

# SIZE AND CONCENTRATION MEASUREMENTS OF PARTICLES PRODUCED IN COMMERCIAL CHROMIUM PLATING PROCESSES

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## ABSTRACT

Optical measurements of particle size and concentration have been made at the chromium plating tank and exhaust system at a commercial hexavalent chromium plating facility. Particles were examined at three locations in the exhaust system: 1) directly at the hexavalent chromium plating bath surface, 2) at the exit of a cyclone separator located in the exhaust system approximately three to four meters downstream of the bath, and, 3) in the exhaust stack, downstream of the induced draft fan and all abatement devices. Particle diameters at the bath surface ranged from 0.3 to 25 micrometers. Downstream of the cyclone exit and mesh pad filters, particle top sizes were approximately 5 and 0.7 micrometers, respectively. On a mass basis, the collection efficiency of all abatement devices was 99.997%. Assuming droplets in the flow consist primarily of water and chromium, correcting the total particle mass flow against water content gives a chromium emission rate of 64,000  $\mu\text{g/hr}$  which compares favorably with a value of 77,000  $\mu\text{g/hr}$  measured with EPA methods. This initial agreement, which should be validated through additional measurements over a broad range of flow conditions, raises the possibility of a continuous monitor for chromium metal emissions using particle size/mass as a surrogate.

## INTRODUCTION

Since chromium is one of the eleven metals specifically regulated under the Clean Air Act Amendment (CAAA), emissions from chromium plating facilities are regulated closely by the state and federal Environmental Protection Agency (EPA). Allowable emissions are typically measured in milligrams of chromium (hexavalent plus trivalent) per ampere-hour of plating bath operation. With the 1990 amendments to the CAA, the allowable chromium emissions rate has decreased substantially. In the San Francisco Bay Area, allowable emissions range between 0.006-0.15 mg/amp-hour, depending on the amount of plating activity [1]. Large plating operations that produce greater amounts of chromium metal per year are typically regulated to the most stringent levels.

In order to meet these increasingly stringent requirements, plating facilities have installed condensed-phase separators, water scrubbers, and mesh-pad abatement devices in the exhaust train to reduce the number of chromium-containing particles entrained in the exhaust stream. The performance and design specifications of these devices depend on particle size. Prior to the present study, little published data existed characterizing the condensed phase emitted from chromium plating processes. Representatives from: 1) plating facilities, 2) emission abatement device vendors, and 3) the Environmental Protection Agency (EPA) suggested a disparate range of particle sizes between 0.5 and 30 micrometers that could be expected in the plating process. These sources also indicated that

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particle size depends on sampling location in the exhaust train, with smaller particles generally expected with increasing penetration into the train. However, little quantitative information was available that explicitly described the reduction in particle size.

To better quantify both the size distribution and concentration of particles released during chromium plating processes, measurements of particle size and concentration have been made at the chromium plating tank and in the exhaust system at a commercial hexavalent chromium plating facility. These data are vital to an on-going study that addresses chromium emissions from plating facilities directly. In addition, these measurements provide insight into the performance of cyclone separation and mesh-pad abatement devices that the plating facility installed to reduce the amount of chromium released to the environment.

## **TECHNICAL APPROACH**

Particle size measurements were made using a laser-based, particle-sizing instrument, the Insitac Particle Counter, Sizer, Velocimeter, (PCSV) fine-particle diagnostic probe. This instrument, illustrated in Fig. 1, is capable of measuring the size, velocity and concentration of particles 0.3 to 25 micrometers in diameter at particle concentrations ranging from sub-part-per-trillion (volume particle/volume gas) to part-per-million levels. A single particle counter, the PCSV is well suited for characterization of more dilute flows, such as those at this facility. Particle size measurements are based on the theory of Mie scattering from a single particle [2]. Particle velocities are determined using a time of flight calculation of the particle through the measurement volume of the PCSV [3]. During a measurement, the PCSV probe is inserted into the flow. Particles to be analyzed pass through the test section, a 4x9 cm slot in the probe body. Flow visualization studies performed during the design of the test section [4] indicate that for flow velocities of up to 100 m/s, the flow is undisturbed at the diagnostic volume (located at the center of the test section) and the flow is effectively sampled iso-kinetically.

For sub-micrometer size classes, the instrument is calibrated with latex spheres. For particle diameters two micrometers and above, an Insitac RS-2 reticle is used for calibration. This reticle consists of an opaque glass disk with monodispersed discs of known size etched on its surface. The glass disk is rotated through the measurement volume of the PCSV probe, enabling dynamic calibration of the instrument. Prior to making the measurements described here, the PCSV probe was calibrated on-site. Over the measurable particle size range of the PCSV, the calibration is within five percent of the known reticle particle size. Particle mass (concentration) uncertainties depend on statistical counting errors and particle velocity measurement errors, in addition to the size uncertainty. For these measurements, mass uncertainties are on the order of 15% [5].

