

California Environmental Protection Agency



SOURCE TESTING GUIDELINE

**Guideline For Determining Chromium Emissions
From Chromium Plating and Chromic Acid Anodizing Operations**

MONITORING AND LABORATORY DIVISION
STATIONARY SOURCE TESTING BRANCH

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California Environmental Protection Agency
AIR RESOURCES BOARD
Monitoring and Laboratory Division

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I. INTRODUCTION

Air Resources Board (ARB) staff provides this guideline to assist local Districts, chrome plating facilities, and source test personnel in collecting relevant chromium emissions data to meet the requirements for the Chromium Airborne Toxic Control Measure for Chrome Plating and Chromic Acid Anodizing Facilities (title 17, California Code of Regulations, sections 93102 – 93102.16) (Chromium Plating ATCM). This guideline may not be applicable to all plating tanks.

Local District staff should be contacted and consulted for specific source testing requirements. District rules, regulations, and permit conditions take precedence over this guideline.

II. PROCESS DESCRIPTION

The three types of processes involving chromium include, decorative chromium plating, hard (or functional) chromium plating, and chromic acid anodizing. The chromium plating process is accomplished by submerging the parts to be plated (cathode) into a plating solution containing hexavalent chromium ions. When an electrical charge is applied to the tank through an anode, the chromium ions precipitate out of solution and adhere to the cathode. During this process, the electrical charge causes the water to split into its constituent components, hydrogen and oxygen. As these gases rise out of the plating solution, they effervesce at the surface of the plating solution. This creates an aerosol mist of hexavalent chromium and other plating solution constituents. These aerosol mists can be entrained in the air and exhausted to the outside.

There are a variety of existing processes currently available for controlling plating tank chromium emissions. Additional processes or control equipment may be available later. Current processes include “in-tank” chemical (fume suppressants) and mechanical (“polyballs”) controls. “Out-of-tank” controls are generally “add-on” and require a tank ventilation system to operate.

III. SAMPLING METHODS AND LOCATIONS

A. SAMPLING METHODS

In accordance with Section 93102.7 (c) of the chromium plating ATCM, any of the following approved test methods may be used to determine hexavalent and total chromium emissions.

- California Air Resources Board Test Method 425 (17 CCR 94135).
(<http://www.arb.ca.gov/testmeth/vol3/vol3.htm>)
- U.S. EPA Method 306 (40 CFR 63 Appendix A).
(<http://www.epa.gov/ttn/emc/promgate.html>)
- South Coast Air Quality Management District (SCAQMD) Method 205.1.
(<http://www.aqmd.gov/tao/methods/stm.html>)

These are isokinetic (particulate) sampling methods. They require the support of Methods 1 through 5 from the appropriate agency (ARB, U.S. EPA, or SCAQMD) for sampling locations and traverses, stack gas flow rates, stack gas density and moisture content, and isokinetic sampling determination.

A complete source test is generally 3 sample runs. A sample run is long enough to determine compliance, even if no chromium is detected. Additional sample runs or sample run times may be required by local districts to adequately monitor any process variations.

In addition to the parameters required to be monitored by the source test methods, ARB staff also recommends that the parameters in Table III-1 be monitored and recorded.

Table III-1

Additional Parameters to be Monitored for Source Testing

Parameter	Frequency
Plating Tank length, width & depth.	Before sampling.
Smoke test of temporary ventilation system.	Before sampling begins for each sample run.
Tank freeboard (solution surface to the top of tank).	Before sample run and after changes in plating bath.
Chromic Solution Surface Tension	Before each run and when chemicals are added during test.
Concentration of Chromic Acid	Once per test.
Plating Solution Temperature	During each run.
Any additions to the bath.	Any time during the source test including between sample runs.
Type of fume suppressant used.	Once per test.
Percentage of polyball coverage (Similar parameters should be recorded for similar emissions controls whose efficiency depends on coverage of the plating solution.)	During each test run and record by taking a picture during each run.
Thickness of foam blanket (Similar parameters should be recorded for similar emissions controls whose efficiency depends on the amount of applied electroplating energy.)	Record the amount of time and amp-hours to fully form the foam blanket during each run. Begin emissions sampling before current is applied to the tank.
Calibration of installed amps, volts, and amp-hour meters	Before source test.
Amps, volts, and amp-hours from installed meters	Start, end, and every ½ hour during sample run.
Description of parts plated. Surface Area of the parts plated, and calculated current density.	For each test run record the parts plated and record surface area.
Record plating schedule	For parts plated intermittently to emulate decorative plating or anodizing (example: every 5 minutes), or plated continuously for hard chromium plating.
Record frequency of disturbing the bath surface during testing	Bath surface should be disturbed intermittently to emulate decorative plating or anodizing (example: every 5 minutes).
Description of the temporary hood	A description of the temporary hood set up and a diagram and picture should also be provided.

