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Workplace Emission Factors for Hexavalent Chromium Plating

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Effective control of emissions from electroplating is necessary to maintain a healthy workplace. However, in many cases the emission rates are not well characterized. This study describes a methodology to determine such rates with application to a hexavalent chromium plating line under production conditions. Area concentrations were determined from particulate samples collected on open-face filters using calibrated personal sampling pumps. Twelve sets of 1-hour samples were collected at six locations at different distances from the plating tanks and in the hood of the local exhaust system. The filters were analyzed using proton-induced X-ray emission spectroscopy. For each 1-hour period, measurements of area concentrations were transformed to emission rates by using a multipoint diffusion mass balance model in conjunction with measured ventilation rates. In addition, source activities such as area plated, ampere·hours consumed, and total power usage were recorded simultaneously with concentration measurements. Comparison of the emission rates with source activities allowed us to determine emission factors as well as the emission rates. The hood emission results were in good agreement with hood emissions measured in a California Air Resources Board study of hard chrome plating (which did not measure workroom emissions). The workroom emissions were related to plating line throughput such as total area plated or ampere·hour of plating current, which was consistent with results from a previous study on another hexavalent chromium line. The emission factors for hood and workroom were 0.0805 and $2.57 \cdot 10^{-4}$ mg/A · h, respectively. The methods provide a first estimate for determining workroom emissions when no other data are available, and are a useful way to extend field test measurements. For systems with local exhaust ventilation the approach also allows determination of mass-based collection efficiency, in this case an average of 99.1 percent based on hourly average emission rates. CONROY, L.M.; WADDEN, R.A.; SCHEFF, P.A.; FRANKE, J.E.; KEIL, C.B.: WORKPLACE EMISSION FACTORS FOR HEXAVALENT CHROMIUM PLATING. APPL. OCCUP. ENVIRON. HYG. ():620–; 19.

Hexavalent chromium plating operations have long been recognized as having the potential to harm worker health. Soluble chromium at this valence is a recognized carcinogen.[1] Releases have ordinarily been characterized in terms of workplace concentrations.[2] However, chromium emission rates and emission factors are much more useful than concentrations for developing emission standards and implementing systematic design of control systems for ambient as well as indoor air in industrial, commercial, and office settings.

Until recently there have been relatively few reports of emission rates from such processes. In 1991 a report from the California Air Resources Board summarized a series of plant tests on emissions from chromium electroplating captured by local exhaust ventilation systems.[3] However, these studies included no measurements of workroom emission rates. A limited study at about the same time on a decorative plating line initiated development of a methodology to determine the in-room emissions.[4] (We have defined workroom emissions as releases not captured by local exhaust ventilation systems.)

This study is a further development of an approach to evaluating workroom releases. We will describe the methodology by which this was done and demonstrate the application for a piston plating line. The study also shows how the results were compared with other process data to establish internal consistency, and includes a comparison with existing hood emission data.

Methodology

During plating, chromium metal is deposited onto the surface of a workpiece suspended in a chromium-containing solution. Chromic acid (CrO_3) is the usual solution form for hexavalent chromium plating. The current that reduces the hexavalent form to metal also causes hydrolysis of water in the bath. The gas bubbles released at the cathode (hydrogen) and anode (oxygen) entrain chromic acid, causing a mist which can be released to the workplace and to ambient air.

The particular site we examined was an electroplating shop containing a piston plating line with nickel and chromium plating tanks, a decorative chrome line plating air cleaner covers for small internal combustion engines (trivalent chromium preceded by nickel), and manual and barrel zinc coating lines (Figure 1). The manual zinc line included one chromium-containing plating tank and the barrel line contained two chromic acid tanks. The detailed sequence of the piston line is shown in Figure 2. Aluminum pistons are loaded into racks and cycled by an automated system through the various tanks. The chromium plating tanks were served with a local exhaust system, as were several of the acid tanks.

Average face velocities at doors and other openings were determined by multipoint traverses using a thermoanemometer; direction of flow was determined by smoke tubes. General ventilation flow rates through the doors are shown in Figure 1. Ventilation rates for the 13 local exhaust hoods (also shown in Figure 1) and for the doors are summarized in Table 1. The local exhaust systems were operating at constant flow rates during the whole period of the test. Total flow into the space (75,307 ft^3/m) agreed quite well with measured flow out (71,638 ft^3/m), and the resulting air change rate was about 5.7 air changes per hour.

