

Evaluation of Parameters Influencing Hexavalent Chromium Mist Sampling: A Full Factorial Design

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ABSTRACT: A chromium electroplating bath with the ability to produce homogenous mist was used to evaluate parameters influencing hexavalent chromium (Cr^{+6}) mist sampling methods. The results of 48 Cr^{+6} mist samples collected using the U.S. National Institute for Occupational Safety and Health method 7600 showed that Cr^{+6} concentration was higher: (1) For sampling by closed-face filter cassettes than for sampling by open-face filter cassettes ($P < 0.001$); (2) for samples collected at 35 cm above the electroplating solution surface than for samples collected at 50 cm ($P < 0.001$); (3) for sampling duration of 30 minutes than for sampling duration of 180 minutes ($P < 0.001$); and, (4) for samples extracted immediately after sampling than for samples with delayed extraction (24 hours after sampling) ($P < 0.001$). It is concluded that the accuracy of Cr^{+6} mist sampling in electroplating shops will be enhanced when: (1) closed-face filter cassette is used to prevent liquid splash contamination; (2) the recommended sampling height is 35 cm above the solution surface; (3) the sampling duration is short--approximately 30 minutes; and, (4) the extraction of the Cr^{+6} sample is performed as soon as the sampling is completed.

KEY WORDS: Hexavalent chromium, Mist, Electroplating, Chromium sampling method, Sampling head, Sampling duration, Storage duration, Sampling height.

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INTRODUCTION

Workers in many occupations are at risk due to exposure to hexavalent chromium (Cr^{6+}). Exposure to this chemical has been associated with cancer [1,2], ulceration, nasal septum perforation [3], contact dermatitis [4], occupational asthma [5], as well as kidney and liver damage [6].

Chromium electroplating is a major source of atmospheric chromium pollution, and a majority of workers in electroplating facilities is exposed to Cr^{6+} mist. While the actual number of non-registered electroplating facilities is unknown, an estimated 2000 or more workers in approximately 400 registered electroplating workshops with the Iranian Electroplating Union in Tehran, Iran, are exposed to Cr^{6+} [7]. Thus, occupational health professionals have a strong interest in accurately determining Cr^{6+} concentrations.

Cr^{6+} is relatively unstable and is likely to be reduced to its trivalent (Cr^{3+}) state [8,9]. Thus, hexavalent chromium sample as mentioned in MDHS 61, should proceed as soon as after sampling [10]. Since the chemical stability and health effects of Cr^{6+} differ significantly from those of Cr^{3+} , the valence states of this chemical should be considered when evaluating potential risk to humans. Therefore, it appears that the sampling duration and sample-storage duration before analysis are two important parameters that should be considered when devising a Cr^{6+} mist sampling method.

Occupational exposure limits for most hazardous aerosols are based on some measure of "total suspended particulates" and samples are typically collected by using a sampling head, which is either a closed-face filter cassette or an open-face filter cassette. Current studies [11,12] have reported differences between the two types of sampling heads for a variety of aerosols and their sampling conditions. On the other hand, there are controversies among different methods and reports. For example, in MDHS 61 and US air force report stated open face and closed face samplers are suitable samplers, respectively [10, 13]. Therefore, choosing an appropriate type of sampling head (closed-face or open-face) seems to be an important Cr^{6+} sampling method parameter.

The height of the sampling location from the electroplating solution surface (sampling height) appears to be another important parameter and conflicting subject, affecting the Cr^{6+} sampling method. In MDHS 52/3,