B. SAMPLING LOCATIONS

If there is no existing plating tank ventilation system, a temporary capture hood and ventilation system will be needed. Temporary systems should be approved by local District staff prior to testing. District approval is no guarantee the temporary system will work as required during sampling. The following documents describe temporary capture systems for source testing purposes.

- U.S. EPA Method 204 (40 CFR 63 Appendix A). (<http://www.epa.gov/ttn/emc/promgate.html>)
- SCAQMD system described in the SCAQMD document “Measurement of Hexavalent Chromium Emissions from Chromium Plating and Chromic Acid Anodizing Operations for Certification of Wetting Agent Chemical Fume Suppressant Subject to SCAQMD Rule 1469,” dated August 14, 2003
- Appropriate American Conference of Government Industrial Hygienists (ACGIH) or American Society of Testing Methods (ASTM) methods subject to the approval of the local district.

In addition to these methods, Appendix A of this document contains specifics on ARB’s temporary hood design.

Both permanent and temporary plating tank ventilation systems need to be “smoke tested” to confirm complete fume capture method. Additionally, temporary capture systems should be smoke tested near the plating bath surface to demonstrate that no emissions are being “scoured” from the plating bath. For monitoring purposes, district representatives should witness these smoke tests.

C. LABORATORY ANALYSIS

The low emission limit of the new Chromium Plating ATCM may require lower laboratory limits of detection (LOD) or quantification than laboratories previously needed. ARB staff has written standard operating procedures (SOP) that may help laboratories lower their LOD for total and hexavalent chromium at <http://www.arb.ca.gov/aaqm/sop/summary/summary.htm#LSOP>. At that site go to SOP 005 for total chromium analysis by atomic absorption (AA) or, if desired and allowed, SOP 061 for total chromium by inductive coupled plasma – mass spectrometry (ICP-MS). Go to SOP 039 for hexavalent chromium analysis by ion chromatography (IC). Contacts for additional laboratory assistance are listed on the LSOP web site listed above. These SOP’s support the ARB ambient air network.

ARB staff recommends analysis for both hexavalent and total chromium. Since hexavalent chromium is relatively unstable, total chromium analysis is an important quality assurance check. Total chromium analysis is separate from analysis for hexavalent chromium.

1. Hexavalent Chromium Analysis Only

ARB staff does not recommend the hexavalent chromium analysis only approach, and suggests a total chromium only approach instead if a single analysis is desired. Hexavalent chromium is relatively unstable. Conversion from hexavalent to trivalent chromium can occur during sampling. The impinger solution of the hexavalent sampling train is designed to prevent conversion, however the sample portion collected before the impingers cannot be stabilized until after sampling when that portion is recovered with stabilizing solution.

A test observer or District inspector can determine if the stabilizing solution is working by its pH per the appropriate chromium source test method. However, either through operator error or source test manipulation, this same observer cannot determine if the nitric acid wash was completely removed from the sampling probe and nozzle. Nitric acid is an important part of the source test train cleaning procedure because it easily converts hexavalent chromium to trivalent during sampling. Based on their knowledge of the control device(s) and the ratio of hexavalent to total chromium, local district staff can usually make a determination of whether or not hexavalent chromium may have been converted during sample collection.

2. Total Chromium Analysis Only

The total chromium analysis only approach is recommended by ARB staff if a single chromium analysis is necessary. All hexavalent chromium including that converted to trivalent during sampling will be reported. Often the laboratory detection limits for total chromium are lower than the detection limits for hexavalent chromium.

Because this approach is usually associated with reducing test costs, ARB staff recommends assuming all total chrome is hexavalent. Alternatively, ARB staff can recommend analyzing the plating bath collected during sampling for hexavalent and trivalent chromium and applying the same ratio to the measured emissions.