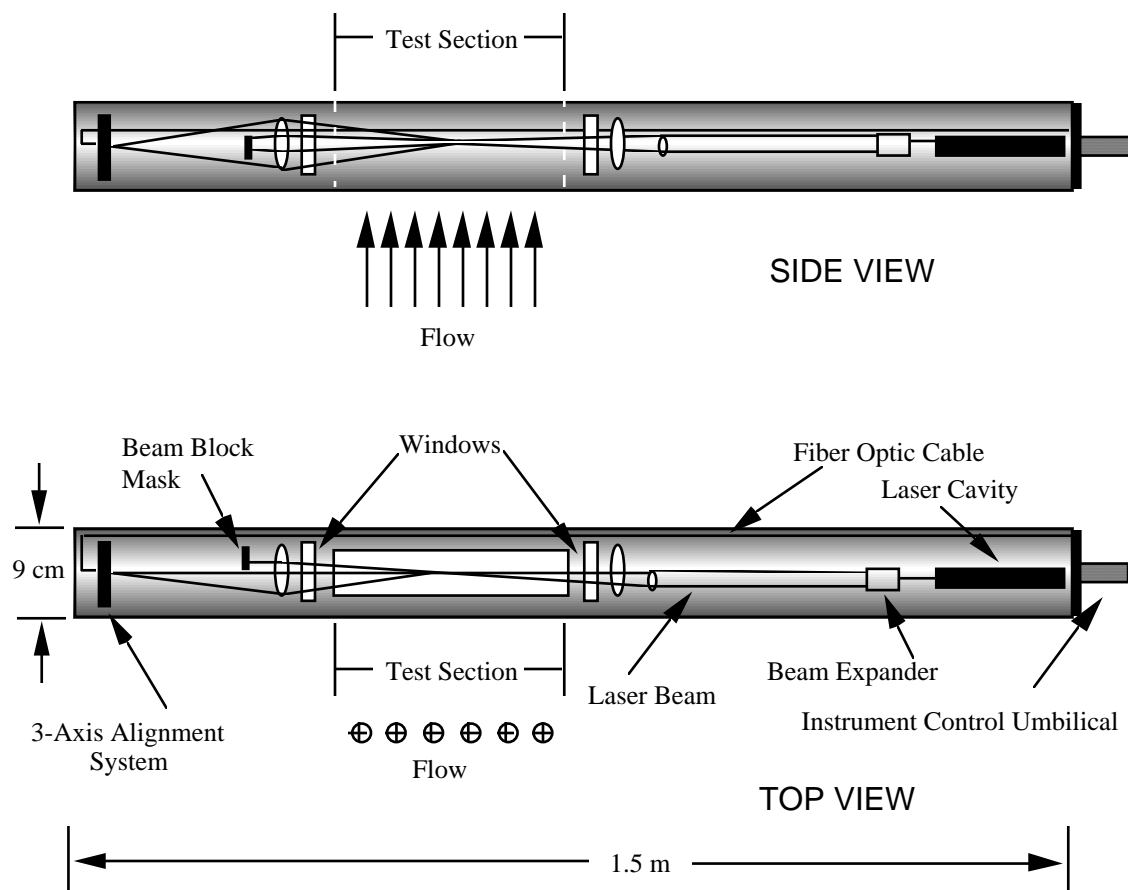


Figure 1. Schematic diagram of the PCSV optical single particle sizing diagnostic used in this study.

Figure 2 illustrates the tank and exhaust system of the plating facility as well as the locations where measurements were made. During the measurement period, no particle/vapor abatement devices were used at the tank surface. Particles were examined at three locations in the exhaust system: 1) directly at the hexavalent chromium plating bath surface; 2) at the exit of a cyclone separator located in the exhaust system approximately three to four meters downstream of the bath; and 3) in the exhaust stack, downstream of the induced draft fan and all abatement devices. Measurements were made under both plating and non-plating conditions. “Plating” indicates that a part has been inserted into the bath, the bath is electrified, and chromium metal is being transferred from the tank solution to the part surface. Under “non-plating” conditions, plating activity has ceased, the parts have been removed from the tank and the tank is not electrified.

