Concentration of Hexavalent and Trivalent Chromium in Electroplating Plants

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Objectives. The objective of this study was to compare the concentrations of hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) in six electroplating factories in central Taiwan.

Methods. The types of electroplating factories included: nickel-Cr $(n = 1)$, mixed (nickel-Cr and hard Cr) Cr ($n = 3$) and hard Cr ($n = 2$). In each factory, area samples and personal samples were taken. Cr(VI) was analyzed by visible absorption spectrophotometry (VAS)- graphite furnace and total Cr was analyzed by atomic absorption spectrophotometry (AAS). Concentration of Cr(III) was determined by subtracting Cr(VI) from total Cr.

Results. The results showed that hard Cr factories had higher concentrations of Cr(VI) and Cr(III) than the other Cr factories. In all factories Cr(VI) concentrations were lower than Cr(III) concentrations. Cr(VI) comprised 5% to 10% of total Cr. For Cr(III), there was a significant positive correlation between area and personal sampling ($r = 0.62$, $p < 0.05$), but for Cr(VI) there was no statistical significance.

Conclusions. Because Cr(VI) is very unstable during the electroplating process, great care must be taken when conducting air sampling and analysis. (Mid Taiwan J Med 2003;8:199-206)

Key words

Cr concentration, electroplating plants, hexavalent chromium, trivalent chromium

INTRODUCTION

Chromium (Cr) is widely used in various industrial processes, such as electroplating, paint and pigment production, wood treatment, and leather tanning. In the natural environment, Cr exists in two oxidized states; trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Cr(VI) is carcinogenic and can cause perforations of the nasal mucosa and severe skin and nasal ulcers. Cr(III) is much less toxic than Cr(VI) but is nevertheless hazardous to health in high concentrations [1]. Airborne Cr(VI) levels are highest in electroplating factories. The most common electrolyte in electroplating baths is composed of Cr₂O₃ and H₂SO₄, but some Cr(III) $(1.5\%$ to 3%) is also added. Cr(VI) is released during electrolysis. Previous studies [2,3] have shown low levels of Cr(VI) in electroplating factories, but this may have been due to the inherent instability of Cr(VI), which readily converts to Cr(III) in the presence of inorganic reducing agents. Therefore, worker exposure to airborne Cr(VI) may be much greater than the current data suggest. There are numerous reductants that could reduce Cr(VI) to Cr(III), such as ferrous iron, reduced sulfur species and organic material in leaching environments [4]. A study in Taiwan in 1991 conducted by the Taiwan Provincial Labor Department measured air-chromium concentrations in various electroplating plants. Of the 56 air chromium samples taken, 5 samples (8.6%) exceeded permissible levels [5]. Previous studies have shown that even when levels of Cr(VI) were low,

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half of the electroplating workers had nose septa problems [2,3]. Soils high in organic matter reduce Cr(VI) to Cr(III) rapidly over a pH range of 4.4 to 7.6. Theoretically, the oxidizing power of Cr(VI) is a function of pH, which means that as the pH value becomes lower, Cr(VI) is more likely to reduce to the trivalent form [6].

This reduction has also been shown to occur in biological environments. For example, white blood cells (WBC) accumulate Cr(VI) following both *in vitro* and *in vivo* exposure [7]. In addition, WBC accumulate Cr(VI) to a greater extent than RBC. These findings indicate that under specific conditions, Cr(VI) is easily reduced to Cr(III). Since Cr(VI) readily converts to Cr(III), true Cr(VI) levels may be underestimated, which means that great care must be taken during the collection and analysis of data. Almost 16% of samples taken from workers occupationally exposed to Cr and nickel exceeded occupational exposure limits for total Cr (500 μ g/m³) and Cr(VI) (50 μ g/m³) in Finland [8]. However, Kiilunen's study did not include any electroplating factories. High concentrations of both Cr(VI) and Cr(III) found in electroplating plants have been linked to a variety of health disorders and, as such, are cause for much concern. There are no available data for Cr(VI) and Cr(III) concentrations in electroplating plants. The objective of the current study was to accurately determine and compare Cr(VI) and Cr(III) levels in three types of electroplating factories.

