \alpha C_{INH} + S, \]

Where \( C_{INH} \) is the personal inhalable exposure level, \( C_{URINE} \) is the corresponding urinary chromium concentration, \( \alpha \) (the regression coefficient) is the slope of the regression model, and \( S \) (the intercept) is the background concentration or the synergistic/antagonistic effect that takes place between individual exposure and the internal dose. In this study, the F-test was used to examine the consistency between the resultant regression results obtained from both types of plating operations. If no statistical difference could be found, then a general regression equation was re-calculated by pooling the sampling results obtained from the above two types of plating operation.

Results and Discussions

1. Personal inhalable Cr⁺⁶ exposure levels

Table 1 shows personal inhalable Cr⁺⁶ exposure levels (\( C_{INH} \)) obtained from both types of chromium-plating operations. It can be seen that both \( C_{INH} \) profiles were log-normally distributed, which suggests that workers selected from each individual chromium plating operation could be regarded as a “similar exposure group” (SEG). In other words, workers performing their tasks in a given type of plating operation could have been exposed to similar exposure scenarios. The above inference is theoretically plausible, since only workers who directly performed their tasks near plating tanks were selected.

Table 1 also shows the estimated AM MVUE, AM UCL-1, 95% and AM LCL-1, 95% for both types of plating operation. It can be seen that the above values for the decorative plating operation (=1.91, 3.03, and 1.42 µg/m³, respectively) were consistently lower than that for the hard-surface plating operation (=25.2, 40.4, and 19.1 µg/m³, respectively). The above results clearly indicate that hard-surface plating workers have been exposed to higher \( C_{INH} \) than decorative plating workers. Considering that thicker chromium films (=5–10 µm) and longer plating duration (=30–60 min) were involved in hard-surface plating than in decorative plating (film=0.5–0.75 µm; duration=5–10 sec), the results obtained in this study are theoretically plausible.

Table 1 also shows the point estimate (F), and the upper and lower 95% confidence limits (F UCL-1, 95% and F LCL-1, 95%, respectively) of the fractions of samples that exceeded the current TLV-TWA of 50 µg/m³ for both selected plating operations. Results show that the above values for decorative plating operations (=0.006%, 0.143%, and <0.001%, respectively) were consistently lower than for hard-surface plating industry (=12.1%, 23.2%, and 5.83%, respectively). The above results suggest that the fraction of Cr⁺⁶ exposure that exceeds the current TLV-TWA value for decorative plating workers is negligible. But for hard-surface plating workers, considering that approximately 12.1% (based on the point estimate; F) of exposures might exceed the TLV-TWA level, more attention should be paid to the hard-surface plating than to the decorative plating operation. Nevertheless, it should be noted that decorating plating workers were simultaneously exposed...
to both sensitizing metals, Ni and Cr, but hard-surface plating workers were only exposed to Cr. The effect of the cross-reaction between sensitizing metals was not discussed, which means that further investigation of the decorative plating industry, might be necessary even though their soluble Cr+6 exposure levels in that industry were significantly lower than the TLV-TWA level.

2. Workers’ urinary chromium concentrations

Table 2 shows workers’ urinary chromium concentrations ($C_{URINE}$) obtained from both types of chromium-plating operations. Here again, it can be seen that the $C_{URINE}$ profiles for both types of chromium plating operations were log-normally distributed, which further confirms that workers selected from each individual plating operation could be regarded as a SEG. Table 2 also shows the estimated $AM_{MVUE}$, $AM_{UCL-1.95%}$ and $AM_{LCL-1.95%}$ for both types of plating operations. It can be seen that the above values for decorative plating operations ($=3.43, 5.31,$ and $2.52 \mu g/g$-creatinine, respectively) were consistently lower than those for hard-surface plating operations ($46.2, 79.3,$ and $33.1 \mu g/g$-creatinine, respectively). That hard-surface plating workers were known to be exposed to higher $C_{INH}$ than decorative plating workers suggests that the results obtained in this study are theoretically plausible.
3. Relationships between personal inhalable Cr\textsuperscript{6+} exposure and corresponding urinary chromium concentration

In this study, the simple linear regression model of \( C_{\text{URINE}} = \alpha C_{\text{INH}} + S \) was adopted to establish the relationship between personal inhalable Cr\textsuperscript{6+} exposure \( (C_{\text{INH}}) \) and the corresponding urinary chromium concentration \( (C_{\text{URINE}}) \). For both types of plating operation, the best-fit regression results were found to be, respectively:

- **Decorative plating:** \( C_{\text{URINE}} = 1.75 \times C_{\text{INH}} + 0.05 \) (\( R^2 = 0.86, n=30 \))
- **Hard-surface plating:** \( C_{\text{URINE}} = 1.86 \times C_{\text{INH}} - 0.33 \) (\( R^2 = 0.81, n=27 \))

In the above two regression models, both regression coefficients (i.e., the \( \alpha \) values=1.75 and 1.86, respectively) were statistically significant (\( p \)-values<<0.000) which suggests that an increase in \( C_{\text{INH}} \) would result in an increase in \( C_{\text{URINE}} \) but it should be noted that both intercepts (i.e., the \( S \) values=0.05 and – 0.33, respectively) were not significantly different from 0 (\( p \)-values>>0.05). The above results suggest that the workers’ background urinary chromium concentrations or the synergistic/antagonistic effects that took place between the individual exposures and the internal doses might be negligible. In addition, both regression models yielded \( R^2 \) of 0.86 and 0.81, which suggests that workers’ inhalable Cr\textsuperscript{6+} exposures were able to explain the variations in the corresponding urinary chromium concentrations up to 86% and 81%, respectively. Based on the above results, it is concluded that use of the inhalable aerosol sampling technique for characterizing workers Cr\textsuperscript{6+} exposure would make it possible to relate their resultant urinary chromium concentrations.