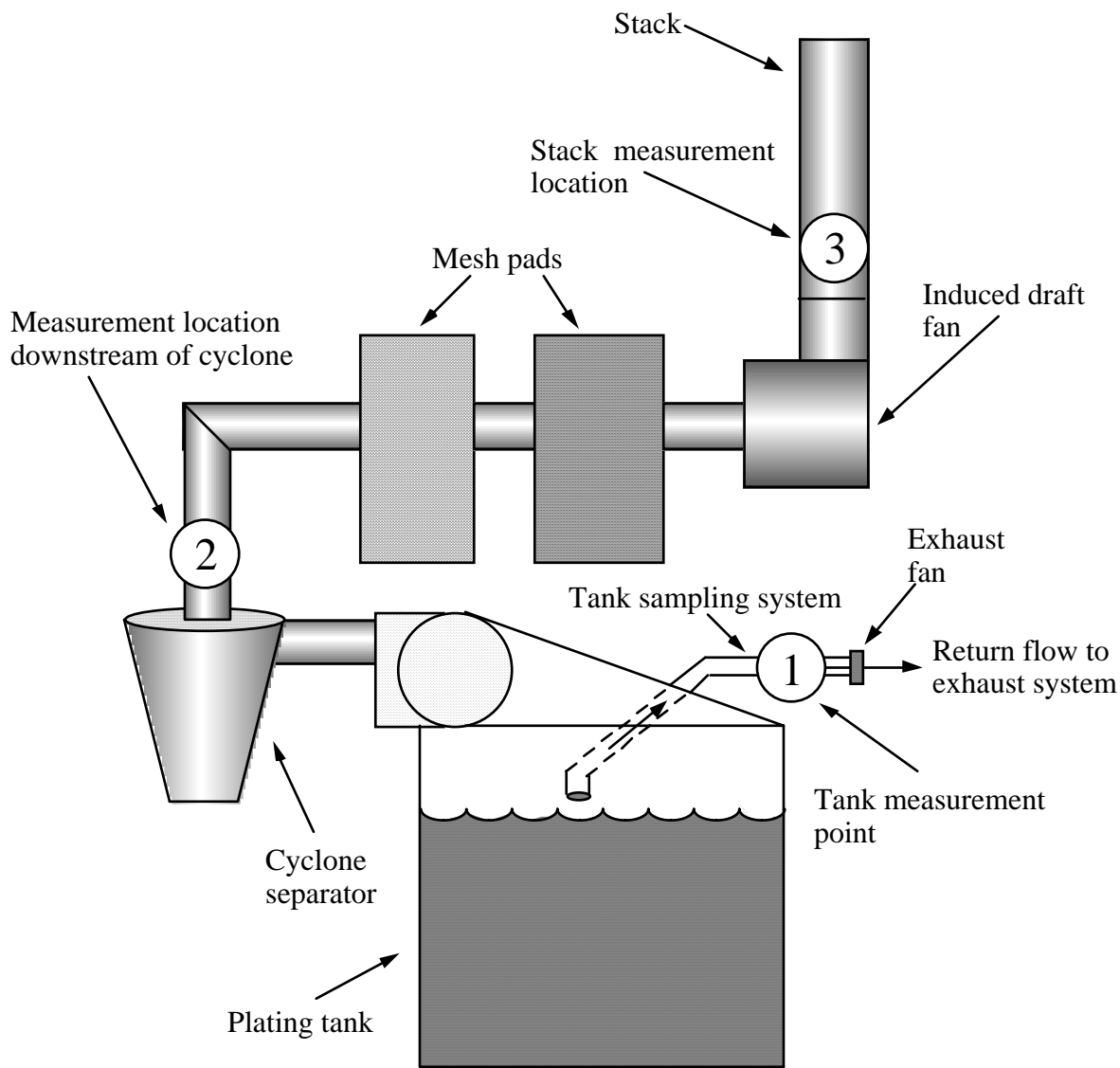


Figure 2. Schematic diagram of the plating facility illustrating measurement locations and pertinent abatement devices. Measurements were made at the tank surface (location 1), downstream of the cyclone (location 2) and in the exhaust stack, downstream of all abatement devices (location 3).

Since the PCSV could not be inserted directly into the hooded area surrounding the bath, an extractor was constructed to pneumatically convey particulates from the bath surface to the PCSV instrument. The extractor consisted of a one-meter length of clear, Plexiglas tube (5 cm I.D.), connected to a flange to accept the PCSV probe and finally to a small exhaust fan. To avoid undesirable room emissions, the flow was routed back into the plating tank exhaust system using flexible ducting. The sampling inlet was positioned two centimeters above the bath surface. In this region of the tank, the influence of the exhaust stack draft fan on particle entrainment was small.

Particle movement was induced primarily by convection currents created by temperature differences between the hot, bath plating solution and the gas immediately above the liquid surface.

Excepting highly turbulent flows, under most conditions small particles less than five micrometers in diameter follow the gas flow stream lines. Thus, it is assumed that small particle concentrations measured in the gas extracted from the tank are representative of the concentration of small particles at the tank surface. Larger particles do not follow the gas flow as closely and, for the in-tank sampling locations, some degree of large-particle under-sampling might be expected that could result in lower-than-actual measurements of concentration for the largest particles. During the bath measurements, discoloration of the inner sampling-tube wall was observed indicating some material deposition on the wall.

Measurements downstream of the cyclone separator and in the exhaust stack were made by inserting the PCSV probe directly into the exhaust duct. Under these test conditions, based on the flow visualization studies described above [4], the flow was sampled iso-kinetically. Particle concentrations measured at these locations, based on measured particle velocity and particle count rate, are therefore representative of the actual concentration in the flow over the measured size distribution.

## RESULTS AND DISCUSSION

### PLATING TANK MEASUREMENTS

Particle size versus concentration curves for all of the measurements made in the plating tank (location 1, Fig. 2) are illustrated in Figure 3. These data were collected successively over a period of approximately one hour. Data acquisition at the in-tank location (location 1, Fig. 2) required approximately 10 minutes per test. Nine measurements were made while plating and two subsequent measurements were made after the part was removed from the plating tank.

