Revised Method 306-A: A Simplified Way for Finishers to Do Certification Testing

Frank R. Clay, Formerly U.S. EPA, Raleigh, NC USA

On October 17, 2000, revised versions of Method 306 and 306-A were published in the *Federal Register*. These methods are used to determine hexavalent chromium emissions from electroplating tanks. Do changes in the methods improve them, and will the changes be of benefit to the plating industry? This presentation will focus on Method 306-A, a simplified method that allows the plater to do his own certification testing.

On October 17, 2000, the <u>FEDERAL REGISTER</u> published changes to Methods 306 and 306-A. Are these changes improvements to the methods and will they be of benefit to the electroplating industry? There is not enough time in this presentation to discuss both methods so this paper will concentrate on Method 306-A.

Before answering the questions about method improvement and industry benefits, let us review briefly Method 306-A. The method was developed as an inexpensive and simple way for electroplaters to show compliance with the U.S. EPA concentration standard of milligrams per dry standard cubic meter. It could be used by the platers, control device suppliers, consultants, or anyone who was willing to assemble the sampling apparatus and collect a sample. It offered an alternative to having only one choice which was to use consultants exclusively.

Does the revised version of Method 306-A actually improve it? Are the revisions of benefit to the plating industry? The answer to both questions is "No." The method is still useable, but corrections to the calculations will have to be made to the October 17, 2000 version in the <u>FEDERAL REGISTER</u> before the method is published in the <u>Code of Federal Regulations</u> if accuracy and correctness are desired. Revising the method created areas that increase the effort required in collecting and handling a sample while adding nothing that benefits the sampling method or the electroplating industry. If the additions found in the most recent version of Method 306-A were removed, it would make no difference in the method at all, except that it would be easier to use, and would contain no superfluous material or errors.

The first clue that there might be problems with Method 306-A can be found on page 62260 of the <u>Federal</u> <u>Register</u> /Vol. 65, No.201/Tuesday, October 17, 2000/Rules and Regulations. The note at the top of the page says that in order to obtain reliable results, persons using this method should have a thorough knowledge of at least Methods 5 and 306. One of the purposes for developing Method 306-A was to eliminate the need for having a thorough knowledge of isokinetic methods (Methods 5 and 306). Although the two methods will give the same results in concentration per dry standard cubic meter, the sampling principles of Methods 5 and 306 do not apply to Method 306-A. If this were an actual requirement, the only people who could perform 306-A would be consultants who would probably opt for the more expensive and profitable Method 306.

One of the problems with the latest version of Method 306-A is the lack of experience with the method of the people who made the changes. An obvious example of this inexperience is on page 62270 which shows a drawing of the sampling train with an optional by-pass valve. Based on my own experience, never in 127 sample runs, (381 mason jars), has a train failed to pass the leak check test at full vacuum. The difference between sample vacuum and maximum vacuum is about 5", and even though the by-pass valve is optional, it would add nothing but labor and expense to the sampling train. If a train will leak check at the higher vacuum, what is the point of performing a leak check at the lower vacuum? The drawing also shows a main valve on the train for starting and stopping the sample run. This is unnecessary, and the train can be more easily started and stopped with an inexpensive power strip. The by-pass valve should not even be considered

Another example of inexperience with the method is the note found in the middle column of page 62262 that talks about high concentrations of acids and sulfur dioxide in the stack gas and the need to use 0.5N reagent to maintain the pH level above 8.5 for sodium hydroxide and 8.0 for sodium bicarbonate if the first run using 0.1 N reagent did not meet the pH requirements. This requirement was taken from the boilers and industrial furnaces standard where there would be high concentrations (10% to 12%) of carbon dioxide and high percentages of acids. Plating facilities have no combustion sources producing high concentration of carbon dioxide and acids. Experience with the method shows that 0.1 N sodium hydroxide would have a pH of 12 at the end of the test run and sodium bicarbonate would be at least 8.0. Measuring the pH level at the end off each run is unnecessary and increases the possibility of contaminating the sample, or losing it entirely.