MATERIALS AND METHODS

Six types of electroplating factories were selected: nickel-Cr $(n = 1)$, mixed Cr $(n = 3)$ (nickel-Cr and hard Cr), and hard Cr $(n = 2)$. Each factory was divided into three areas: electroplating bath, post-processing area (including cleaning, spraying, polishing, cutting and packing areas) and administrative area.

Personal and area samples were taken in each of the three areas in the factory. Area samples were taken by a personal sampling pump that was calibrated with a soap bubble meter. A 37 mm diameter PVC filter with a pore size of 0.5 µm was used in the pump. The flow rate was 2 L/min. Sampling height for each of the area samples was approximately 100 to 150 cm. Three areas were selected for area sampling: electroplating bath, post-processing area (including cleaning, spraying, polishing, cutting and packing areas) and administrative area. The personal samples were taken from the breathing zone i.e. from the workers' collars. For area and personal sampling, the dust in the filter was collected and weighed. Samples were taken once in the morning and again in the afternoon. Each sampling period was three hours and the sampling volume was 360 liters. Two blank filters ensured that no contamination occurred during sampling and storage. TWA was calculated from the personal samples. Strict adherence to the decontamination protocol was necessary to prevent contamination of the sampling equipment. Because of the extremely low detection limit, great care was taken during the sampling, shipping, and analytical process. Personnel wore clean latex gloves to prevent contamination during assembly of all components. Prior to sampling, the apparatus was soaked in a diluted nitric acid (1%) bath and rinsed three times with distilled water. Field blanks were included with every sample set. After sampling, filters were stored (with great care to avoid any possibility of contamination) and analysis was completed within two weeks. In addition, laboratory ware (including pipette tips and micro-vials) was soaked in 0.5 N sulfuric acid for a minimum of 24 hours. The glassware was rinsed with deionized water, and the water was tested for the presence of Cr. Only analytical grade reagents were used.

The analytical method for detecting Cr(VI) followed the NIOSH 7600 guidelines [9] and was consistent with the method in Sheehan's study [10]. Visible absorption spectrophotometry (VAS) was also used in the analysis. A calibration curve was established with six standard solutions at concentrations of 0.0072, 0.024, 0.048, 0.12, 0.24 and 0.4 µg/mL. A calibration curve revealed that Area sampling $(N = 35)$

 $Cr(VI)$ ($\mu g/m^3$)

 $Cr(III)$ ($\mu g/m^3$)

Total Cr $(\mu g/m^3)$

 $Cr(VI)$ ($\mu g/m^3$)

 $Cr(III)$ (µg/m³)

Total Cr $(\mu g/m^3)$

Personal sampling $(N = 35)$

 \mathbf{M}

GM Range

 $Mean \pm SD$ **GM** Range $Mean \pm SD$ GM Range $Mean \pm SD$ **GM** Range

3.27 $0.76 - 9.46$

 $(n = 5)$ 0.32 ± 0.41 0.18 $0.07 - 1.13$ 5.77 ± 3.74 4.82 $2.70 - 12.81$ 6.09 ± 4.13 5.02 $2.78 - 12.94$

Table 1. Concentration of Cr(VI) and Cr(III) by area and personal sampling based on three kinds of electroplating plants $(\mu g/m^3)$

1.83 $0.51 - 5.36$

 $(n = 3)$ 0.20 ± 0.12 0.15 $0.05 - 0.34$ 4.29 ± 4.02 2.64 $0.91 - 9.95$ 3.75 ± 3.63 2.55 $1.25 - 9.99$

There were significant differences between the three kinds of electroplating plants in concentrations of Cr species by the Kuskal-Wallis test. GM = geomatric mean.

the correlation coefficient was 0.999. A filter blank and a laboratory blank were prepared by depositing 50 μ L of 2% (v/v) sulfuric acid onto the membrane surface. The detectionlimit of Cr(VI) was $0.0055 \mu g/L$. The instrument was tested after every 10 samples to ensure that the values were reliable ($CV = 6.1\%$). The total Cr was analyzed by an AAS-graphite furnace (Perkin Elmer 5100): wavelength, 357.9 nm, slit width, 0.7 nm. Temperature program was set as follows: drying $(120^{\circ}C)$, ashing $(1650^{\circ}C)$, atomizing $(2400^{\circ}$ C), cleaning $(2650^{\circ}$ C). The repeatability (CV) was 1.41%. For analyses in this study, it was assumed that total Cr was comprised of only Cr(III) and Cr(VI). Thus, Cr(III) concentrations were determined by subtracting Cr(VI) from total Cr.