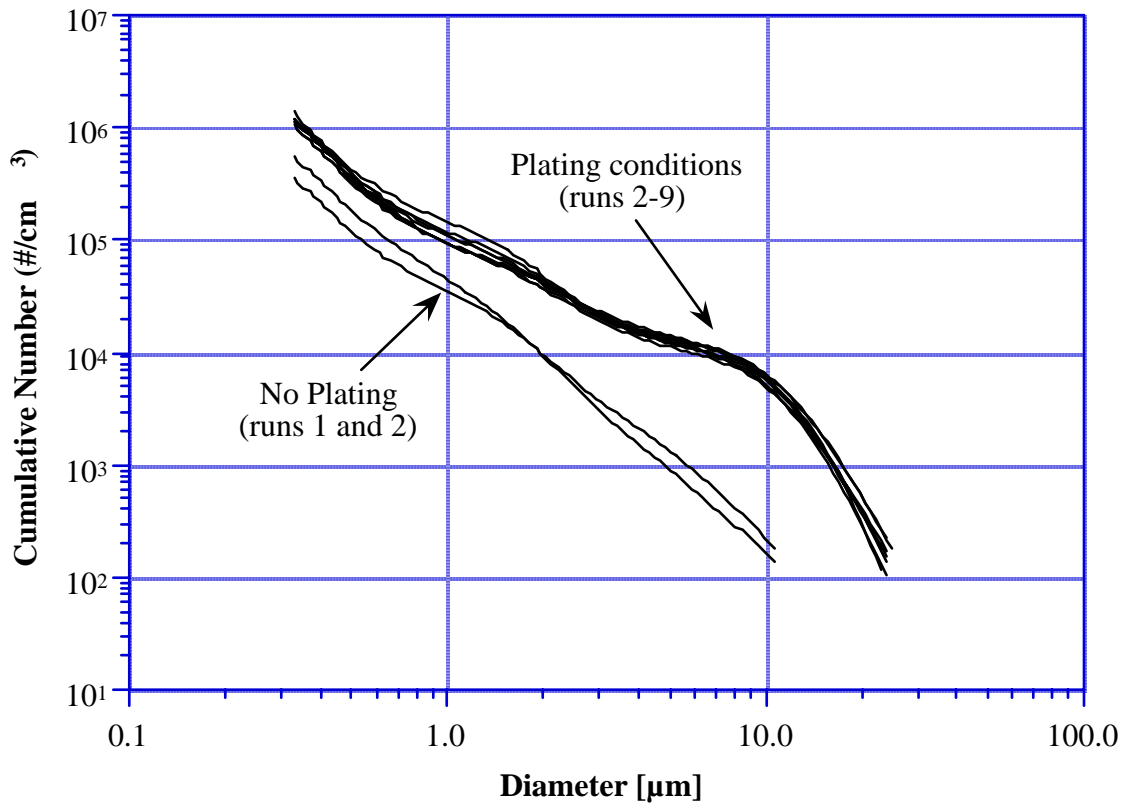


Figure 3. Comparison of in-tank size distributions between plating and non-plating conditions. Non-plating conditions show considerable reduction in particle concentration and reduction of maximum particle size. Tank conditions: approximately 12.9 amperes/cm<sup>2</sup> plating density when plating, 53 °C bath temperature.

Figure 3 shows that the measurements are reproducible, indicating that the measurement time was sufficiently long to allow adequate sampling statistics. Interestingly, for the first five measurements during plating, the power supply

for the muffin fan was set at 100%. During the final four measurements, fan speed was increased to 150% percent of full power. Increasing the fan speed by this amount resulted in a 20% increase in particle velocity measured by the PCSV probe. Initially, it was suspected that an increase in fan speed would improve entrainment of the larger particles in the flow. However, the similarity between all measurements during plating suggests that the fan speed increase had little influence on entrainment. Particles extracted from the plating bath hood ranges between 0.3 and 25 micrometers in diameter, equalling the upper and lower size limits of the PCSV. These sizes are similar to those observed in the Sandia plating laboratory during a study made under more carefully controlled plating conditions [6].

Figure 3 also illustrates measurements made under the same flow conditions as those of runs 2-9 but in the absence of any plating action in the tank. These “background” distributions indicate that an appreciable quantity of material was released from the bath surface even in the absence of plating activity. A visible mist was observed by eye under these conditions. The background is believed to result from the high bath temperature that contributed to formation of the mist. Particle number densities measured under non-plating conditions are a factor of 3-10 lower than those measured while plating. The plating/non-plating number density ratio is a function of particle size; the smallest ratio occurring at small particle sizes and the greatest ratio occurring in the large size classes.

Figure 4 illustrates the mass distributions calculated from the concentration information of Fig. 3. Because the parent solution forming the particles is primarily water, we assume that individual particles have a density of 1 g/cm<sup>3</sup> to obtain mass concentration from the size distribution measurements. The measurements made under plating conditions are again well grouped, with the average cumulative particle mass equaling 1.05x10<sup>-5</sup> g/cm<sup>3</sup>. The background measurements are characterized by an average cumulative mass of approximately 3.7x10<sup>-7</sup> g/cm<sup>3</sup>, a factor of 30 lower than the cumulative particle mass measured under plating conditions. Since we believe that some particles larger than the maximum measurable limit of the PCSV are present during plating, the actual ratio of cumulative masses is slightly larger.