The next item concerns paragraph 8.1.1.3.1 and 8.1.1.3.2 on page 62262, saying that to demonstrate that the flow rate is constant over several days, perform velocity traverses at the beginning and end of each day's test effort. Nobody cares what the flow rate is. The standard is a concentration standard in milligrams per dry standard cubic meter. The control equipment should be in good working order, but measuring the flow rate over several days is not the job of EPA. If the EPA had looked at its own test data, it would have realized that the flow rates of ventilation systems in the plating industry are virtually constant and these two paragraphs

probably would not have been written. An analysis of test data for 54 sampling runs for 10 plating facilities tested by the EPA was done by ratioing the average volumetric flow rate for all the sample runs at a particular site with the individual runs at that site. The values were converted into an absolute value average %, (all positive numbers). The average of these 54 runs was 1.7%. To get a higher average, the highest flow rate from a site was ratioed with the other values and the highest flow rate per cent (which would have been zero) was omitted from the average. In this worst case calculation, the average was 2.7%.

Paragraph 8.1.1.3.2 says to record only the delta p (velocity pressures) for the duct. Comparing just the velocity pressures is no way to determine flow rate. The square roots of the velocity pressures would be a less inaccurate way to do this. The last sentence says to determine an average stack velocity pressure to get a mass emission rate. This too, is in error. Velocity should be determined for each point and averaged, not from an average velocity pressure. How to determine the deviation is not specified. All of this certainly does not enhance the plater's desire to do his own testing. The best way to avoid these problems is to do all the sampling on one day.

The first column on page 62263 gives a procedure for cleaning glassware. Glassware is found in the train in the Mason jars and possibly the nozzle. Glass tubing could be used in fabrication of the impingers, but the glass tubing is easily broken and difficult to repair. The most trouble free sampling train uses glass in the Mason jars only. Paragraphs 8.1.1.8. and 8.1.1.8.1 are unnecessary. Cleaning two brand new Mason jars with nitric acid makes no sense. The effect of a 10 per cent nitric acid solution on the plastic components has not been determined, and was never done when Method 306-A was being developed. Recent analysis of the rinse solutions (tubing, nozzle, and Mason jars) has shown that the positive hexavalent chromium bias is very close to the minimum detectable limit of the analytical method. Since the Mason jars are already rinsed before collecting the sample, the plater can live with a reagent rinse of then nozzle and tubing. Even the mention of nitric acid cleaning of the train components does nothing but make the Agency look foolish.

Paragraph 8.1.1.9.2 on page 62263 says to use a small cotton ball in the outlet tube of the third impinger. In over 127 sample runs in more than five years of chromium sampling, this has not been necessary. The reason that the cotton ball is in the method is that someone called the Agency and said that the desiccant in the third impinger was going out the impinger, through the critical orifice, and damaging the pump. Since the orifice tubing is 3/32 inches in diameter, it is obvious t the desiccant size was smaller than the 6 to 16 mesh recommended in paragraph 8.1.1.9.1. The Agency should have told the source sampler to make sure his desiccant was the correct mesh size and left the cotton ball out of the method.

On page 62264, a procedure is given for sample recovery. It is incorrect. Paragraph 8.2.1.3 says to position the nozzle, probe, and connecting plastic tubing in a vertical position so that the tubing forms a "U". The nozzle, probe, and connecting tubing will be very difficult to recover unless the nozzle and tubing are removed from the sheath (usually a piece of steel conduit). The nozzle/tubing should be rinsed three times, not two as is written in the latest version of the method. Thus, there are 6 rinses for the nozzle/tubing (3 in each direction) and the same is true of the short tubing that connects the first and second impingers.

On page 62265, paragraph 8.3.2 says to refrigerate the samples at 4 degrees C or -40 degrees F (-40 is an error). Whether this is necessary or not is unknown since the EPA has no such data on chromium samples from electroplaters. When I was at the Agency, I saw either a letter or a memo that said that if samples were refrigerated prior to analysis, some of the chromium would adhere to the walls of the glass container and not be analyzed. Since we never refrigerated samples at that point in time, I paid little attention to a possible problem with refrigeration of samples. Now refrigeration is in the method in order to maintain consistency with the sample handling specifications of the boilers and industrial furnaces standard. Recent samples collected from electroplaters seem to suggest that part of the sample (if refrigerated) may be lost to the walls of the collection jar, but whether or not this is actually true is still indeterminate.

