Air Emission Factors for Metals Finishing Operations

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It is widely known that limited air emission factor data related to electroplating and metals finishing operations are available. In recent years, EPA has published AP-42 emission factors related to certain electroplating operations, and other emission factors have been published by various sources. In addition, various methodologies have been presented and/or are used in practice to estimate emissions. These methodologies include the use of vapor pressures, activity coefficients and physical factors such as temperature, current density and agitation in order to estimate emissions.

This paper presents the results of a survey of metals finishing related emission factors and emissions estimation methodologies, identifies data gaps in the form of missing or poorly documented emission factors, and begins discussion on priorities for filling the data gaps.

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Introduction

This paper primarily focuses on the results of a survey of metal finishing related air emission factors and a compilation of these factors, including US EPA AP-42, results of South Coast Air Quality Management District (SCAQMD) studies, other papers presenting emission factors and a brief overview of methods used to estimate emissions other than the use of emission factors.

The use of emission factors is well documented and typically use of such factors is straight forward. The introduction of US EPA AP-42 emission factors provided a limited range of usable emission factors. Presently, US EPA AP-42 and other emission factors exist for the processes listed in Table 1 through 4. When compared with the number of processes in extensive use industry-wide, there are significant data gaps of emission factors.

In addition, there are emission studies that are conducted for specific facitities but are unpublished. These sources include emissions data as a result of state regulatory agency requests for emission verification tests.

Use of Emission Factors

The use of emission factors is the simplest method to estimate emissions from surface finishing process sources. An emission factor relates the quantity of a pollutant released to the atmosphere with a specific activity or in this case a specific process. Emission factors summarized for each process are expressed as a weight of pollutant divided by the unit weight, work, and/or duration.[1]

$$(1)\ E = EF \times A \times [1-(ER/100)]$$

where:

E = emissions,
EF = emission factor - uncontrolled,
A = activity rate, and
ER = overall emission factor reduction efficiency, %.

Emissions from Agitation Activities

Emissions to the atmosphere are result from turbulence caused by air agitation. US EPA, in AP-42, provides the following algorithm for mixing process tanks with air:

$$(2)\ E = 1.9 \times o/R_b * ((1 - 2A + 9A^2) / (1 + 3A) - (1 - 2A + 9A^2)^{0.5})^{0.5}$$

[1] US EPA, AP-42, Fifth Edition, 1996

Where

E = emission factor in grains/cu. ft. aeration air

o= surface tension of bath, in pounds force per foot

R_b= Average bubble radius, in inches

A= $0.072R_b^2/o$

As written in AP-42, emission factors are most often averages of available data that are considered of acceptable quality and are considered to be representative of long-term averages for all facilities in the source category. US EPA does comment that the data that is available is usually insufficient to indicate the influence of other process and external variables that influence emissions. US EPA does provide emission factor ratings that provide some indication of robustness or appropriateness of the emission factors. In a way, this is a quality rating of an emission factor. As an example, emission factor ratings for AP-42 electroplating emission factors range from a "B" for one emission factor, chromium to an "E" for other metal electroplating factors.

Caution must be exercised when applying any emission factor. There are variables that affect emissions that are not always considered. There are a number of factors that affect the emissions rate and total emissions of contaminants from surface finishing process tanks. These are summarized and briefly described below.

Temperature: Temperature of a process solution has the greatest effect on the emissions of acids, solvents and other process solution additives. Increasing temperature can increase emissions rate through volatilization. Surface tension tends to decrease with increasing temperature and this typically lowers emissions from misting when bubbles burst at the surface of the process tank.

Agitation: Agitation of process tanks by mechanical mixing and air agitation affect both process solution components and increasing agitation affects volatilization and potentially increases misting. Mechanical agitation typically will promote volatilization, and air agitation both increase volatilization through mild stripping and create misting.

Active Surface Area: Active surface area of parts, racks and fixtures need to be considered in developing dependable emission factors.

Concentration: Emissions are proportional to the concentration of the "pollutant" of concern in the process solution.

Current Density, efficiency: The concentration of metal emissions from process tanks is influenced by and proportional to the current density applied to the process.

Surface Area of process solution exposed: Emissions are directly proportional to the tank surface area.

Ventilation: Occupational Safety and Health Administration (OSHA) prescribes the minimum ventilation rates for various electroplating process tanks. The OSHA ventilation categories consist of a code that relates the hazard level to the chemical component based on toxicity. The numeric designation relates primarily to the temperature/volatility characteristics. OSHA specifies the minimum ventilation rate based on the minimum ventilation rate.[2] Typically higher ventilation rates across the surface of a process solution lead to higher emission rates, essentially there is a mild stripping effect.

Part Type: The shape of the parts affect emissions. Part complexity can influence current density and efficiencies that impact air emissions as described above. Part complexity also influences solution dragout that can impact air emissions.

Surface Tension: The surface tension affects emissions from an electroplating tank. As the surface tension is lowered, hydrogen bubbles generated will not have the same burst effect at the surface and misting is substantially reduced.