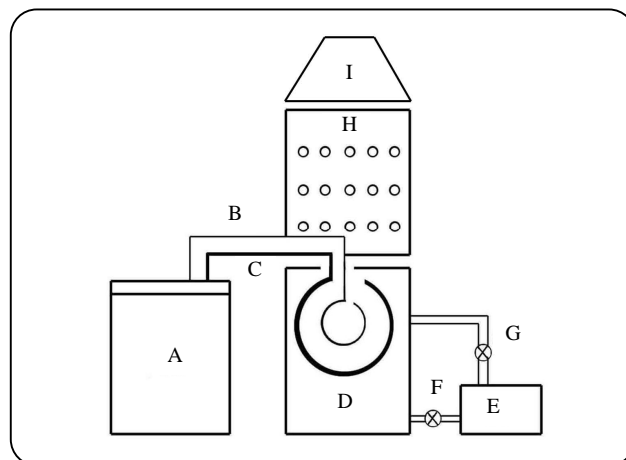


Fig. 1: Set up of chromium mist generation system. A) Rectifier, B) Cathode, C) Anode, D) Electroplating bath, E) Anti acid pump, F&G) Valves, H) Plexiglas case, I) Hood.

proposed sampling height from electroplating bath was determined 30 cm above the edge of the bath [14]. Kuo and Wang placed the sampling probes at 35 cm above the solution surface [15]. Boiano *et al.*, collected samples at height higher than 50 cm in their studies [16]. In our previous project, the lowest mean and standard deviation of coefficient of variations (CVs) for several simultaneous samples belong to samples collected at 50 cm above the solution surface (compared to 35 and 65 cm) [17].

This study was initiated to evaluate the effects of these four Cr^{6+} mist sampling parameters: Type of sampling head, sampling height from the electroplating solution surface, sampling duration, and sample-storage duration.

MATERIALS AND METHOD

Mist Generation System

A continuous stream of Cr^{6+} mist was generated using a chromium electroplating bath (in pilot scale) equipped with a special sampling chamber (Fig. 1). A detailed description of this system has been reported elsewhere [17].

The 2⁴ Factorial Design

To study the effects of four Cr^{6+} mist sampling parameters including, type of sampling head, sampling height from the electroplating solution surface, sampling duration, and sample-storage duration, the 2⁴ factorial design was applied under controlled electroplating

conditions. As shown in table 1, samples were collected at 16 different factor levels. At each factor level, 3 samples were collected and the average value of the three readings was reported as the Cr^{6+} mist concentration for that factor level. The total resulting number of samples was 48. Multiple analyses of variance (ANOVA) and Duncan test were used to analyze the data and P-Value less than 0.05 considered as significant. The data were processed by SAS statistical program version 9.

Chromium Mist Collection and Analysis

The U.S. National Institute for Occupational Safety and Health (NIOSH) method 7600 [18], developed primarily for measuring chromic acid concentrations, was used to determine the Cr^{6+} concentrations. Each sampling train consisted of either a closed-face or an open-face 37-mm polystyrene filter cassette. Each filter cassette, containing a 5.0 μm pore size polyvinyl chloride (PVC) membrane filter (MSA, Pittsburgh, USA), was connected to a personal sampling pump (Model 224-PCXR3; SKC, Blandford Forum, UK). The sampling pump was calibrated for airflow rate of 2.0 ± 0.1 l/min. The inlet of the filter cassette turned downward at an angle of approximately 45° normal to the solution surface.

Twenty four samples were collected using a closed-face filter cassette and 24 were collected using an open-face filter cassette. Samples in each of these two categories were collected at sampling heights of either 35 cm (24 samples) or 50 cm (24 samples) above the electroplating solution surface. Samples at each height were collected for the durations of either 30 minutes (24 samples) or 180 minutes (24 samples). Samples at each sampling duration were extracted and analyzed either immediately (24 samples) or 24 hours after sample collection (24 samples).

Analytical Method Summary

Using NIOSH method 7600 [18], each sampled PVC filter was extracted. The absorbance of the color complex was measured at 540 nm by ultraviolet-visible (UV-VIS) spectrophotometer (Model DU640; Beckman, Fullerton, USA). The calibration curve was established with seven standard solutions at concentrations of 0.04, 0.08, 0.12, 0.16, 0.20, 0.24, and 0.28 $\mu\text{g}/\text{ml}$ of Cr^{6+} . The calibration curve revealed a correlation coefficient of 0.998.