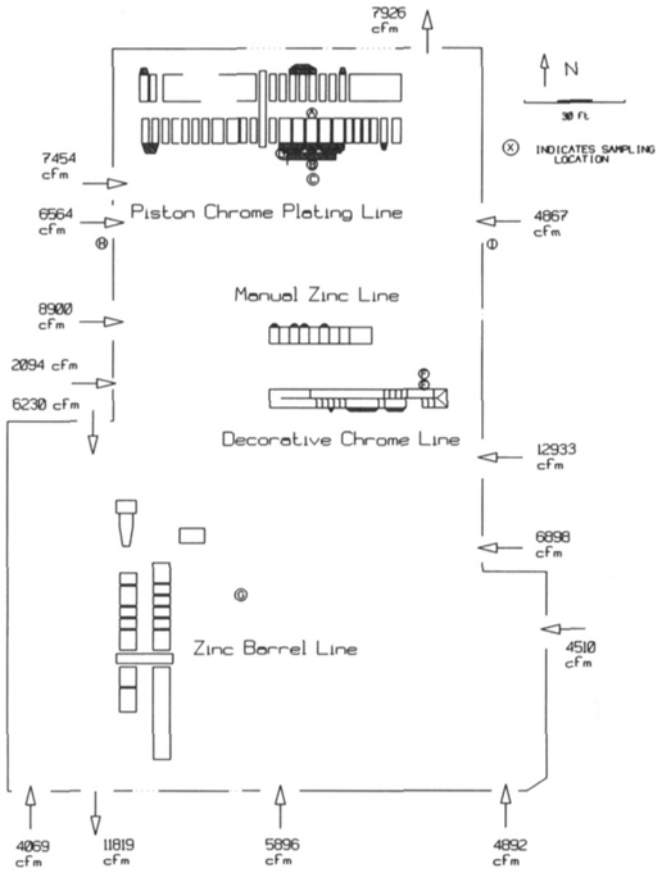

FIGURE 1. Plan view of electroplating shop.

The general approach to development of emission rates and emission factors has been described in several previous reports.[5-8] Simultaneous area concentration data are collected at various distances away from an emission source along with measurements of ventilation. These data are transformed to emission rates by using mass balance models which are appropriate for the geometry and patterns of work in the space. If observations of source activity are made concurrently with the concentration and ventilation measurements, emission rates can often be characterized as emission factors.

For this particular setting the appropriate model was a multipoint diffusion model. This form has been used to determine emission rates when one pollution source is the major contributor to concentrations in the surrounding space. A solution for the mass balance on the pollutant for a hemispherical space, neglecting deposition on the surface, is[9]

TABLE 1. Summary of Ventilation Measurements

Direction of Flow	Location	Q (ft^3/m)	
In	Doors	75,307	
Total in			75,307
Out	Doors	19,745	
Out	Chromium piston line, all LEVs	28,556	
Out	Chromium decorative line, all LEVs	4,994	
Out	Manual zinc line, all LEVs	18,343	
Total out			71,638

LEV = local exhaust ventilation systems.

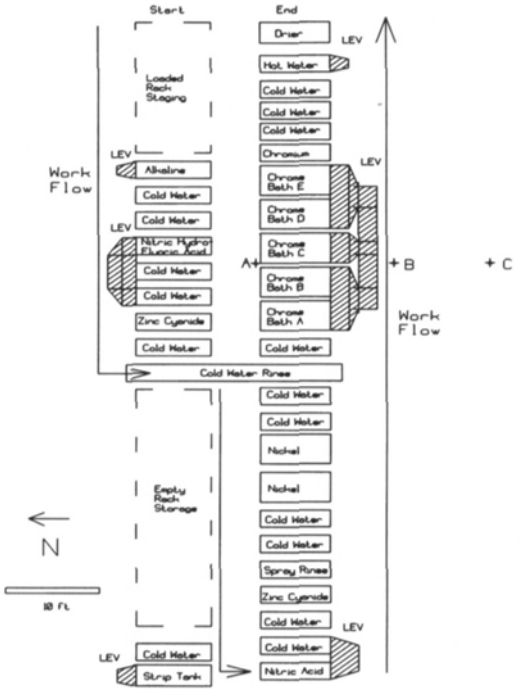

FIGURE 2. Piston chrome plating line schematic.

$$C = \frac{S}{2\pi Dr}\,\mathrm{erfc}\left[\frac{r}{(4Dt)^{0.5}}\right] \quad (1)$$

where:

C (mass/volume) = the concentration at any location r (the radius of the hemisphere), produced by an emission rate S (mass/time) which is constant with respect to the time t since the start of emission release

D (area/time) = an eddy diffusivity for the workplace setting[10]

$erfc$ = 1 − the error function

Manipulation of Equation 1, and those which follow, is most conveniently carried out with the aid of a programmable calculator, or personal computer software, which incorporates the error function and integration capability.