Survey of Available Emission Factors

1. US EPA AP-42

The US EPA AP-42 (Section 12.20) Electroplating emission factors as published by US EPA, Office of Air Quality Planning and Standards, Emission Factor and Inventory Group includes the most comprehensive set of emission factors and emission factor data that is currently available. Good data documentation exists for chromium electroplating processes, and data and emission factors are summarized for other electroplating processes. All are presented that are summarized below on Table 1. The AP-42 reports are readily available, but for convenience of the reader, the emission factors and methodologies are summarized below:

Table 1 AP-42 Emission Factor Summary [3]

PROCESS	CONTROL	POLLUTANT/EMISSION FACTOR	
		Cr	PM
Hard Chrome Electroplating	Uncontrolled	0.12 grains/A-hr	0.25 grains/A-hr
Hard Chrome Electroplating	With moisture extractor	1.4 x 10-4 grains/dscf	2.8 x 10-4 grains/dscf
Hard Chrome Electroplating	With poly propylene balls	4.2 x 10-4 grains/dscf	8.8 x 10-4 grains/dscf
Hard Chrome Electroplating	With fume suppressant	1.6 x 10-4 grains/dscf	3.4 x 10-4 grains/dscf
Hard Chrome Electroplating	With fume suppressant and polypropylene balls	3.0 x 10-5 grains/dscf	6.3 x 10-5 grains/dscf
Hard Chrome Electroplating	With packed bed scrubber	2.1 x 10-5 grains/dscf	4.4 x 10-5 grains/dscf
Hard Chrome Electroplating	With packed-bed scrubber, fume suppressant and polypropylene balls	2.6 x 10-5 grains/dscf	5.5 x 10-6 grains/dscf
Hard Chrome Electroplating	With chevron-blade mist eliminator	8.8 x 10-5 grains/dscf	1.8 x 10-4 grains dscf

[2] S. Schwartz and M. Lorber, Proc. AESF/EPA Conference for Environmental Excellence, p. 7, 1999
[3] US EPA, AP-42, Fifth Edition, Section 12.20 Electroplating, 1996

Table 1 AP-42 Emission Factor Summary continued

PROCESS	CONTROL	Cr	PM
Hard Chrome Electroplating	With mesh pad mist eliminator	1.2 x 10-5 grains/dscf	2.6 x 10-5 grains/dscf
Hard Chrome Electroplating	With packed-bed scrubber and mesh-pad eliminator	3.2 x 10-8 grains/dscf	6.7 x 10-8 grains/dscf
Hard Chrome Electroplating	With composite mesh-pad mist eliminator	3.8 x 10-6 grains/dscf	8.0 x 10-6 grains/dscf
Decorative Chrome Electroplating	Uncontrolled	0.033 grains/A-hr	0.069 grains/A-hr
Decorative Chrome Electroplating	With fume suppressant	1.2 x 10-6 grains/dscf	2.5 x 10-6 grains/dscf
Chromic Acid Anodize	Uncontrolled	2.0 grains/hr-ft^2	4.2 grains/hr-ft^2
Chromic Acid Anodize	With poly propylene balls	1.7 grains/hr-ft^2	3.6 grains/hr-ft^2
Chromic Acid Anodize	With fume suppressant	0.064 grains/hr-ft^2	0.13 grains/hr-ft^2
Chromic Acid Anodize	With fume suppressant and polypropylene balls	0.025 grains/hr-ft^2	0.053 grains/hr-ft^2
Chromic Acid Anodize	With packed bed scrubber	0.0096 grains/hr-ft^2	0.020 grains/hr-ft^2
Chromic Acid Anodize	With packed-bed scrubber and fume suppressant	7.5 x 10-4 grains/hr-ft^2	0.0016 grains/hr-ft^2
Chromic Acid Anodize	With mesh pad mist eliminator	0.0051 grains/hr-ft^2	0.011 grains/hr-ft^2
Chromic Acid Anodize	Packed bed srubber, mist eliminator	5.4 x 10-4 grains/hr-ft^2	0.0011 grains/hr-ft^2
Other Metals		**Pollutant**	**Emission Factor**
Copper Cyanide Electroplating	Mesh-pad eliminator	Cyanide	2.7 x 10-6 grains/dscf
Copper Sulfate Electroplating	With wet scrubber	Copper	8.1 x 10-5 grains/dscf
Cadmium Cyanide Electroplating	Uncontrolled	Cadmium	0.040 grains/A-hr
Cadmium Cyanide Electroplating	With mesh pad mist eliminator	Cyanide	1.0 x 10-4 grains/dscf
Cadmium Cyanide Electroplating	With mesh pad mist eliminator	Cadmium	1.4 x 10-7 grains/dscf
Cadmium Cyanide Electroplating	With packed-bed scrubber	Cyanide	5.9 x 10-5 grains/dscf
Cadmium Cyanide Electroplating	With packed-bed scrubber	Cadmium	1.7 x 10-6 grains/dscf
Cadmium Cyanide Electroplating	With packed-bed scrubber	Ammonia	4.2 x 10-5 grains/dscf
Nickel Electroplating	Uncontrolled	Nickel	0.63 grains/A-hr
Nickel Electroplating	With wet scrubber	Nickel	6.7 x 10-6 grains/dscf