D. QUALITY ASSURANCE

Quality assurance (QA) for supporting emissions results may be especially important where hexavalent chromium sampling is concerned. This is because of the relative instability of hexavalent chromium and its relatively high risk to public health. The recommended source test methods include specific QA measures such as monitoring the pH of hexavalent chromium stabilizing solutions before and after sample collection.

Local districts may require additional QA measures for their purposes, especially if a District inspector is not available to observe the source test. Private source testing businesses and analytical labs may include additional internal quality assurance procedures for their own purposes or to better explain source test results.

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Unless specifically stated in the test method, quality assurance measures are not designed to correct emissions results. They are available to help determine whether or not test results are acceptable; whether or not a source test should be repeated.

For example, smoke testing of the fume capture system does not affect the results of the source test method, but it does assure all emissions are directed to the sampling site. OSHA already controls indoor chromium emissions to an acceptable level, so indoor ambient samplers should not be needed to evaluate dilution air for the ventilation system.

IV. PLATING OPERATIONS DURING SAMPLING

It is best to sample during a facility's normal plating production. This is the best representation of emissions from the facility, and because source testing may not be exempt from district imposed amp-hour limits. However, sampling configurations, variation of plated parts, plating configurations, low amp-hour usage, and other factors may limit a facility's ability to use normal plating production during sampling.

"Dummy" parts may be used to extend, or in place of, normal production parts. Dummy parts should be similar to normal production parts and their configuration and surface area should be recorded before testing. Old dummy parts should not be used for emissions sampling purposes if they have metal spikes.

Plating tank operations should also be near normal, even with dummy parts. Some emissions controls may become more effective as plating current is applied to the plating tank (i.e. foam blankets). When plating current stops, some foam blankets lose their effectiveness (i.e. foam disappears). It is important to include sampling during these variations in emissions control effectiveness. Sampling should begin before the foam blanket forms to include these emissions in the source test. The local District and plating facility should agree on plating tank operation during sampling before sampling begins.

Also, to emulate decorative chromium plating and chromic acid anodizing, parts should be plated intermittently. The current should be turned on and off at specified intervals. Also, the plating bath should be disturbed intermittently to emulate parts going in and out of the tank.

V. SOURCE TESTER AND ANALYTICAL LABORATORY SELECTION

A plating facility's ability to select a source tester or analytical laboratory may be restricted by the local District's rules or regulations. The local District may have a list of District approved source testers or analytical laboratories a facility must use for emissions measurement. In the absence of those restrictions, a facility may use the source tester and analytical laboratory of their choice. Experience in chromium testing is important.

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It is usually best to select an appropriate source tester and allow them to select the analytical laboratory. However, plating facilities, because of their internal needs, may be more “comfortable” with their analytical laboratory recommending a source tester. Recommendations from other plating facilities and local plating associations are also appropriate.

For a list of ARB source tester recommendations, go to the ARB Independent Contractor (source tester) program at <http://www.arb.ca.gov/ba/icp/icp.htm>. There is no requirement to use an ARB approved source tester. And, there may not be any ARB approved source testers for ARB Method 425. ARB approves private source testers only for those methods the source testing organization can perform completely within the company, including sample analysis. Because chromium analysis may be expensive for a source testing company, analysis is usually subcontracted. In the absence of ARB Method 425 approval, the company should be approved for ARB Methods 1 through 5. Then ask the company if they can do ARB Method 425, or any of the other recommended chromium sampling methods.

VI. DETERMINING ACCEPTABLE SAMPLE SIZE

This section is for local districts and plating facilities who are evaluating a source tester’s source test protocol. Good, experienced source testers should already know how to determine an acceptable sample size.

To demonstrate compliance with the ARB hexavalent chromium ATCM, it is not necessary to collect a detectable amount of chromium. It is only necessary to show the source does not exceed the appropriate emissions limit of the ATCM by proving the level of detection is below the regulated emissions limit. A local District’s hexavalent chromium rule or regulation may be more stringent than the ARB and may require a detectable amount of chromium. This may be especially true if the District needs to determine public risk near the plating facility.

Below is one way to determine appropriate sample size to show compliance with the regulated emissions limit. Other methods also exist.