The integral of Equation 1 is the appropriate form to characterize area concentrations C_{av} collected over sampling time Δt. If we simultaneously sample concentrations over the same averaging time at two different distances from the source, r_1 and r_2, the integral form of Equation 1 gives two independent equations:

$$C_{av,r_1} = \frac{\bar{S}}{\Delta t}\int_0^{\Delta t}\left\{\frac{1}{(2\pi Dr_1)}\,\mathrm{erfc}\left[\frac{r_1}{(4Dt)^{0.5}}\right]\right\}dt \quad (2a)$$

TABLE 2. Hourly Chromium Concentrations (micrograms/cubic meter)

		Piston Line				Decorative Line		Background		
Date	Start Time	A Near (49.6 inches)	B Mid (137 inches)	C Far (249 inches)	D Duct	E Near (23.9 inches)	F Far (47.2 inches)	G Room	H Plant	I Plant
6/11/91	8:00	1.39	1.50	0.49	33.10	1.95	1.66	<0.43	0.01	<.07
	9:00	6.88	0.35	0.26	47.44	0.27	0.41	<0.18		
	10:00	8.59	2.07	1.38	58.82	1.18	0.52	0.02		
	11:00	3.10	1.91	0.40	54.21	0.66	0.02	<0.27		
	12:00	5.36	3.87	1.23	81.16	0.43	0.12	0.18		
	13:00	2.56	4.11	3.32	85.39	0.25	0.43	<0.20		
6/12/91	8:00	2.40	1.01	0.21	9.39	0.77	0.51	0.26	0.08	0.05
	9:00	1.77	1.77	0.34	16.12	0.59	0.08	0.30		
	10:00	1.62	3.86	0.44	17.48	0.97	0.32	1.16		
	11:00	1.31	3.60	0.20	11.13	0.22	0.25	0.03		
	12:00	2.76	4.71	0.74	23.55	0.36	0.34	0.38		
	13:00	1.09	1.60	0.20	7.53	0.32	0.32	0.33		
Average		3.24	2.53	0.77	37.11	0.66	0.42	0.31	0.04	0.06

$$C_{av,r2} = \frac{\bar{S}}{\Delta t}\int_0^{\Delta t}\left\{\frac{1}{(2\pi\, Dr_2)}\,\mathrm{erfc}\left[\frac{r_2}{(4\,Dt)^{0.5}}\right]\right\}dt \qquad (2b)$$

where:

$\bar{S}$ = the average emission rate over the sampling interval

Since the concentrations have been measured over a particular averaging time, the emission rate will also be an average value. An assumption of the model is that the average concentration is essentially the result only of emissions that occur during the sampling interval. Equations 2a and 2b can then be solved simultaneously for D and $\bar{S}$. A procedure for the solution which uses the Mathcad software[11] is given in the Appendix. Since, in this model, the pollutant is assumed to diffuse independent of direction, the sampling locations do not have to be in line.

Twelve separate hourly periods were monitored over 2 days for chromium concentrations at six locations in the workplace and in the ventilation duct on the chrome plating tanks (Figure 1). Six-hour average concentrations were also determined at two locations (H and I) just outside the plating room. Air samples were collected on open-face 25-mm polycarbonate filters using calibrated flow rates of 2 to 3 L/min. Filters were analyzed by proton-induced X-ray emission spectroscopy (PIXE). Samples B and C (Figure 2) were 3.48 m (137 inches) and 6.33 m (249 inches) from the center of the five chrome plating tanks. Sample D was taken in the local exhaust ventilation duct immediately prior to the wet scrubber air cleaner.

Results

Chromium concentrations for each hour are shown in Table 2. Although the PIXE method does not discriminate between ionic forms, it is likely that most of the chromium release from the piston line is in the hexavalent form since the California measurements showed that based on 14 tests at seven sites 86.8 percent of total chromium was chromium^{+6}.[3] None of the workplace concentrations were above the threshold limit value (TLV) of 50 $\mu g/m^3$ for chromium^{+6}.[1] (The TLV for chromium^{+3} is 0.5 mg/m^3, and this form of the metal has not been identified as a carcinogen). The area of each piston type is given in Table 3. During the test, only plating tanks A, B, C, and E were in operation (Figure 2). Actual plating time was 18 minutes for each rack of pistons. The plating bath composition was 260 g chromium^{+6}/L and the bath was agitated with an air sparger. The composition of chromium^{+3} in the decorative line baths was 6 g/L, the plating time/part was about 4 minutes, and this bath was also air agitated.