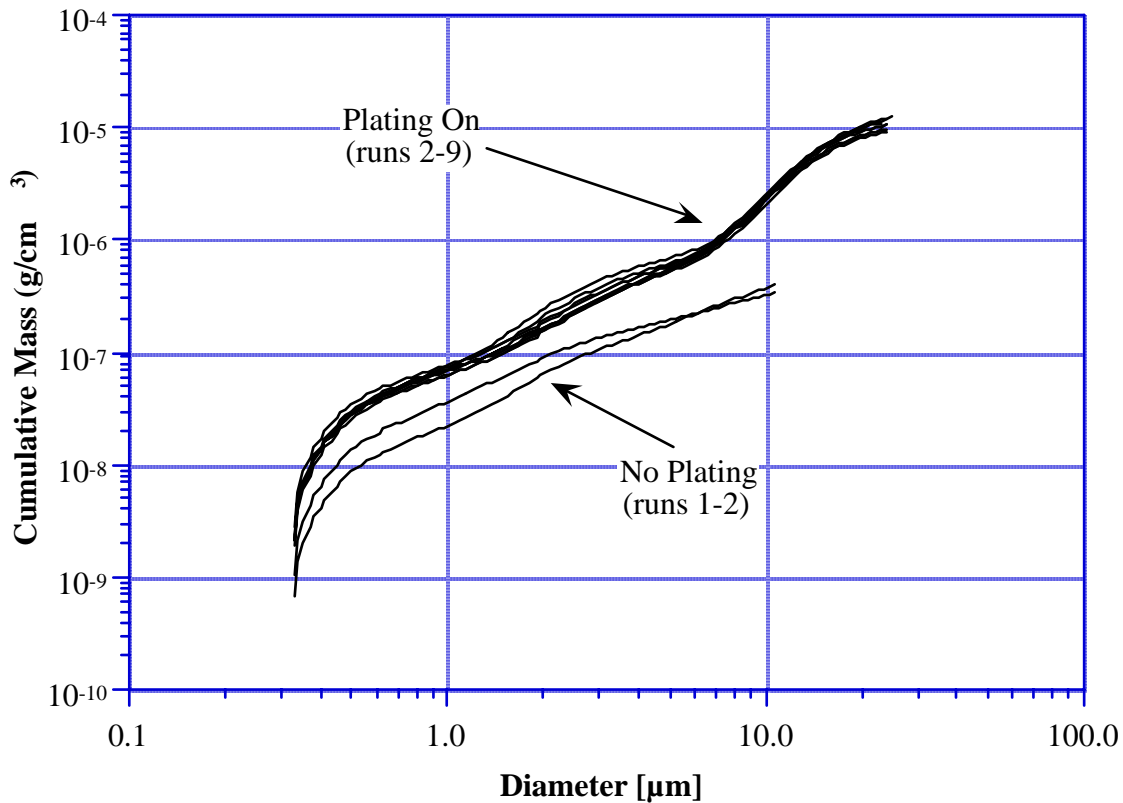


Figure 4. Particle mass distributions between plating and non-plating conditions calculated from the data of Fig. 3. Plating tank conditions identical to those indicated in Fig. 3.

#### POST-CYCLONE SEPARATOR AND EXHAUST STACK MEASUREMENTS

Figure 5 illustrates particle size distributions measured at the exit of the cyclone separator and in the exhaust stack, downstream of all abatement devices. A single size distribution measured under non-plating conditions downstream of all abatement devices is also depicted. The minimum particle size observed is 0.3 micrometers, the lower measurable limit of the PCSV. Maximum particle sizes observed are all less than 5 micrometers, well within the upper measurable size limit of the PCSV probe. Of the data collected in the plating tank exhaust system (locations 2 and 3, Fig. 2), the measurements made immediately downstream of the cyclone are characterized by the highest particle concentrations and, most significantly, by the largest particles. The data acquired