- 1) Start with the Laboratory LOD (from the laboratory contracted to do chromium analyses of the samples).
 - a) For example ARB Northern Laboratory Branch has a 1.0 nanogram/milliliter (ng/ml) LOD using a 15 ml injection sample (or $1.0 \text{ ng/ml} \times 15 \text{ ml} = 15 \text{ ng LOD/sample}$). (*This detection limit may be lower than similar detection limits at commercial analytical labs.*)
 - b) “Safety factor” of 2 to 5 would be useful to guarantee a suitable sample size.
 - c) If the LOD is “single digit” (implying +/- 50%) and the local District requires “double digit” results (implying +/- 10%) then the “safety factor” is needed and may be 10 or higher.

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- 2) For detectable amount(s) in the sample train:
 - a) Sample train Impingers 1 & 2 - 100 ml each of stabilizing solution (per the test methods).
 - b) Sample probe rinse – (assume) about 100 ml of stabilizing solution. (Actual amount will vary per source tester. Most will be less than 100 ml.)
 - c) Sample size:
 $100 \text{ ml (Imp. 1)} + 100 \text{ ml (Imp. 2)} + 100 \text{ ml (probe)} = 300 \text{ ml.}$
 - d) Detectable sample size:
 $300 \text{ ml (fm 2c)} \times 1.0 \text{ ng/ml (from 1a, b, or c above)} = 300 \text{ ng per sample train}$

- 3) Proportion of emissions collected by the sample train:
 - a) Ventilation system flow (measured by stack sampling methods 1 – 4).
Use 1,000 cfm for this example.
 - b) Sample gas collection rate measured by sampling console dry gas meter – generally averages about 0.75 to 0.5 cfm.
Use 0.75 cfm for this example.
 - c) Proportion of collected sample to vented emissions;
 $0.75 \text{ cfm (from 3b above)} / 1,000 \text{ cfm (from 3a)} = 0.00075$, or
Sample train collects 75 ng for every 100,000 ng passing the sample probe.

- 4) Amount of chrome needed to pass the sample probe to collect a detectable amount in the sample train:
 $300 \text{ ng (from 2c)} / 0.00075 \text{ (from 3c)} = 400,000 \text{ ng}$

- 5) Determine applicable hexavalent chromium emissions limit.
 - a) Per 17 CCR Table 93102.4, 0.0011 or 0.0015 milligrams/ampere-hour (mg/amp-hr) (1100 or 1500 ng/amp-hr respectively).
 - b) Local District may require a lower emissions limit for specific facilities.
 - c) Maybe use a lower emission limit to insure suitable sample detection limit (in place of the “safety factor” from 1b or 1c above).
Use 1000 ng/amp-hour for this example.

- 6) Source test sample run ampere-hour requirement:
 $400,000 \text{ ng (from 4a)} / 1000 \text{ ng/amp-hr (from 5c)} = 400 \text{ ampere-hours}$

- 7) Sample train run time is beyond the scope of this example. Sample run times are a combination of the ampere-hour requirements from 6) above and how the plating tank is operated over time to meet or exceed that ampere hour requirement during the sample run.

For example, a hard chrome plater or high output decorative plater may meet the ampere-hour requirements within an hour with their normal production plating. A low output decorative plater may not plate that many ampere-hours in a normal week of plating. This low output decorative chrome plater may have to compress several days of normal plating into a day. When approving this type of sampling protocol,

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district staffs should be careful that emissions and emissions control operations for these “compressed plating days” are consistent with normal operations.

For example, a foam blanket, a type of in-tank emissions control, may not be completely effective without a certain amount of amperes applied to the tank during plating operations. That is, if the foam blanket takes 3 minutes to fully form during “normal” plating and normal plating is less than 2 minutes, then the tank needs to be operated in this manner during each source test run.

It is permissible and may be desirable to continue running the sample train when the tank is not plating. It is generally accepted that the plating tank will not be emitting chromium while the tank is “idle.” Water may evaporate from the plating tank solution at that time, but this water vapor does not include chromium. Instead, chromium concentrates within the plating solution.

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Appendix A

ARB STAFF DESIGNED CAPTURE HOOD

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PLATING TANK SOURCE TEST CAPTURE HOOD

This appendix includes an example of a capture hood and exhaust system used by ARB staff to collect chromium emissions from electroplating tanks without tank ventilation systems. This design may not be suitable for all plating tank configurations. Also, other designs may be acceptable. Contact the local air pollution control district regarding acceptable designs. District approval is not a guarantee a design will work as required.

