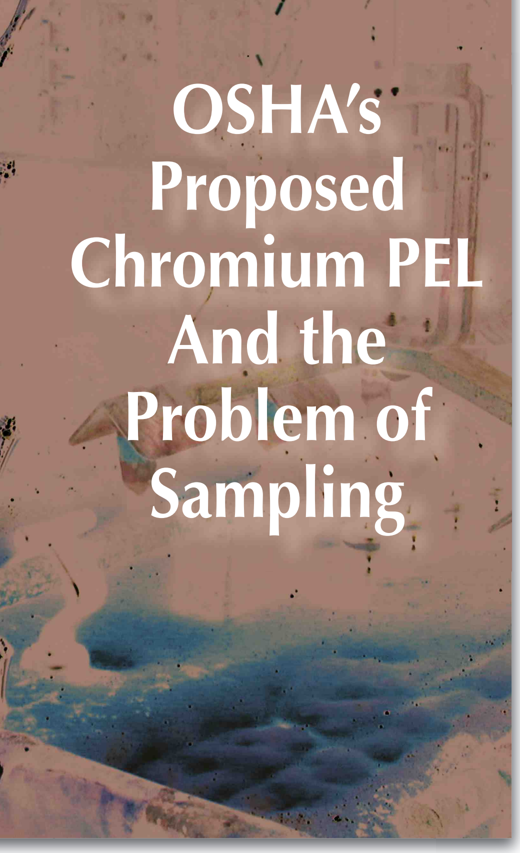


OSHA's Proposed Chromium PEL And the Problem of Sampling

By Bill Corzine

Once again, the metal finishing industry is faced with a new regulatory proposal dramatically impacting finishing operations—this time involving the permissible workplace exposures levels of hexavalent chromium. And once again, the industry is mounting a defense revolving around technical and economic flaws in OSHA's analysis for the proposed workplace exposure level of 1 $\mu g/m^3$—a 50-fold decrease from the current standard. [69 *Fed. Reg.* 59306 (October 4, 2004)]. No one argues that the installation and upgrading of the requisite control technology to approach the proposed standard creates economic hardship for the small businesses that, in large part, make up the metal finishing industry. Most importantly, are such measures needed and justified to protect the health of workers in the plating industry? We don't think so, because OSHA's proposed rule is based on some flawed technical assumptions and data.

Should the metal finishing industry simply bow its head and accept OSHA's proposed standard? If the data are examined and OSHA has sound technical and economic bases for the proposal, then the answer must be "yes." But, if flaws exist in the technical arguments presented by OSHA, the industry should, at very least, expose these flaws and force the regulators to re-examine their premises.

Flawed Methods

As one critical example, OSHA's Inorganic Method #215, *Hexavalent Chromium in Workplace Atmospheres*, (a 29-page document describing the analytical method used to monitor hexavalent chromium in the air that can be downloaded from OSHA's website) has at least one major flaw. While the test method, by itself, seems to be sound, the inherent sampling issues associated with the method are largely ignored. This paper is an attempt to examine these sampling problems with OSHA's analytical methods and relate these problems to potential variability of analytical results.

Sampling, as described in the OSHA document, is performed by filtration through a PVC filter with a specific pore size, a typical method of separating particulate matter from gaseous samples. By virtue of the fact that the chromium filtrate is in the solid and/or liquid state, while the filtered substrate is a mixture of gases (air), the filter is likely to trap the bulk of the chromium particles as they are expected to be larger than the specified pore size. Assuming that there is no reason to question the validity of the results with respect to the subject sample and that the reported statistics are repeatable, the analytical result depends only on the sample that is subjected to the analytical procedure.

Closer examination of OSHA's sampling procedure, however, exposes potential problems with the quality of samples. Inherent in the collection of samples by filtration is the problem of repeatability, which incidentally is not necessarily due to the sampling method. For example, consider the accepted method for determining total suspended solids in a wastewater sample as given in *Standard Methods 209C* (16th edition, 1985). The method is simple gravimetric analysis; *i.e.*, the difference in filter weight before and after filtration is expected to be equal to the weight of suspended solids in the sample. Repeatable results from such a method are highly dependent on how the sample is collected. In practice, the sampling is performed by simply dipping a container into the wastewater and pouring off the excess until the proper volume of sample is collected. Because the solids are suspended (not dissolved) the likelihood of their equal distribution throughout the waste stream is extremely small.