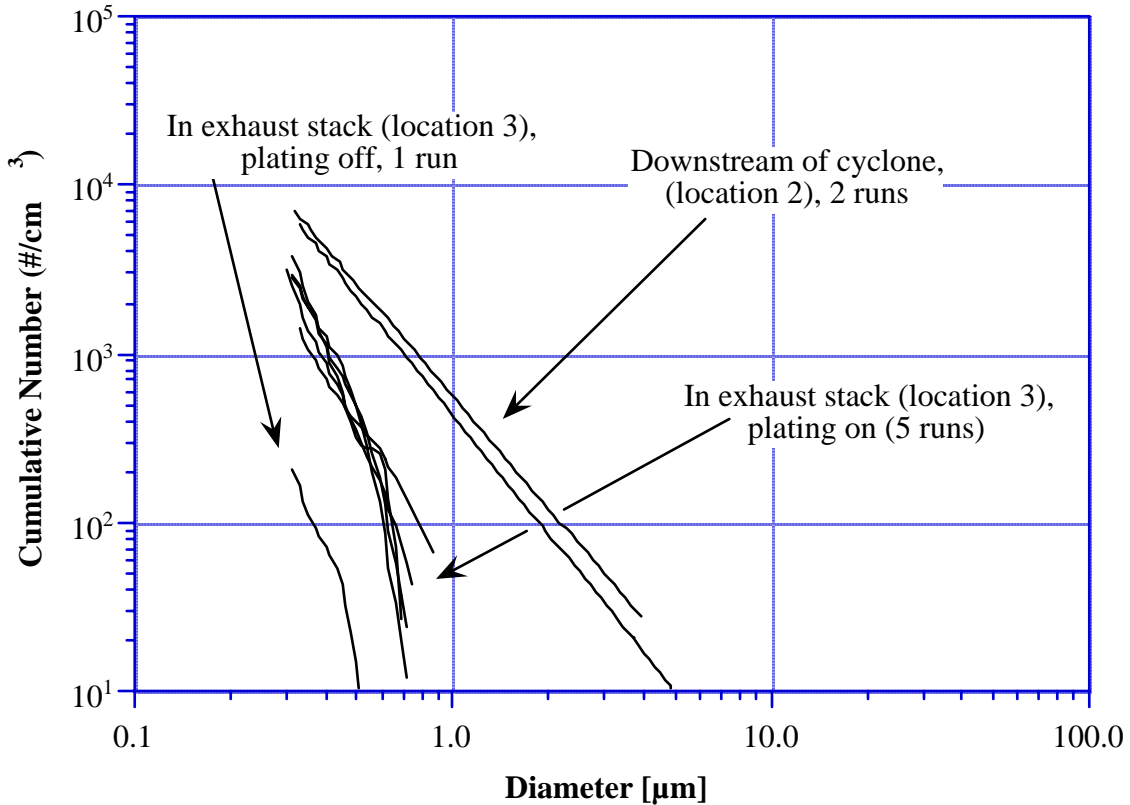


Figure 5. Particle size versus particle concentration measured at the cyclone exit and in the exhaust stack under plating and non-plating conditions. Reduction of particle concentration as a function of measurement location is indicative of particle removal by abatement processes. Locations reference Fig. 2. Plating tank conditions identical to those indicated in Fig. 3.

in the exhaust stack itself were collected over a period of one hour, corresponding to a complete plating run for a single machine part. These data are reasonably well grouped, excepting the first measurement that exhibits higher concentrations in the larger particle size classes. This data set was acquired over a time interval nearly coincident with the start of the plating run, suggesting that the difference resulted from a start-up transient of the plating process. The reduction in particle loading and size downstream of the abatement devices is apparent in the data of Fig. 5. Measured particle concentrations are nearly an order of magnitude higher at the cyclone exit (location 2, Fig. 2) than in the stack (location 3, Fig. 2), and the majority of the large particles have been removed from the flow at the final measurement point. The manufacturer of the mesh-pad filters has indicated that the system is capable of total particulate removal to particle sizes as small as 1  $\mu\text{m}$ . Since the transformation from particle size to particle

volume (mass) depends on the cube of particle diameter, we conclude that the amount of mass exiting the stack is significantly lower than that measured at the exit of the cyclone separator. These relationships are presented in Fig. 6, which depicts the same information as Fig. 5, but on a mass basis. Again, multiple runs are

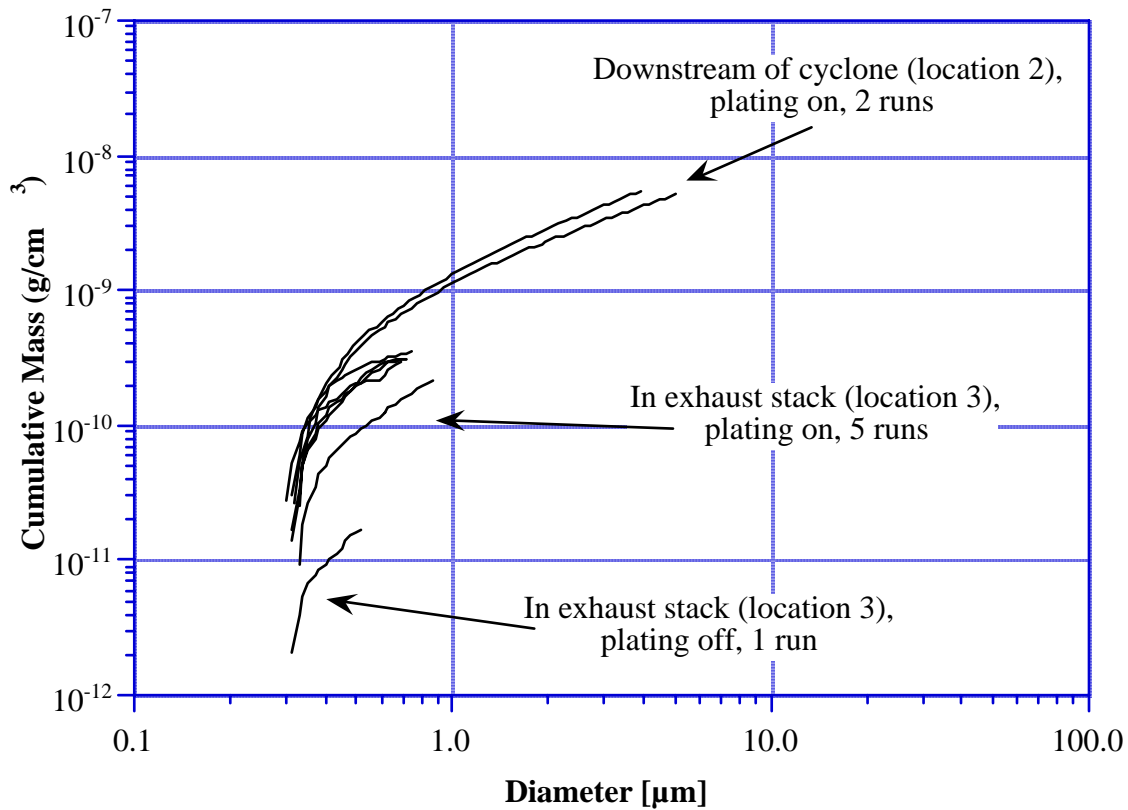


Figure 6. Particle size versus particle mass measured at the cyclone exit and in the exhaust stack illustrating the reduction of particle mass by successive abatement devices as well as the variation in loading between plating and non-plating conditions. Locations reference Fig. 2. Particle mass assumes a density of 1 g/cm<sup>3</sup>. Plating tank conditions identical to those indicated in Fig. 3.