Table 1: Factor levels for the 2^4 factorial design.

Factor	Level	
	1	2
Sampling head	Open	Close
Sampling height (cm)	35	50
Sample storage duration (h)	0	24
Sampling duration (min)	30	180

RESULTS AND DISCUSSION

Effect of Types of Sampling Head

The results obtained by the two types of sampling head (closed-face filter cassettes and open-face filter cassettes) are presented in table 2. The Cr^{6+} concentrations in samples collected by closed-face filter cassettes were higher than those in samples collected by open-face filter cassettes (377.5 ± 120.5 Vs. 337.5 ± 91.5 , $P < 0.001$). That is, on the average, the Cr^{6+} concentrations in the closed-face filter cassettes were approximately 11% higher than the open-face filter cassettes.

Effect of Sampling Height

Results of Cr^{6+} concentrations in samples collected at sampling heights of 35 cm and 50 cm above the electroplating solution surface are presented in table 2. On the average, Cr^{6+} concentrations in samples collected at 35 cm were approximately 16% higher than those samples collected at 50 cm, a statistically significant ($P < 0.001$) difference.

Effect of Sampling Duration

Table 2 presents Cr^{6+} concentrations of samples collected for 30 min. or 180 min. On the average, Cr^{6+} concentrations in samples collected for 30 min were approximately 32% higher than those samples collected for 180 min. ($P < 0.001$).

Fig. 2 shows average values of Cr^{6+} concentrations arranged at each of the two sampling durations of 30 min and 180 min for samples from lowest to highest concentrations.

The results also indicate that Cr^{6+} reduced in all samples and that reduction was greater in higher concentrations.

Table 2: Descriptive data for samples collected under a full factorial design.

Factors		Number	Mean ($\mu\text{g}/\text{m}^3$)	S.D. ($\mu\text{g}/\text{m}^3$)	P-Value
Sampling head	Closed-face	24	377.6	120.5	0.001
	Open-face	24	337.5	91.5	
Sampling height (cm)	35	24	388.9	95.5	0.001
	50	24	326.2	112.1	
Sampling duration (min)	30	24	425.5	111.0	0.001
	180	24	289.6	42.1	
Sample-storage duration (hour)	0	24	408.6	111.3	0.001
	24	24	306.5	76.8	

Effect of Sample-Storage Duration

To determine the effects of sample-storage duration on the reduction of Cr^{6+} to Cr^{3+} , 24 samples were extracted immediately and 24 samples were stored for 24 hours in capped cassettes in a laboratory where the temperature ranged from 16-21 °C and the average relative humidity was approximately 58 %.

Table 2 shows that Cr^{6+} concentrations in samples extracted immediately after sampling were higher than concentrations in samples extracted 24 hours later. The difference was statistically significant ($P < 0.001$) at approximately 25%.

Interactions

The ANOVA test results also indicated that, there have been statistically significant interactions ($P < 0.001$) between storage duration and other main factors (i.e. sampling head, sampling duration, and sampling height) (Fig. 3). There were no other statistically significant interactions between factors.

Optimum condition

The statistical method of Duncan test was used in order to search for the optimum condition or the best situation to yield the maximum concentration value. Table 3, shows the means for groups in homogeneous subsets. Results show that, the best condition is: immediate extraction, sampling duration of 30 min, sampling head of closed-face filter cassette, and sampling at height 35 or 50 cm.

Cr^{6+} concentrations were significantly higher when samples were collected by closed-face filter cassettes than when collected by open face filter cassettes. According to

Kenny *et al.*, [11] this preference is probably due to the better performance of closed-face sampler in low external wind speeds.

Since particle diameters at the electroplating bath surface ranged from 0.3 to 25 μm [19], and the actual wind speeds in workplaces where ventilation is not forced rarely exceed 0.2 ms^{-1} [20], the same behavior of closed-face compared to open face cassette is predictable in actual conditions.