Table 4 shows the duct emissions for the plating line, the workplace emissions and diffusivity calculated from Equations 2a and 2b, the corresponding throughput in terms of total area/hour in all plating tanks and current as ampere·hours/hour, and the percentage not collected by the local exhaust ventilation system (% penetration). The workplace emissions were calculated using concentrations from locations B and C.

Discussion

One useful check on the activity data is whether the observed amperage is consistent with the amount of chromium applied. The plating thickness on the pistons was 0.15 mils or $1.5 \cdot 10^{-4}$ inches. Figure 3 shows a strong hourly association between ampere · hours and square inches of piston surface. The average area/amperage value, based on 105 individual racks of pistons, was 3.56 inches^2/A · h. (Alternately, the slope of Figure 3 is 3.48 inches^2/A · h.) The plating efficiency (*Eff*) for a chromium^{+6} system is given by the equation[12]

TABLE 3. Piston Plating Line Parts

Part Number	Surface Area (square inches)	Description
8	40	Small piston
9	40	Small piston
19	55	Medium piston
25	71	Large piston

TABLE 4. Hourly Emission Rates and Source Activities for Piston Line

Duct Emission Rate (milligrams chromium/hour)	Workroom Emission Rate (milligrams chromium/hour)	Eddy Diffusivity (meters²/minute)	Total Area Plated (inches²/hour)	Ampere · hours/hour	Penetration (%)
562.2	3.09	0.884	32,383	9,110	0.55
805.8			47,405	13,487	
999.1			47,032	13,367	
920.8	2.12	0.310	46,650	13,170	0.23
1378.5	7.43	0.802	47,441	13,597	0.54
1450.3			23,209	6,990	
159.5	1.13	0.313	31,814	8,604	0.70
273.8	1.87	0.279	30,769	8,713	0.68
296.9	3.42	0.149	33,058	9,406	1.14
189.0	3.26	0.085	17,684	4,920	1.70
400.0	4.48	0.206	24,902	6,907	1.11
127.9	1.43	0.159	13,196	3,624	1.11
Averages					
630.3	3.14	0.354	32,962	9,325	0.86

$$\text{Eff} = \left[\frac{\frac{\text{inches}^2}{\text{A} \cdot \text{h}} \cdot (\text{plating thickness}) \cdot \left(\rho \frac{\text{g Cr}}{\text{cm}^3}\right)}{\frac{0.0611 \text{ inches}^3}{\text{cm}^3} \cdot \frac{\text{g Cr}^{+6}}{\text{equivalent}}}\right] \cdot \frac{96{,}450\text{A} \cdot \text{s}}{\text{equivalent}} \cdot \frac{\text{h}}{3600 \text{ s}} \quad (3)$$

or

$$\text{Eff} = \left[\frac{3.56 \frac{\text{inches}^2}{\text{A} \cdot \text{h}} \cdot (0.00015 \text{ inches}) \cdot \left(6.9 \frac{\text{g Cr}}{\text{cm}^3}\right)}{\frac{0.0611 \text{ inches}^3}{\text{cm}^3} \cdot 8.67 \frac{\text{g Cr}^{+6}}{\text{equivalent}}}\right] \cdot \frac{96{,}450 \text{ A} \cdot \text{s}}{\text{equivalent}} \cdot \frac{\text{h}}{3600\text{s}} \quad (4)$$

$$\text{Eff} = 0.180 \text{ or } 18.6\%$$

This value is in very good agreement with the typical range of efficiencies, which range from 10 to 20 percent.[13] In addition, the current density for this process was calculated from the observational data to be 131 A/m², which is consistent with usual reported ranges of 50 to 200 A/m². Consequently, we had considerable confidence that the data we were recording were accurate (i.e., consistent with the production objectives of the process). A similar evaluation was carried out for the decorative line. In this case the thickness was 0.03 mils with an average area to current consumption ratio of 93.9 inches²/A · h (Figure 4). The resulting average plating efficiency from Equation 4 (recognizing that there are 17.3 g chromium^{+3}/equivalent) was 52 percent.