The ARB designed capture hood consists of a rigid frame covered with flexible sheet plastic on the sides and top (See Figure A-1.) An exhaust duct of rigid and flexible PVC tubing connected the hood to a sample collection site and variable speed, in-line fan. The variable speed, in-line fan draws dilution air into the capture hood. The dilution air carries plating tank emissions in the capture hood through the ventilation system, past the sampling site, and out of the area.

The sampling site consists of a straight section meeting the requirements of ARB Methods 1 through 5. The sampling site includes two perpendicular ports placed in a single cross sectional plane. The in-line fan is located downstream of the sampling site.

The face velocity between the tank and capture hood should be equal to or less than 50 feet/minute. Fifty feet/minute is the indoor air velocity created by an effective air conditioning system according to the American Conference of Government Industrial Hygienist. Face velocity changes can be achieved by controlling fan velocity, adjusting the height of the capture hood above the tank, and adding dilution air between the sampling site and the in-line fan.

Duct flows at the sampling location can be determined by ARB Methods 1 through 4 for ducts 12 inches or larger in diameter. (Other methods are available for ducts 4 to 12 inches in diameter.) Method 1 determines the velocity and sampling traverses. Method 2 determines stack gas velocity head with a pitot tube and is used to calculate volumetric flow. Method 3 determines dry molecular weight (the dry molecular weight of atmospheric constituents may be used for ventilation systems such as those at electroplating facilities. Method 4 is used to determine stack gas moisture content. These methods also require the measurement and recording of stack temperature, ambient temperature, and barometric pressure during sampling.

ARB Method 425 – Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources is used to determine the chromium emissions. Other methods are available. These methods collect samples isokinetically. See ARB Method 5 for more information on isokinetic sampling.