These data were analyzed by SAS software. [11] Since area and personal sampling for the concentrations of the Cr species had log normal distributions, the mean and geometric mean were calculated. The sample size was small and the data showed log normal distribution. Therefore, ratios of Cr species in different electroplating plants and areas within the plants were compared by non-parametric method (Kuskal-Wallis test). The concentrations of Cr species between personal and area samples were correlated by Pearson's correlation.

RESULTS

Cr levels were highest in hard Cr factories, followed by mixed Cr and nickel-Cr plants. Cr(III) concentrations were much higher than Cr(VI) in both the personal and area samples. There was wide variation of Cr concentrations in hard Cr factories. The range of Cr(VI) concentrations of the area samples was 0.01 to 26.98 μ g/m³ and for Cr(III), the range was 0.65 to 295.65 μ g/m³. For personal samples, the range of Cr(VI) concentrations was 0.02 to 35.32 μ g/m³ and for Cr(III), the range was 0.54 to 183.33 μ g/m³. The lowest range of Cr concentrations was found in nickel-Cr plants. There was a significant difference between the three kinds of electroplating plants in

10.19 $0.68 - 295.95$

 $(n = 12)$ 0.80 ± 11.86 0.87 $0.02 - 35.32$ $30.29 + 47.57$ 11.32 $0.54 - 183.33$ 35.45 ± 47.34 12.13 $0.55 - 183.69$

	Cr(VI)/Cr(III)	$Cr(VI)$ / Total Cr	Cr(VI) / dust	Total Cr / Dust
Area sampling				
Electroplating plants				
Hard Cr plant	0.07	0.06	0.02	0.14
Mix Cr plant	0.38	0.10	0.001	0.02
Ni- Cr plant	0.05	0.05	0.001	0.02
Electroplating location				
Electroplating bath	0.44	0.12	0.02	0.12
Post processing	0.04	0.03	0.001	0.03
Administrative room	0.05	0.05	0.000	0.07
Personal sampling				
Electroplating plants				
Hard Cr plant	0.39	0.19	0.02	0.05
Mix Cr plant	0.04	0.04	0.001	0.02
Ni- Cr plant	0.16	0.12	0.001	0.01
Electroplating location				
Electroplating task	0.53	0.24	0.02	0.04
Post processing	0.11	0.08	0.001	0.04
Administrative room	0.03	0.03	0.000	0.01

Table 2. Comparison of ratios between Cr(VI), Cr(III), total Cr and dust concentrations

There were no significant differences between the electroplating plants and areas within the plant in concentrations of Cr species and dust ratios by the Kuskal-Wallis test.

Table 3. Correlation between personal and area samples for Cr(VI) and Cr(III) concentrations in hard and mixed chromium electroplating plants

	Hard Cr plants	Mixed Cr plants	All Cr plant
Cr(III)	$0.70*$	$0.59*$	$0.66*$
Cr(VI)	-0.14	-0.40	-0.28
Total Cr	$0.76**$	$0.74**$	$0.75**$

 $*_{p}$ < 0.05, $*_{p}$ < 0.01.

concentrations of Cr species according to the Kuskal-Wallis test (Table 1).

Table 2 compares the ratios of concentrations of Cr species and dust in the three types of factories and areas within each factory. Cr(VI) levels were much lower than Cr(III). The Cr(VI)/Cr(III) ratios in area samples ranged from 0.05 to 0.38 and personal samples ranged from 0.04 to 0.39. Cr(VI)/total Cr ratio in area samples ranged from 0.05 to 0.1. For personal samples, the range was 0.04 to 0.19. Total chromium/dust ratio ranged from 0.02 to 0.14 for area samples. For personal samples, the range was 0.01 to 0.05. In the electroplating bath area, Cr(VI)/Cr(III) and total chromium/dust ratios were highest compared to the after-processing and administrative areas for both area and personal samples. No significant difference was found between the electroplating plants and areas within the plant in Cr species' and dust ratios according to the Kuskal-Wallis test.