Concentrations at locations H and I were much lower than those measured in the room. Consequently, the major chromium sources were assumed to be located within the space. The concentration gradient defined by locations B and C was used in Equations 2a and 2b to determine workroom release rates from the piston line. While the concentration gradient was consistently negative for all 12 measurement periods (decreasing concentration with increasing distance from the source), we were not able to calculate an emission rate for three of the hourly periods (Table 4). The reason for this is likely to be the presence of other chromium sources in the space, and the possibility that cross-drafts may have contributed an advective flow from the south end of the room which was great enough to disrupt the concentration gradient for these three sets of observations. The range of diffusion coefficients shown in Table 4 is within the usual range which we have observed in the past (0.1 to 10 m²/min).[10]

It is useful to note that the solution of Equations 2a and 2b depends on the slope of the concentration gradient with distance away from the source. A necessary condition for solution

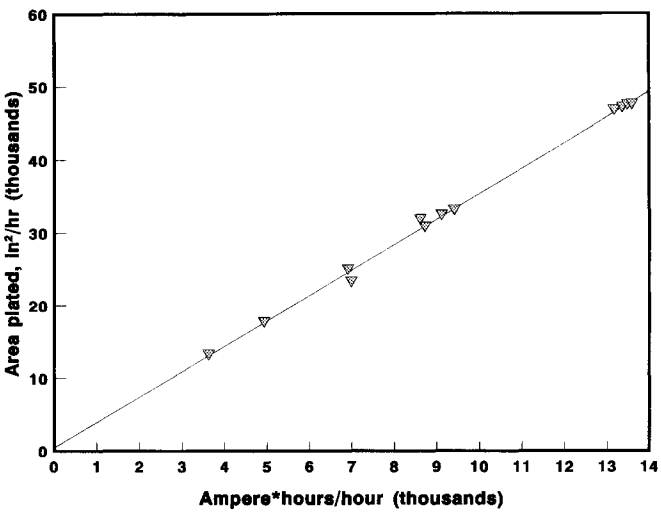

FIGURE 3. Area plated as a function of ampere · hours; chromium plating on pistons. Inches²/h = 3.485 × A · h/h + 463.4.

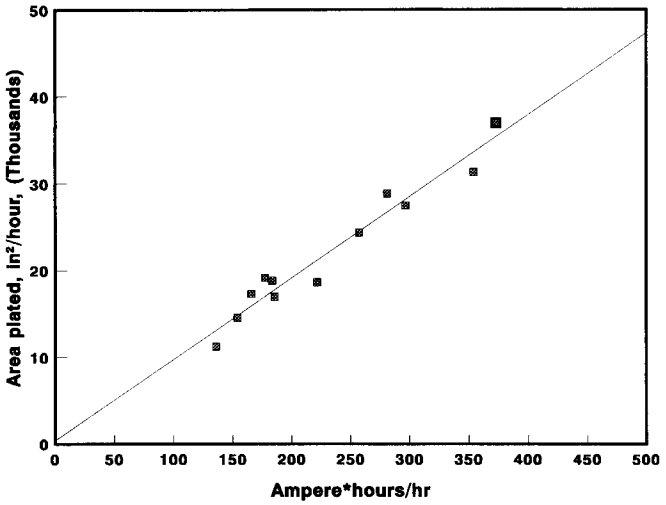

FIGURE 4. Area plated as a function of ampere · hours; trivalent chromium plating. Inches^2/h = 93.9 × A · h/h + 360.

is that the concentration decrease with increasing distance. However, this is not a sufficient condition. Even with a decreasing gradient, a physically realistic solution (i.e., one for which the calculated value of D is greater than zero) may not be possible. It is likely that concentration patterns that do not result in solutions are caused by violations of the basic assumptions of the mathematical form such as emissions from other sources; significant residual emissions from the previous sampling period; excessive cross-drafts leading to advective flow in excess of diffusion; low ceilings, walls, or other geometric configurations which may distort the hemispherical geometry; or significant deposition or, for particles, coagulation. At this stage of model application we are not able to *a priori* specify numerical limits for these assumptions. However, the model is, to some extent, self-regulating in this regard because it will not return a realistic solution if the assumptions are not approximated closely enough. Our general approach, if there is not strong persistent advective flow (which requires a different form of the mass balance[7]), is to apply the model and see if a solution results. If a physically realistic solution is determined, we then compare this with some measure of source activity, such as throughput, to determine whether the mathematical solution is consistent with process operation.

As a further example, we also used the edge concentration (location A in Figure 2) in conjunction with the concentration at location B or C to solve Equations 2a and 2b. Generally, we were not able to calculate an emission rate for any physically realistic value of diffusivity (cannot be <0, and is unlikely to be >100 m^2/min). Since site A is on the opposite side of the tank from the local exhaust ventilation, there is likely to be a significant advective air flow in the direction of the hood and away from A. Consequently, the edge concentration does not fulfill the physical assumptions of the diffusion model and we would not expect Equation 1 to apply.