reasonably well grouped at each measurement location, excepting the anomalous run of the data collected in the exhaust stack. The mass distribution of this data set is significantly lower than that of the other runs, supporting the previous conclusion that this data set was collected before the plating/exhaust system had reached steady-state operating conditions.

#### ABATEMENT DEVICE PERFORMANCE

Fig. 7 shows the variation in cumulative particle mass with measurement location and plating conditions (on or off). Note that the concentration axis of Fig. 7 is logarithmic. Particle mass measured at the tank surface under plating conditions is a factor of 30 higher than under non-

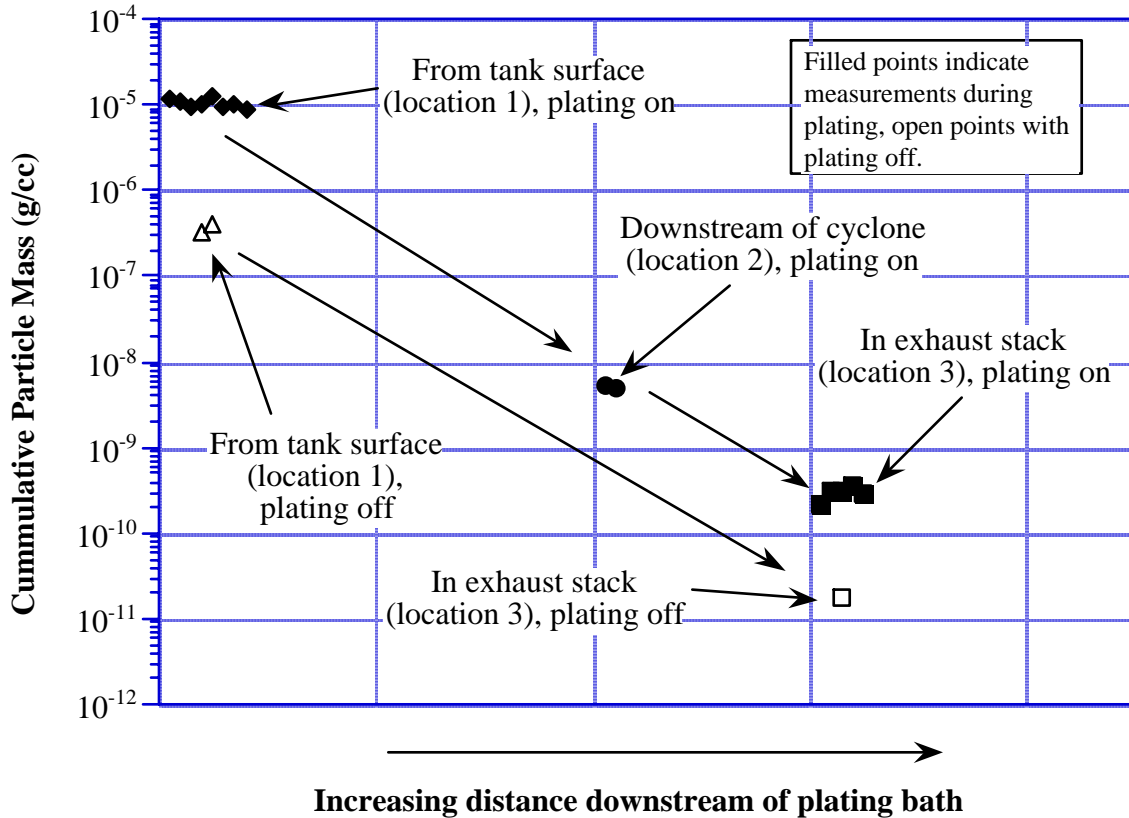


Figure 7. Comparison of total, measured cumulative mass at several locations for both plating and non-plating operations. Locations reference Fig. 2.

plating conditions. Under plating conditions, the particle mass at the exit of the cyclone is a factor of 2000 lower than at the bath surface. The reduction in mass from the cyclone to the exhaust stack is also evident, changing by a factor of 17.

Comparing the particle mass measurements made at the bath surface and in the exhaust stack downstream of all abatement devices, we calculate that the collection efficiency of the emissions control system is at least 99.997%. For the cyclone alone, the collection efficiency was 99.949% (also relative to the bath mass measurement). Clearly,

the cyclone provides the greatest amount of abatement. However, it predominately removes the largest particles that contain the majority of the particle mass. Alternate means of condensed-phase separation (such as mesh-pad filters) are required to eliminate the small particle fraction from the flow exiting the cyclone. The mesh-pad filters installed in this system have a collection efficiency of  $94\pm 2\%$ , assuming the instrument uncertainties described previously. The lower efficiency is consistent with the increased difficulty of removing smaller particles from the flow.