The results of this study revealed significantly higher Cr^{6+} concentrations collected at 35 cm from the electroplating solution surface than those collected at 50 cm. Suitable sampling height from electroplating solution surfaces has not been identified in available reports [16] nor in standard methods such as NIOSH 7600, 7605, 7703 [18,21,22].

Lack of recommended sampling height is an obvious omission. However, in lower height sampling, the liquid splash from the electroplating bath is greater than the liquid splash in higher height sampling; that is, the liquid particles can enter directly into sampler's head at higher rates in lower heights. Tsai *et al.*, [23] in their study in two electroplating shops reported that 19 samples out of 74 actual pairs of samples (approximately 25%) had to be rejected due to the inadvertent liquid splash into the sampler head. Thus, it seems reasonable to standardize the height where Cr^{6+} mist sampling is to be performed.

As shown in table 2 and Fig. 2, increased sampling duration has resulted in a reduction of collected Cr^{6+} on sampled filters and this is more obvious in higher concentrations. This may have occurred due to the susceptibility of Cr^{6+} mist to dry after generation and disperse into the air. The change of mist size, due to

Table 3: Duncan comparison of the mean run concentration values .(n=3).

Run Number	Con. ($\mu\text{g}/\text{m}^3$)	Subset*
8	226.7	A
6	261.6	A B
16	264.3	A B C
7	267.5	A B C
15	279.7	A B C
12	285.4	B C
4	293.5	B C D
14	314.8	B C D
2	321.5	C D
10	348.9	D E
11	397.6	E F
5	434.4	F G
3	437.2	F G
1	457.7	G
13	570.1	H
9	572.1	H

* Subset with letters in common indicates no statistically difference in the mean concentration.

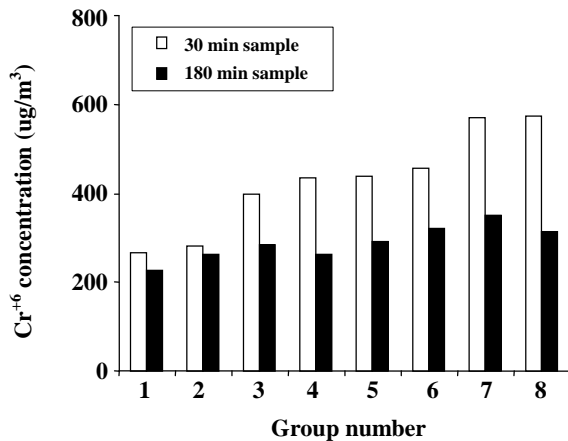


Fig. 2: Average of Cr^{6+} concentration in 8 clusters of samples at each of the two sampling durations.

drying, alters both the pH and Cr^{6+} concentrations in the mist as reported by *Shin et al.*, [8]. The reduction of collected Cr^{6+} on sampled filters also may have been due to the interaction of Cr^{6+} mist with acids and other reducing agents in the air surrounding the electroplating bath. The greater reduction in higher concentration might be due to high sensitivity of Cr^{6+} to pH [24].