Concentrations in the vicinity of the decorative trivalent chromium line (locations E and F) were generally much lower than those close to the piston line. There was no local exhaust ventilation system on the decorative line chromium bath. In three cases the gradient was actually positive away from the line, and in two other sampling periods there was essentially no gradient. Application of Equations 2a and 2b to the remaining concentration pairs did not yield realistic solutions. The major reason for the lack of a consistent gradient may have been the activity at the nearby manual zinc plating line, which included a chromium plating tank. Consequently, the assumption underlying Equation 1 that only a single source was contributing to the measured concentrations was not met. Although it is possible to apply Equation 1 for multiple sources,[6,7] we did not have the resources to collect the many more samples which would have been required to distinguish multiple contributions.

Comparison of duct emissions with ampere·hours of input is shown in Figure 5. The data suggest a positive association. In addition, the least-squares fit of the data gives an emission factor of 0.0805 mg chromium released/A · h. Figure 6 shows the emission rates from the piston line into the workspace. A least-squares fit of the emission data provides an emission factor of about $2.6 \cdot 10^{-4}$ mg chromium/A · h. Emissions into the workspace and hood emissions are compared in Figure 7. The positive relationship between workroom and duct emissions is an indication of the consistency of the methodology.

Hood and workroom emissions are summarized in Table 5. Results from another test on a line coating hexavalent chromium on automobile ignition lock caps are also listed.[4] Hood emissions from both the piston line and the ignition lock cap line are well within the range of values reported from the California studies.[3] Workroom releases were not measured in the California studies. The values shown for the piston and ignition lock cap operations are consistent with the respective efficiencies of control systems for the two processes on an hour-by-hour basis.

Conclusions

We have described a methodology for determining workroom emissions from chromium plating. Application of this ap-

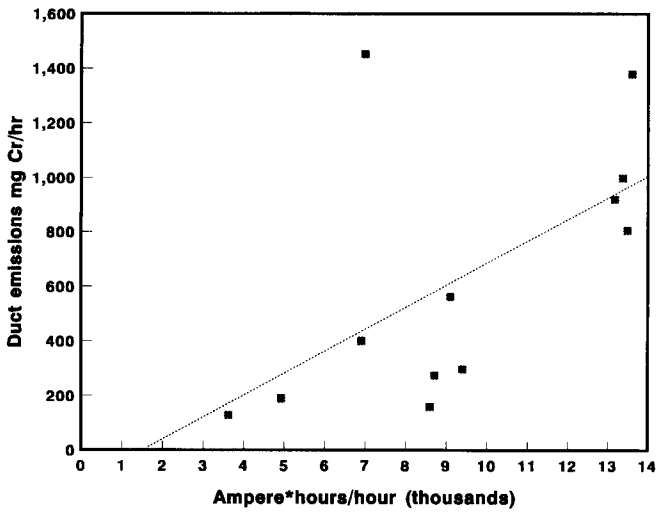

FIGURE 5. Duct emissions of chromium versus ampere · hours; chromium plating on pistons. Emission factor = 0.0805 mg/A · h from least-squares fit of data.

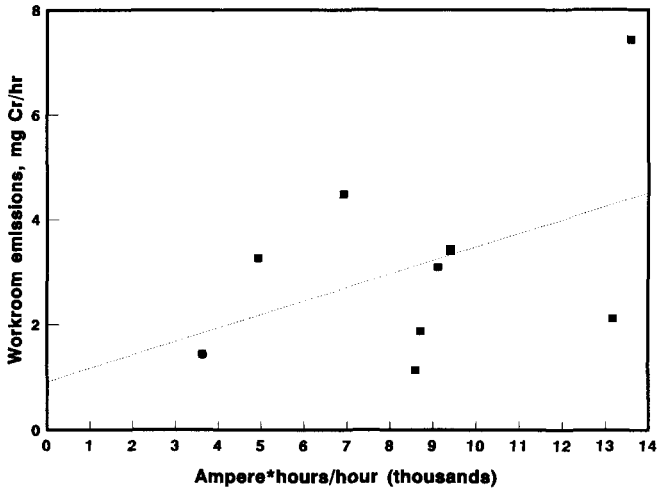

FIGURE 6. Room emissions of chromium versus ampere • hours; chromium plating on pistons. Emission factor = $2.57 \cdot 10^{-4}$ mg chromium/A • h from least-squares fit of data. Hood efficiency ≈99 percent.