A quick look at this waste stream will verify that different concentrations of solids are visible at different places. If agitation is slowed, the solids will tend to sink (as in a pretreatment clarifier). No matter how well the stream is agitated, it is physically impossible to have equal agitation everywhere and, therefore, impossible to have equal solids distribution everywhere. Further, since the zones of distribution tend to be in constant motion, it is practically impossible to repeat the sample collection. Thus, while the analysis of the collected sample may be quite accurate *for that sample*, analysis of subsequent samples will likely yield different results.

The *Standard Methods* procedure, under the heading Precision and Accuracy, gives standard deviations and coefficients of variation for different concentrations of suspended solids. The coefficients of variance range from 0.76% for a concentration of 1707 mg/L to 33% for a concentration of 15 mg/L. Note that relative standard deviations, as reflected in variance coefficients, increase with decreasing concentration, which is the usual case. This behavior is commonly reflected in standard deviations that are given as equations, which can be solved by plugging in the analysis results. Typically, within the acceptable range of the method, as concentration increases, relative standard deviation (and, consequently variance) decreases.

The same is true with airborne particles, which is easily illustrated by the dispersion of a visible cloud of small particles. As more particles are generated, clouds form in various places. If enough particles are present, the clouds may combine to form a single cloud of particles, but the density of the cloud will vary from place to place depending on air motion, varying temperatures, the amount of particles generated from different sources, *etc*. If one were to analyze the air from different zones of the cloud, one would certainly get widely varying amounts of particles from sample to sample. These potentially wide differences in concentrations within the cloud would be evident, even if one were to take eight-hour averages (as described in OSHA's Method #215).

Unfortunately, we usually can't see chromium particles in the air. But, we can often pinpoint the sources of chromium emission and, from that information, we can estimate their relative concentrations at different places. During the plating operation, gas bubbles rise to the surface around the electrodes due to the hydrolysis of water. Molecular oxygen is formed at the anode while hydrogen forms at the cathode. As the gas bubbles reach the solution surface, they suddenly burst into the air carrying chromic acid mist with them. Thus, the major emission sources are identified with the locations of the electrodes.

Higher current densities in the plating process increase the rate of hydrolysis and, therefore, the amount of chromium emitted in a given time period. Longer plating times simply allow more chromium to be emitted into the air. Because we can, to some extent, identify the point sources of the emitted chromium, we can expect certain behaviors from the airborne particles.

The particles, as they enter the atmosphere, are obviously not going to follow a constant path. Such behavior would require all the particles to be precisely the same size, weight, and shape and, further, would require that all local conditions (*e.g.*, physical forces, air movement, temperature, etc.) remain absolutely constant, a situation that isn't likely to occur in the real world. When the bubbles burst, the particles are sent into three-dimensional space in directions perpendicular to the surface of the bubble. It is interesting to note that, if the paths remained linear, the density of particles from a single incident emission would be expected to decrease with distance as particles of different sizes change direction. The paths, however, cannot remain linear and are affected by air motion and other physical phenomena. Therefore, we can expect the density of the chromium particles to be greatest in areas generally defined by the emission sources and air movement. From this, we can say with some certainty that the amount of chromium collected in a sampling filter is completely dependent upon (1) the location of the sampler, (2) the specific environmental conditions (*e.g.*, air speed, temperature, barometric pressure, *etc*.) at the time of sampling, and (3) the process conditions (*e.g.*, current density, bath temperature, process time, *etc*.) during sampling.

The Sampling Device

OSHA's method of sampling as described in Inorganic Method #215 attempts to overcome these problems by placing the sampling device on the worker and in the worker's "breathing zone", *i.e*., near the nose and mouth area. The amount of hexavalent chromium collected in the sample will vary from employee to employee depending on where each individual's "breathing zone" actually lies. A worker's habits will certainly affect his/her exposure according to how he/she is positioned around the plating system.