Page 6f2265, paragraph 10.1 says the pitot tube shall be calibrated. During the development of the chromium standard, no pitot tubes were calibrated and the pitot tube coefficient was assumed to be 0.84. Since this is a concentration standard, it is not necessary to calibrate the pitot tube, nor is calibration necessary for an approximate (and optional) mass emission rate. Experience shows that the stack temperature will remain

constant across the duct and before and after velocity traverses are redundant. The pitot coefficient will make no difference in calculating point sample times since the square roots of the velocity pressure readings are used for that purpose. All that is necessary is that the pitot be properly constructed.

A serious problem exists on page 62267 in calculating the chromium concentration in milligrams per dry standard cubic meter (12.5, 12.6, and 12.7). Determining this concentration is the whole point of Method 306-A. The revised method has made this determination more difficult and also is incomplete. Paragraph 12.7 goes to the trouble to tell how to convert micrograms to milligrams by dividing by 1000, but there is no conversion of cubic feet to cubic meters. Dry standard cubic feet should be divided by 35.31 to get cubic meters. Most sampling in this country is done in cubic feet, but the allowable concentration is in milligrams per dry standard cubic meter for electroplaters. Paragraph 12.7 also mentions micrograms per dry standard cubic foot. This is a mixture of English and Metric units, and this policy was dropped in 1977 by the Emission Measurement Branch. There is also a half page wasted on calculating a volumetric flow rate. The standard is a concentration standard, not a pounds per hour standard. Paragraphs 12.8 through 12.11 are non-productive and show a lot of effort put into something that is completely unnecessary.

The preceding discussion has presented some (but not All) of the problems with revised Method 306-A. It is one of the poorest documents to be written by the Emission Measurement Center of the Office of Air Quality, Planning, and Standards, in Research Triangle Park, NC. It is filled with needless material, calculation mistakes, and shows a lack of knowledge of both the method and the standard. This version of the method should be replaced with the original version until personnel who are qualified could make some additions that are improvements.

It is not difficult to criticize a piece of work that is as poorly done as the latest version of Method 306-A. Aside from correcting the multitude of flaws in the October 17, 2000 version, what improvements could be made in the method? Here are four:

First, the use of Method 306-A for systems that have dilution air should be approved. This was supposed to have been done back in 1997 but the Agency never got around to it.

Second, the method for sampling multiple ducts to a control device where some of the ducts contained dilution air was cumbersome to use and required extra long sampling times. Is there another way to sample these systems without the excessively long sample times?

Third, there are processes such as reverse etching that produce chromic acid mist and the mist is also routed into a control device that controls plating emissions. Should the reverse etching gas streams be considered process air or dilution air?

Fourth, how should a cyclic process be sampled? An example would be a process where the plating time to finish a part was less than the time required to change the finished part for another part to be plated. Is it possible to sample this type of cyclic operation without using an excessively long sampling time?

It is difficult to say how long the EPA will take to correct the current version of Method 306-A. If the need arises to perform a test using Method 306-A before the method is corrected, the following recommendations may help:

- 1. Work with state or local regulatory personnel.
- 2. Forget the by-pass valve; it is useless. Use a power strip with a rocker switch to start and stop the train.
- 3. Perform all runs in a single day.
- 4. Use laboratory grade 0.1N sodium hydroxide to rinse the nozzle, tubing and Mason jars.
- 5. Omit the cotton ball from the third impinger and fill the Mason jar about half full using 6 to 16 mesh silica gel.
- 6. When recovering the sample, rinse the tubing and nozzle 3 times in each direction. Use the same procedure on the connecting tubing from the first to the second impinger.
- 7. As soon as each sample is collected, refrigerate it until it reaches the laboratory. This may help the platers.
- 8. Construct the pitot tube properly but do not bother with calibration.

9. When doing calculations to determine the milligrams per dry standard cubic meter, be sure to divide dry standard cubic feet from the dry gas meter by 35.31 to get dry standard cubic meters if sample collection involves using a meter that records volumes in cubic feet.

CONCLUSION

Hexavalent chromium is one of the deadliest carcinogens in the environment. If the plating industry is to be regulated by U.S. EPA standards, it has the right to expect sampling methods that are fair, accurate, and have been developed by qualified personnel. This is the AESF/EPA Conference for Environmental Excellence. The current version of Method 306-A does not qualify as excellent. The general public, the platers, and the American taxpayers deserve better than the current version of Method 306-A found in the October 17, 2000 <u>FEDERAL REGISTER</u>.