In order to establish a general regression model for the two types of chromium plating operations, the consistency of the above two resultant regression models was further examined in this study. The result shows no significant difference between the above two regression models \((F*=0.0012<<F(0.95; 2, 53)=3.2)\). By combining all the data sets, this study yielded a general regression model as (see also Fig. 1):

- **Chromium plating:** \( C_{\text{URINE}} = 1.86 \times C_{\text{INH}} - 0.21 \) (\( R^2 = 0.87, n=57 \))

In the above regression model, the regression coefficient \((=1.86)\) was statistically significant \((p\)-value<<0.000) which again indicates that the increase in \( C_{\text{INH}} \) would result in an increase in \( C_{\text{URINE}} \). In addition, the intercept \( (= -0.21)\) was found insignificantly different from 0 (with \( p \)-value=0.93), which again indicates that workers’ background urinary chromium concentrations or the synergistic/antagonistic effects that took place between the individual exposures and the internal doses might be negligible. The regression model yielded an \( R^2 \) value of 0.87, which suggests that \( C_{\text{URINE}} \) could explain the variation in \( C_{\text{INH}} \) up to 87%.

Assuming that the exposure level of \( C_{\text{INH}} \) is equivalent...
to the current TLV-TWA of 50 µg/m³, the above regression model suggests a corresponding $C_{\text{URINE}}$ level of approximately 93 µg/g-creatinine. Obviously, the above value is greater than the current BEI value of 30 µg/g-creatinine which was suggested by ACGIH (applicable for welding workers when exposure to soluble Cr+6 fumes at the same level of 50 µg/m³). It is known that the particle size distribution of soluble Cr+6 droplets generated by the plating operation might be quite different from the particle size distribution of soluble Cr+6 fumes generated by the welding operation. For example, one recent laboratory study focussed on investigating the characteristics of droplets generated from the chromium plating process has shown that the size distribution of Cr+6 droplets was in a bimodal form [37, 38]. The mass median aerodynamic diameters (MMAD) for the fine mode and the coarse mode were <4 µm and 10–15 µm, respectively. On the other hand, the size distribution of metal fumes generated by the welding operation was in a single modal form with MMAD<1 µm [39]. Based on these figures, it is expected that plating workers would be exposed to coarser aerosols than welding workers. Here it should be noted that the coarser the aerosols in size, the greater the deposits would be in the upper region of the respiratory tract. Therefore, workers exposed to Cr+6 droplets would have greater deposits in the upper respiratory tract than workers exposed to Cr+6 fumes. It should also be noted that aerosols deposited on different regions of the respiratory tract might lead to different contributions to $C_{\text{URINE}}$. Therefore, on condition that both chromium plating workers and welding workers were exposed to the same exposure levels, it would be reasonable to expect that their resultant urinary chromium concentrations could be different. In this study, we also found that the BEI value for chromium plating workers ($\geq$93 µg/g-creatinine) was greater than that for welding workers ($\geq$30 µg/g-creatinine). Particularly plating workers are known to be exposed to coarser aerosols than welding workers, which suggests that soluble Cr+6 might be more easily absorbed in the upper airway than in the lower respiratory tract. Considering that soluble Cr+6 droplets are known to easily cross the mucous membrane of the nose (thereby causing perforation of the nasal septum), from the physiological viewpoint the above inference is theoretically plausible.

Conclusions and Recommendations

Because hard-surface plating workers were found with higher exposure levels and higher urinary chromium concentrations than decorative plating workers, this study suggests that more attention should be paid to the hard-surface plating operation, rather than to the decorating plating operation. Clear relationships were found between personal inhalable soluble Cr+6 exposure levels and urinary chromium concentrations for both plating operations, which indicates the use of an inhalable aerosol sampling technique would be useful in characterizing workers’ true exposures. Assuming the $C_{\text{URINE}}$ of plating workers is equivalent to the current TLV-TWA of 50 µg/m³, this study yielded a level of $C_{\text{URINE}}$ of approximately 93 µg/g-creatinine. The above value is clearly different from the current BEI of 30 µg/g-creatinine suggested by ACGIH for the welding industry. The above discrepancy might be due to the fact that soluble Cr+6 droplets generated during the plating process are coarser than soluble Cr+6 fumes generated during the welding operation. Considering that no BEI has been suggested by ACGIH for the chromium plating industry, the results obtained in this study might be helpful for establishing a new BEI in the future.

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