The correlations between personal and area samples and concentrations of Cr(VI), Cr(III) and total Cr are shown in Table 3. Only one nickel-Cr plant was studied; however, because there were only 7 workers at this plant, it was excluded from this table. There was a negative correlation between personal and area sampling for Cr(VI), but it was not statistically significant. However, there was a statistically significant positive correlation between personal and area sampling for Cr(III) ($r = 0.70$ and $r = 0.59$) and total Cr ($r =$ 0.76 and $r = 0.74$) in hard Cr plants and mixed Cr plants, respectively.

DISCUSSION

Chromium is one of the contaminants present in the ecosystems around mining regions and electroplating industries. It exists in two different oxidation states, Cr(III) and Cr(VI). Reduction of toxic Cr(VI) to non-toxic Cr(III) in the environment is a desirable, but potentially reversible process. Redox reactions with Cr are largely kinetically controlled by pH, organic ligands and surfaces which strongly influence rates and reaction pathways [12]. Bartlett and Kimble (1976) showed that small amounts of Cr(III) in soil convert to Cr(VI) in the presence of manganese dioxide. However, in the presence of MnO2, Cr(VI) reduces to Cr(III) more readily. If $MnO₂$ is present in high concentrations, the Cr(VI) concentration decreases rapidly [6]. Hara (1976) reported that if the concentration of sulfuric acid exceeds 0.2 N, Cr(VI) decreases in proportion to the increased amount of $MnO₂$ [13]. The average half-life of airborne Cr(VI) is approximately 13 hours according to chamber studies that closely approximated actual ambient atmospheric conditions. Because of the unstable nature of Cr(VI), sampling and analysis were completed as quickly as possible. When Cr(VI) was desorbed from the PVC filters, the solution ensured that the Cr(VI) present in the sample remained stable. NIOSH 7600 guidelines recommend 0.5 N sulfuric acid to desorb Cr(VI) in the filters, but this provides insufficient sensitivity for the measurement of low levels of Cr(VI) [9]. The detection limit for the NIOSH method is 500 ng/m³, which is approximately 100 times higher than typical environmental concentrations of total Cr [14]. Cr(VI) dissolved in sulfuric acid is not stable under storage conditions [15]. The current study analyzed fresh standard solutions of Cr(VI), since stock solution stored for long periods of time can result in the conversion of Cr(VI) to Cr(III).

When the wavelength of the spectrophotometer was set to 540 nm (for measuring concentration of Cr(VI) after a period of storage), the absorbance decreased, but increased when the wavelength was 240 nm (for measuring Cr(III)). This phenomenon

demonstrates that Cr(VI) reduces to Cr(III) during storage over a long period of time. The NIOSH 7600 method was modified by adding a buffer solution (sodium bicarbonate) instead of sulfuric acid. Cr(VI) is stable in the buffered impinger solution for samples held up to 100 days [10]. In the initial assessment, the pH range after sampling was 8.6 to 9.1, but in the field study, the pH range was 7.2 to 9.2 which prevents the reduction of Cr(VI). The slightly alkaline pH of the system ensures that Cr(VI) is stable during preparation and analysis.

The results of the current study show that Cr(VI) comprised only 4% to 19% of total Cr in personal samples and 5% to 10% in area samples. The different processes that occur within the plant generate varying amounts of dust (from polishing/grinding) and mist (electroplating bath), which may include Cr species. We felt that it was important to determine the ratios of Cr/dust in order to estimate which fraction of the Cr species was derived from dust. Hard Cr plants had the highest Cr species/dust ratios, especially around the electroplating bath, which indicates that mist was the main source of airborne Cr. We suggest that airborne Cr levels of the plant could be greatly reduced by covering the electroplating bath.

We speculate that most (80% to 90%) of the Cr(VI) rapidly converted to Cr(III). There are three possible reasons for this: 1) the addition of chromate and sulfuric acid to the electroplating tank results in the conversion of Cr(VI) to Cr(III). The oxygen and hydrogen gas produced during electrolysis vaporizes in the air, taking with it $Cr(VI)$ and $Cr(III)$; 2) interference, such as interaction with airborne chemicals may convert airborne Cr(VI) to Cr(III); 3) sampling, shipping and analyses of Cr(VI) may have resulted in conversion of Cr(VI) to Cr(III). Kuo (1998) demonstrated that concentrations of Cr(VI) decrease in the presence of sulfuric acid and MnO2 (reasons 2 and 3), but further research is needed to investigate the factors affecting the reduction of Cr in and around the electroplating bath, since the process of sampling and analysis in electroplating manufacturing plants can easily

result in bias [15].