Assuming the presence of a functional exhaust system around the top of the tank, a taller worker will likely be less exposed to chromium particles than one of shorter stature. The nature of the work being plated will also affect the amount of chromium emitted. Smaller parts are often plated at higher current densities, thus causing the emission of more chromium. Even barometric pressure can affect the paths by which particulate matter travels by changing the exhaust pressure differential. If outside pressure is lower, air will be exhausted more rapidly, air speed is increased, and particles are removed more quickly. High pressure has the opposite effect. Further, unless the plating shop does exactly the same work every time with exactly the same bath chemistry, there can be little indication of a worker's exposure level based on a single sample collection. Plating is a business and, like all businesses, there are busy days and slow days. All of these variables will dictate the amount of chromium collected by the sampling device, which is likely to show considerable variability from sample to sample.

Finally, the precision of the test method is normally assessed by analyzing aliquots of the same sample, while the accuracy is determined by analyses of spiked samples, where known additions of hexavalent chromium are added to the sample. Ideally, the results should be the sum of the previously determined concentration, plus the addition. While these methods have been used since the advent of analytical chemistry, we must not forget that the statistics fail to take sample variance into consideration. Usually, a sample can be collected several times from the same source. For example, ten samples taken from a plating bath at approximately the same time and analyzed using the same method should yield (within reason) the same result. If the samples are taken from a freshly made bath, where the concentration of analyte is known, then the results are expected to be very close to what is known as the true value.

Where the source is constantly changing, such as in a waste stream, composite samples are taken either by means of a sampler that collects some volume per unit time over a longer period (*e.g*., 24 hours) or by a series of timed "grab" samples that are mixed together prior to analysis. These methods are not perfect, but because the analytes are usually dissolved (and, therefore, expected to be equally distributed throughout the wastewater) results are expected to be reasonably accurate for the time the samples are taken. In theory, two or three wastewater samples drawn at the same time, even from different locations in the stream, should yield very similar results.

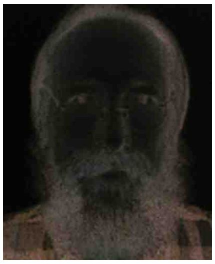
With respect to particulate matter separated by means of a filter, the distribution is suspect and, in reality, expected to be discontinuous. Hence, duplicating the sampling in a different location is likely to yield a substantially different result. Due to the unpredictable behavior of solid/liquid particles in air, it cannot be assumed that a sample is truly representative of the source.

In summary, a solution of a dissolved specie (such as hexavalent chromium) in a liquid substrate (such as water) can easily be made up in the lab and used to test the precision and accuracy of an analytical method. With such a sample, analyte distribution is not an issue, because sufficient stirring will cause the solute to be equally distributed throughout the solvent. Solids and liquids, on the other hand, are not usually soluble in or miscible with air and, therefore cannot be evenly distributed. Without the ability to produce a known standard with an evenly distributed analyte, the method cannot be properly tested nor can the effects of sampling be quantified. It follows, then, that analysis results will always be suspect and likely affected by the position of the sampling device. These sampling limitations pose some serious problems in demonstrating compliance with a workplace exposure level, particularly one as low as OSHA's proposed level of 1 μg/m^3.

With these technical limitations in mind, one cannot help but wonder how OSHA can rely on analytical results of questionable samples to enforce the proposed workplace exposure standard, especially at concentrations as low as 1 μg/m^3 where statistics of precision become even less precise. In reading Inorganic Method #215, OSHA's scientists seem to have devoted the bulk of their research to proving the method, and have missed the critical issues associated with sampling and variability. To paraphrase the Bard, *the government doth protest too much, methinks*.

In any case, if OSHA is allowed to implement the proposed standard of 1 μg/m^3, woe to employers who provide jobs to thousands of families and who make concerted efforts to protect workers' health. Void of any scientific certainty and repeatability associated with OSHA's test method, proving compliance with the proposed standard will be a "crap shoot." And, the house rarely loses.

About the Author



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