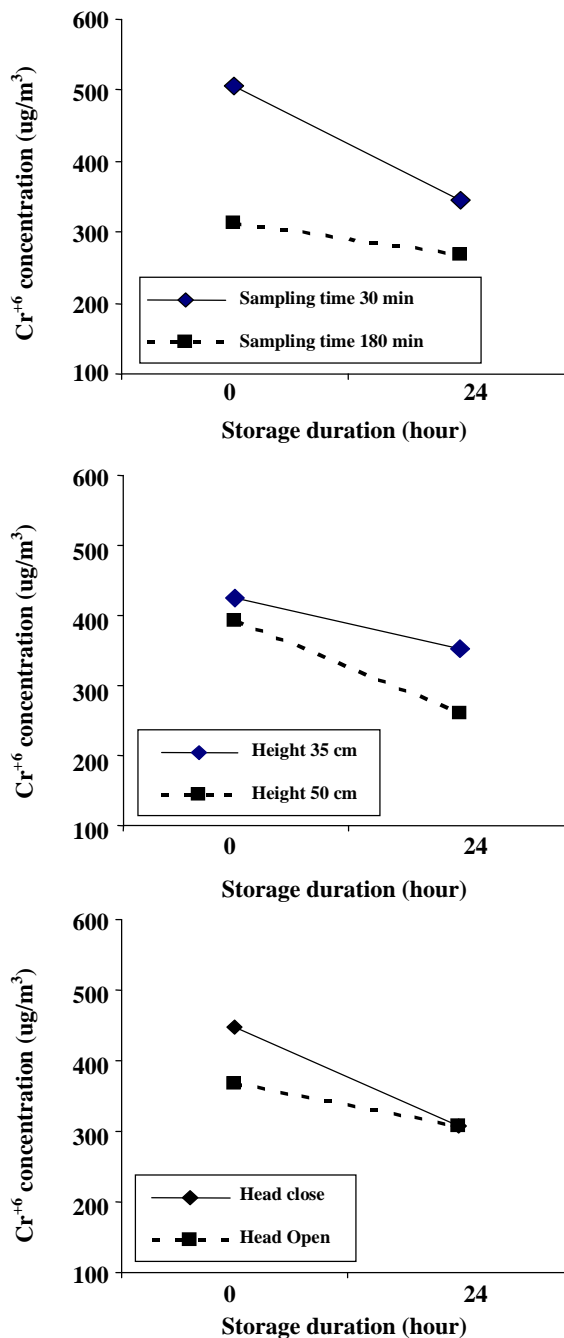


Fig. 3: Interactions between sample storage duration and other main factors.

As shown in table 2, Cr^{6+} concentrations in samples extracted immediately after sampling were higher than concentrations in samples extracted 24 hours after sampling. This finding may provide evidence of instantaneous reduction of Cr^{6+} taking place during sampling, sample transport and sample-storage, and confirm MDHS 61st suggestion that sample analysis

should not exceed 3 days [10]. The results obtained in this study agree with the findings of *Shin et al.*, [8] and *Marlow et al.*, [25]. The ratio of reduction of Cr^{6+} to Cr^{3+} averaged approximately 25%. This is not in agreement with the findings of another study in which the average half-life of Cr^{6+} in an environmental chamber was reported as 13 hours [8]. The reduction of Cr^{6+} to Cr^{3+} appears to be less problematic, however, when samples are analyzed as soon as possible at the sampling day [25].

All samples in this study were collected in an enclosed sampling chamber located in a controlled laboratory. In actual work conditions, however, the presence of reducing agents in the air (such as organic matters, $\text{Fe}(0)$, $\text{Fe}(\text{II})$ and vanadium) may cause Cr^{6+} to reduce to Cr^{3+} [8,26]. This can be particularly problematic when determining Cr^{6+} concentration in chromic mist, since Cr^{6+} is easily reduced in an acidic environment [26].

As shown in Fig. 3, although there are interactions between sample storage and other factors, the effect of these factors did not reverse and the general conclusion on the average effects were still valid.

In addition, with regards to storage duration and sampling head, for example, it seems to be reasonable thinking that contribution of sampling duration in Cr^{6+} concentration determination is much greater than sampling head.

Duncan test result indicated that, the optimum condition for Cr^{6+} collection is: immediate extraction, sampling duration of 30 min, sampling head of closed-face filter cassette, and sampling at the height of 35 cm.

CONCLUSIONS

It is concluded that the accuracy of Cr^{6+} mist sampling in electroplating shops will be enhanced when:

- 1- a closed-face cassette (rather than an open-face cassette) is used.
- 2- the sampling duration is short (approximately 30 minutes).
- 3- the extraction of Cr^{6+} in samples is conducted as soon as the sampling is completed (preferably the same day).
- 4- the recommended sampling height is 35 cm or 50 cm, but preferably 35 cm.

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