Figure A-1
Capture Hood

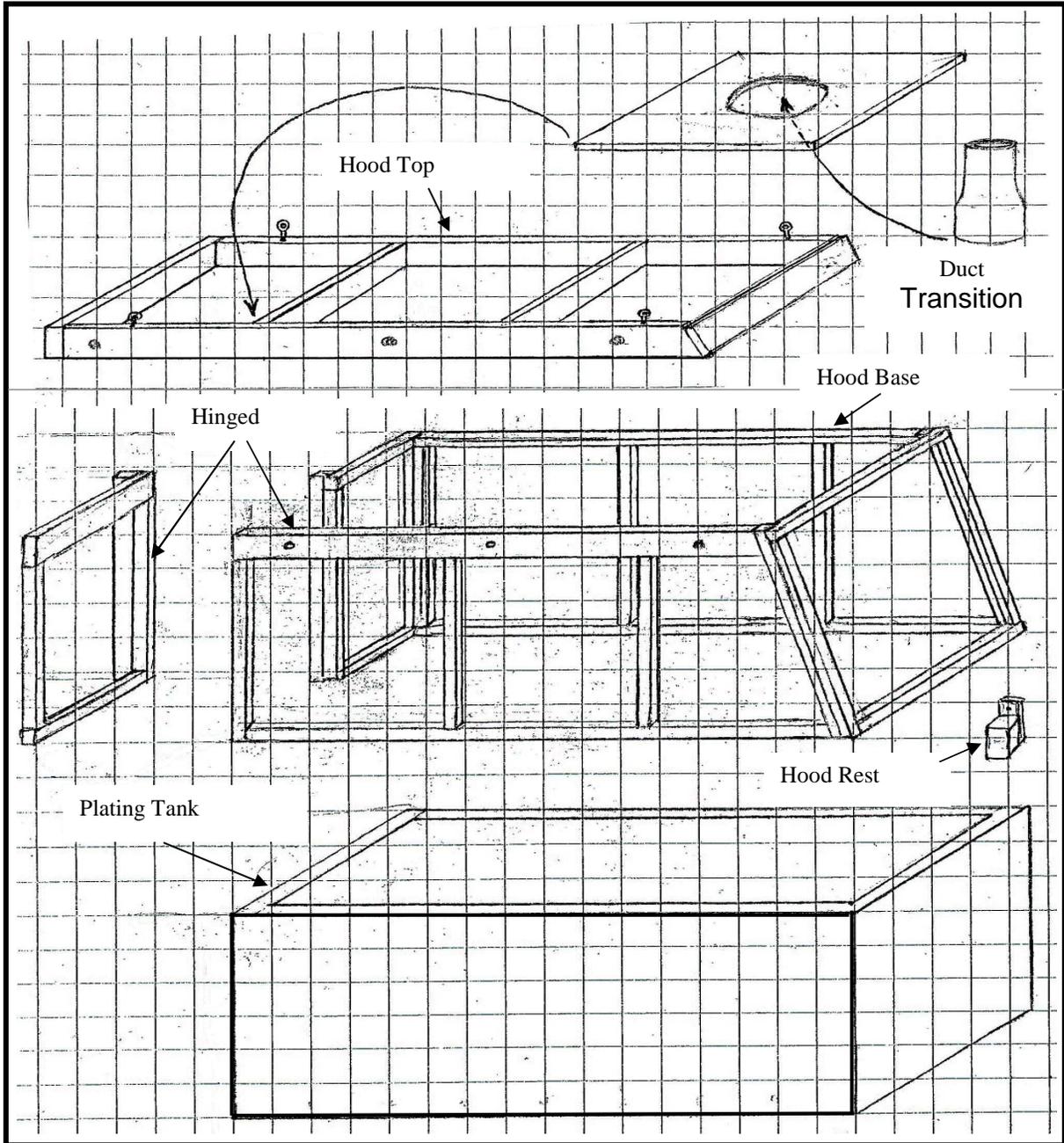




Figure A-2: Chromium plating tank and rectifier with ARB capture hood and ducting.

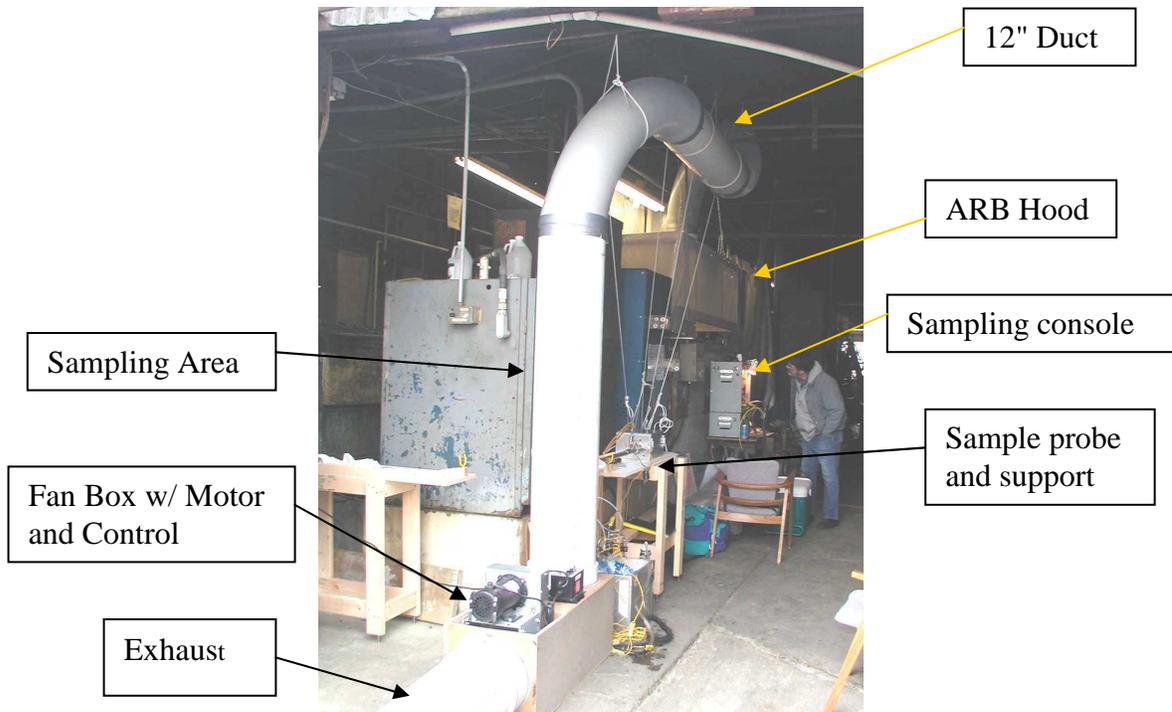


Figure A-3: ARB sampling location behind chrome plating tank, including vertical sampling pipe (12-inch diameter), fan box with controller, and exhaust ducting.

Figure A-4

**Alternate Capture Hood Design
With Connected Ventilation Duct**