DPC for measuring concentrations of Cr(VI) could result in inaccuracies. Existing methods for the colorimetric determination of microgram quantities of Cr with DPC give poor recovery, unstable colors and unreliable results. Saltzman developed a new method for oxidizing Cr in acid medium with permanganate; the excess oxidant was destroyed with sodium azide. The color obtained by DPC was stabilized by the addition of a phosphate buffer. The method is suitable for measuring Cr in air, water and urine samples with a sensitivity of 0.03μ g in a volume of 25 mL [16].

For the current study, Cr(VI) and Cr(III) concentrations were determined simultaneously. Total Cr concentration was measured by AAS, and Cr(VI) concentration was determined by VAS. Because other valences of Cr have a very short half-life, and are so unstable in the natural environment, it was assumed for the purposes of this study that the remaining Cr was in the trivalent form. Therefore, Cr(III) concentration was calculated by subtracting the Cr(VI) concentration from total Cr concentration. Simultaneous measurement of Cr(III) and Cr(VI) can be achieved by high performance atomic emission spectrometry (HPLC-ICP-AES) [17], direct current plasma atomic emission spectrometry (HPLC-DCP-AES) or ion chromatography/chemiluminescence detection [18]. Since these methods are extremely complicated and require sophisticated laboratory equipment, the current study relied on AAS and VAS to determine total Cr and Cr(VI), respectively. VAS is recommended by NIOSH 7600 and AAS is recommended by CFR part 50 (California Air Resources Board) [19]. Even if more sophisticated equipment were used to detect and analyze the speciation of Cr, the problem of Cr(VI) converting to Cr(III) in and around the electroplating tank would still remain. Therefore, it is extremely difficult to determine how much Cr(III) has been converted from Cr(VI) and how much was already present. Hara (1976) reported that Cr(III) is stable in an acidic state and Cr(VI) is stable in an alkaline state [13]. Even though the total Cr concentration is constant, the process of Cr determination and the transition between Cr(VI) and Cr(III) means that measurement of the true concentration of $Cr(III)$ and $Cr(VI)$ is very difficult. We speculate that there is a dynamic relationship between Cr(VI) and Cr(III) under acidic conditions. Therefore, strictly observing quality control in the laboratory, performing analysis of samples in a short span of time after sampling, and keeping Cr(VI) samples under stable conditions during sampling and analysis, are all of paramount importance to industrial hygienists. We recommend that NIOSH 7600 guidelines for measuring Cr(VI) be revised to allow for greater sensitivity and accuracy.

In conclusion, hard chromium factories had higher concentrations of Cr(VI) and Cr(III) than the other Cr factories. There was a significant difference between the three kinds of electroplating plants and areas within the plants for all Cr species. Cr(VI) concentrations were much lower than Cr(III) concentrations in area and personal samples in all factories. Cr(VI) comprised 5% to 10% of total Cr. Because of the inherent instability of Cr(VI) during sampling and analysis, there must be strict observance of methodology protocol.

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電鍍工廠六價鉻及三價鉻濃度之測定

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目的 本研究之目的在比較中部地區六家電鍍工廠空氣中六價鉻及三價鉻濃度之分 布。

方法 選自中部地區六家電鍍工廠包括一家鎳鋁電鍍工廠、三家混合工廠鎳鋁及硬鉻 及二家硬鉻電鍍工廠,每家電鍍工廠都進行區域及個人採樣,利用可見光吸收光譜儀 (VAS)分析六價鉻濃度,而鉻以原子吸收光譜儀(AAS)來分析總鉻濃度,以總鉻濃度扣 除六價濃度得知三價鉻濃度。

結果 硬鉻電鍍工廠之六價鉻及三價鉻濃度均高於其他電鍍工廠,六價鉻濃度在所有 電鍍工廠均低於三價鉻濃度,六價鉻濃度大約為總鉻濃度之5%至10%,三價鉻濃度在 區域及個人採樣呈現正相關($r = 0.62$, $p < 0.05$), 但在六價鉻濃度則無統計性之相關。 結論 六價鉻濃度在電鍍作業非常不穩定,必須特別注意採樣與分析過程六價鉻之變 化。(中台灣醫誌 2003;8:199-206)

關鍵詞

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