Measurements in the exhaust indicate that net particle mass emissions are a factor of 17 greater under plating conditions than with no plating. At this point, it is not clear whether the particles observed under non-plating conditions result from the “mists” described earlier in conjunction with the in-tank measurements (location 1, Fig. 2), or whether these particles represent ambient dusts that can normally be expected at these operating conditions. The total (water, chromium and additional elements of the plating solution) particle emission rate under non-plating conditions amounts to  $30,000 \mu\text{g/hr}$ , five percent of the total emissions observed under plating conditions.

The total particle emissions from the stack can also be obtained from the average cumulative particle mass measured in the exhaust stack ( $320 \mu\text{g/m}^3$ ), an assumed particle density of  $1 \text{ g/cm}^3$  and a stack flow rate of 29 actual  $\text{m}^3/\text{min}$ . Based on these values, for the conditions measured the total particulate mass emissions are  $560,000 \mu\text{g/hr}$ . However, this value represents total mass of particulates being emitted, not the total amount of chromium metal emission alone. The particulate measured include not only chromium metal, but also water (the primary constituent), ambient room dusts, and other contaminants in the plating tank solution that are all emitted as particulates from the bath surface.

To estimate the amount of chromium being released based on the particle size measurements, the relative proportions between chromium metal in the plating bath solution and water (the primary plating bath constituent) must be known. At this facility, the chromium content is examined weekly and is maintained over a range of 11.0 to 11.8% chromium metal in water, on a mass basis. Assuming that the particulate measured in the exhaust stack consists only of chromium and water, based on an average chromium metal content of 11.4% the calculated chromium metal emission rate is  $64,000 \mu\text{g/hr}$ . This value compares favorably (within 18%) with a value of  $77,000 \mu\text{g/hr}$ , measured shortly before this study in the same stack using EPA method CARB 425.

Uncertainties in the emission rate calculated from the particle measurements include the lack of spatial averaging over the stack diameter, droplet vaporization over the lifetime of the droplet while in the stack, fluctuating contaminant levels in the plating bath and the aforementioned uncertainty associated with the PCSV itself. The PCSV measurements were made on the stack centerline. Off-centerline PCSV measurements in other stacks have shown five to twenty percent reductions in measured particle mass depending on proximity to the inner stack wall. As a competing influence, droplet vaporization over the lifetime of the droplet in the exhaust system could increase

the chromium content of individual droplets above the concentration level calculated from the plating solution formulation.

The agreement between the chromium emissions rate calculated from aerosol particle mass measurements and that of the EPA method suggests using total mass measured to determine chromium emissions for these conditions. With this approach, a Continuous Emissions Monitor (CEM) for chromium metal emissions using particle size/concentration measurements as a surrogate for chromium emission may be practical. However, it is emphasized that repeated testing at various chromium plating facilities over a broad range of documented flow conditions will be required to confirm that this approach has universal applicability.

## CONCLUSIONS

Particle size, concentration and velocity measurements have been made using a laser based optical diagnostic in the exhaust system of a commercial, hexavalent-chromium plating facility. These measurements, made both at the tank surface and at several points in the exhaust system, illustrate the reduction in particle concentration (and particle mass) that occurs with the implementation of mesh-type abatement devices. Measurements made directly above the bath are characterized by particles sizes in the range of 0.3 to 25 micrometers. However, these values represent the measurable size range of the instrumentation used in this study, and the complete particle size distribution is likely to lie outside these limits.

Particle characterizations were also made downstream of the cyclone separator and downstream of the abatement installation and induced draft fan in the exhaust stack. Downstream of the cyclone separator, the particle mass is a factor of 2,000 lower than at the bath surface. Maximum particle sizes are on the order of 5 micrometers at the same location. In-stack, maximum particle sizes are on the order of 0.7 micrometers and the particle mass at the final measurement point is a factor of 17 lower than at the cyclone exit and a factor of 34,000 lower than at the tank surface. Comparing the particle mass measurements made at the tank surface and in the stack, on a mass basis the collection efficiency of all abatement devices combined is approximately 99.997%. The collection efficiency of the mesh-pad abatement devices alone is approximately  $94\pm 2\%$ .

Based on the exhaust flow rate and average cumulative mass measurement, the total particle mass emission from the stack is approximately 560,000  $\mu\text{g/hr}$ . Assuming that the droplets in the exhaust flow consist primarily of water and chromium, correcting the total particle mass flow for the chromium content alone content gives a chromium metal emissions rate of 64,000  $\mu\text{g/hr}$ . This value compares reasonably well with a value of 77,000  $\mu\text{g/hr}$  measured in the same stack using EPA regulated method CARB 425.

Uncertainties in the emissions rate calculated from the optical measurements arise from the assumed water/chromium ratio, spatial variations in the stack flow, droplet vaporization and errors in the optical measurement itself. Nevertheless, the agreement between the chromium emission rate calculated from the optical measurements and the EPA regulated method suggests a correlation between particle mass flux in the stack and chromium metal emission. Establishing this correlation through additional comparison measurements over a broad range of test conditions raises the possibility of devising a CEM for chromium metal emissions that uses particle mass as a surrogate.

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