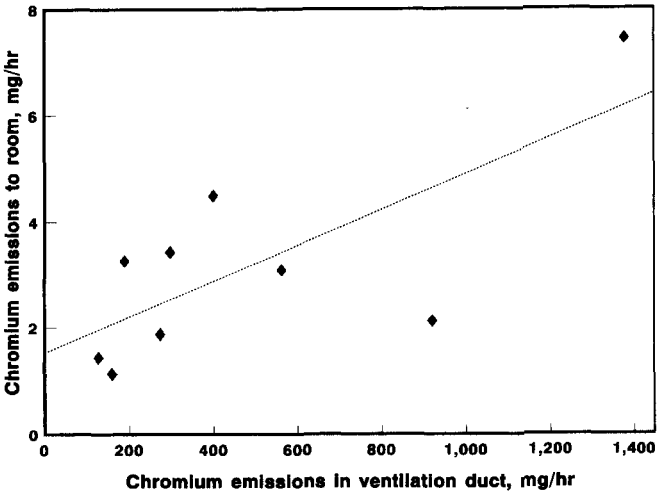

FIGURE 7. Room emissions of chromium as a function of duct emissions; chromium plating on pistons. Emissions to room (mg/h) = 0.0034 • duct emissions (mg/h) + 1.53. LEV efficiency, ≈99 percent.

proach to a piston plating line resulted in an average workroom release rate of 3.1 mg chromium^{+6}/h and a determination of an actual hood efficiency of >99 percent (99.1% based on the average values in Table 4, or 99.7% based on the average hood and workplace emission factors in Table 5). The workroom emission rates were in agreement with the ampere•hours of plating current consumed and, expressed as an average emission factor, were equal to $2.6 \cdot 10^{-4}$ mg chromium/A • h. Description of release rates in this form provides a more systematic basis for emission control both into the workplace and into ambient air.

Acknowledgments

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TABLE 5. Comparison of Hood and Workplace Emissions for Hexavalent Chromium Plating

Hood Emissions (milligrams/ampere • hour)				Workroom Emissions (milligrams/ampere • hour)	
California Air Resources Board[3]		Ignition Locks[4]	Pistons	Ignition Locks[4]	Pistons
3.8[A]	0.0106–3.107[B]	1.47	0.0805	0.412[C]	0.000257[D]

[A]Average of 10 field tests (reported separately from Footnote B).
[B]Range of 14 tests on 7 systems.
[C]Hood control efficiency of 81 percent; 148 g chromium^{+6}/L plating solution; 2700 to 9900 inches^2 plated/h.
[D]Hood control efficiency of >99 percent.

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Appendix: Calculation of D and S Based on Mathcad 4.0[11]

$C_{av_1} = 1.599\ \mu g\ chromium/m^3$;

$C_{av_2} = 0.197\ \mu g\ chromium/m^3$;

$t_{av} = 60$ minutes (13:00 to 14:00, 6/12/91)

Assume $D = 0.1\ m^2/min$ as a first estimate, and define

$$erfc_{r1}(D,t) = 1 - erf\left(\frac{r_1}{\sqrt{4 \cdot D \cdot t}}\right)$$

$$erfc_{r2}(D,t) = 1 - erf\left(\frac{r_2}{\sqrt{4 \cdot D \cdot t}}\right)$$

$$R(D) = \left(\frac{r_2}{r_1}\right) \cdot \frac{\int_{10^{-9}}^{t_{av}} erfc_{r1}(D,t)\,dt}{\int_{10^{-9}}^{t_{av}} erfc_{r2}(D,t)\,dt}$$

$$z = \frac{C_{av_1}}{C_{av_2}}$$

Mathcad commands:

$R(D) \cong z$

$D = Find(D)$

Resulting in:

$D = 0.159\ m^2/min$. S is calculated from

$$S = \frac{C_{av_2} \cdot (2 \cdot \pi \cdot D \cdot r_2) \cdot \int_{10^{-9}}^{t_{av}} dt}{\int_{10^{-9}}^{t_{av}} erfc_{r2}(D,t)\,dt} = 23.9\ \mu g\ chromium/min$$

The lower limit is set to a small number (10^{-9} minutes) instead of 0 to avoid any singularities at $t = 0$. The Mathcad program uses a numerical algorithm called Romberg integration (a modification of the trapezoidal rule) to approximate the integral of the expression. The solution was the same when the tolerance variable, TOL (set = 0.001), was varied from 10^{-5} to 0.1. The calculation is not strongly a function of the assumed value. The value of D shown above will be reached for assumed values between 0.01 and 0.19 m^2/min. If one assumed value does not give a solution, choice of one or two others will show which direction to search for solutions. Figure 8 shows the variation in the two complementary error functions with variation in t, Figure 9 shows how the value of $R(D, t_{av})$ varies with t_{av}. Figure 10 shows the variation with time in the instantaneous concentration calculated at r_1 using the values of $\bar{S}$ and D determined from the solution of Equation 2(a and b) with concentration data from 13:00–14:00, 6/12/91. The average concentration, which is what we measured, will be the area under the curve divided by the averaging time.

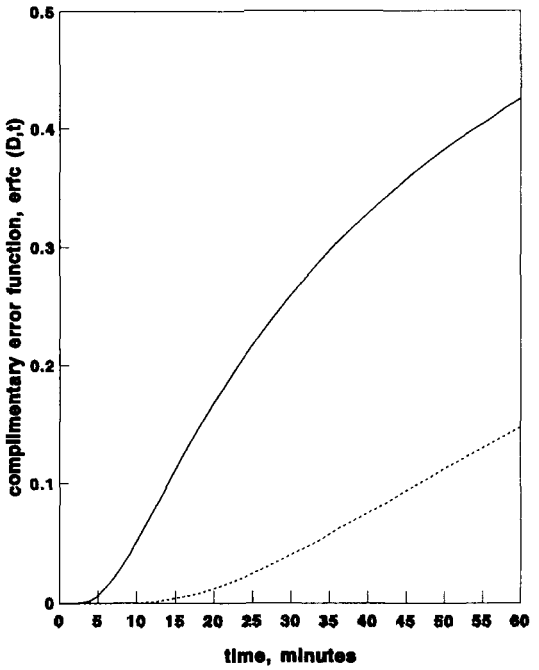

FIGURE 8. Variation in complementary error function with time (data for 13:00 to 14:00, 6/12/91). — $erfc._{r1}(D,t)$ - - - - $erfc._{r2}(D,t)$. D = 0.159 m^2/min; piston line, run 12.

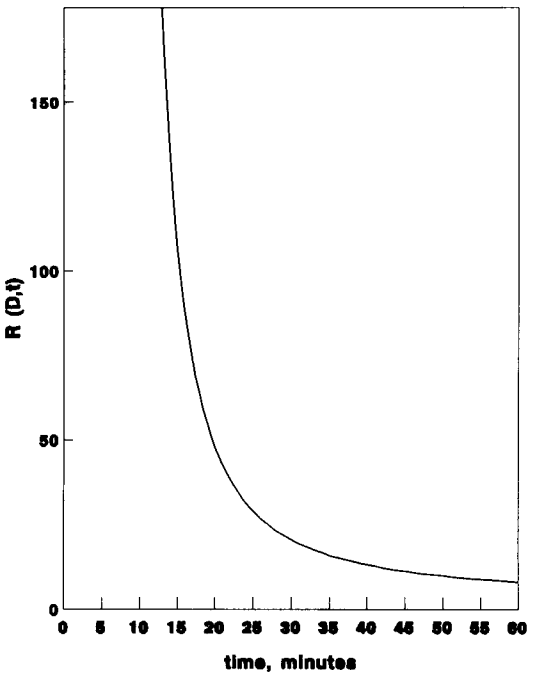

FIGURE 9. Variation of $R(D,t_{av})$ with averaging time (data from 13:00 to 14:00, 6/12/91). D = 0.159 m^2/min; piston line, run 12. C_{r1}/C_{r2} = 1.599/0.197 = 8.117.

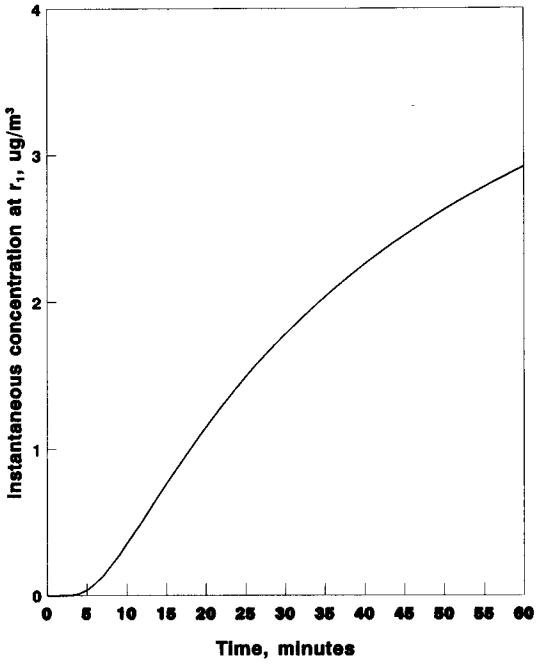

FIGURE 10. Variation of instantaneous concentration calculated from Equation 1 with time at r_1 based on emission rate and diffusivity determined from concentration data (13:00 to 14:00, 6/12/91). D = 0.159 m^2/min; piston line, run 12. S = 23.86 μg chromium/min; r_1 = 3.48 m. $C_{r1} = [S/(2\pi D\ r_1)]\ erfc\ [r_1/(4\ D\ t)^{0.5}]$.