In brief, US EPA's methodologies and criteria used in rating emissions data and the overall emission factors is sound. US EPA utilized a screening approach wherein;

a. emissions data must be from a primary reference
b. the referenced study should contain test results based on more than one test run
c. the report must contain sufficient data to evaluate the testing procedures and operating conditions

US EPA evaluated data and excluded certain data from consideration, including data that;

a. test series averages reported in units that cannot be converted to selected reporting units
b. test series representing incompatible test methods
c. test series of controlled emissions for which the control device is not specified
d. test series in which the source process is not clearly identified/described
e. test series in which t is not clear whether emissions were measure before or after the control device

US EPA went on to assign a quality rating to the data that was not excluded and the data is rated as follows;

A – multiple tests that were performed on the same source using sound methodology and report in enough detail for adequate validation

B- tests that were performed by a generally sound methodology but lack enough detail for adequate validation

C- tests that were performed by a generally sound methodology or that lacked a significant amount of background data

D- tests that were based on generally unacceptable method but provide an order of magnitude value for the source.

US EPA established a quality rating system for the emission factors based on an analysis of the test data. The quality ratings are as follows:

A – Excellent: Developed from A and B rated source test data from many randomly chosen facilities in the industry population. The source category is specific enough so that variability within the source category population may be minimized.

B- Above average. Developed only from A- or B- rated test data from a reasonable number of facilities. Although no specific bias is evident, it s not clear if the facilities tested represent a random sample of the industries Variability within the source category population may be minimized.

C- Average. Developed only from A, B and/or C rated test data from a reasonable number of facilities. No specific bias is present, but it is not clear if the facilities tested represent a random sample of the industry. May be evidence of variability within the source category.

D- Below Average. The emission factor was developed only from A, B and/or C rated test data from a small number of facilities, and there is reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population.

E- Poor. The emission factor was developed from C and D rated test data, and there is reason to suspect that the facilities tested do not represent a random sample of the industry.

As noted, AP-42 emission factors rate from a “B” rating to an “E” rating where chromium emission from hard chrome plating rate with no emission control a high of B. There are sixteen different studies that are evaluated and included with this uncontrolled chromium emission factor. Emission factors for other processes only rate with D and E emission factor qualities.

2. MFASC and SCAQMD Emission Factors for Toxic Air Contaminants of Concern to the Metal Finishing Industry

The Metal Finishing Association of Southern California (MFASC), with the South Coast Air Quality Management District (SCAQMD) and collaboration by the California Air Resources Board published **Emission Factors for Toxic Air Contaminants of Concern to the Metal Finishing Industry**. This is a report of source tests and development of emission factors for tin, zinc, nickel, electroless nickel plating, hydrochloric acid associated with etching, sodium hydroxide from spray, electroclean, etch and soak. Data and results of these tests as related to Nickel and Electroless Nickel plating have been presented at this conference in recent years.

The following tables are the resulting emission factors from the source test work and are in use by the SCAQMD.

Table 2 SCAQMD Emission Factor Summary from Emissions Test Reports[4]

Process	Pollutant	Emission Factor
Electroless Nickel	Ni	7.5 x 10 -7 lb./hr-ft2 tank
Nickel Plating w/o air agitation	Ni	0.057 mg/A-Hr
Nickel Plating w/ air agitation	Ni	6.5 x 10-6 lb/hr-ft2 tank
Hydrochloric Acid Etching	HCl	3.0 x 10-5 lb/hr-ft2 tank
Sodium Hydroxide Electroclean	NaOH	5.4 x 10-7 lb/hr-ft2 tank

Other emission factors where no study data exists, but are reported in the **Emission Factors for Toxic Air Contaminants of Concern to the Metal Finishing Industry** include:

Table 3 SCAQMD Emission Factor Summary from Other Sources

Process	Pollutant	Emission Factor
Tin Plating	Sn	3.86 mg/A-hr
Zinc Plating	Zn	6.40 mg/A-hr

The limitation with the emission factors developed by this study is that the each emission factor is based on the testing at one facility only. The methods, data, and approach to developing emission factors are sound. However, each emission factor was developed from a series of three tests at one facility.

3. US EPA Factor Information Retrieval (FIRE) Data System

US EPA maintains the Factor Information Retrieval (FIRE) Data System. Perceptions are that this source is not in widespread use for the metal and surface finishing industry. The author’s first experience with

[4] Metal Finishing Association of Southern California, Emission Factors for Toxic Air Contaminants of Concern to the Metal Finishing Industry, Sherman Oaks, CA, p. 10

this reference came from the Michigan DEQ Environmental Assistance website – the Emission Calculation Fact Sheet - Electroplating Operations. The following emission factors are summarized

Table 4 Emission Factor Summary from US EPA FIRE Data System[5]

Process	Pollutant	Emission Factor
Electroplating – Entire Process General	NOX	9.0 x 10-3 lb/ft2 plated item
Electroplating – Entire Process General	VOC	2.6 x 10 -2 lb/ft2 plated item

Note that much of the supporting data is unavailable at the time of this writing. In general, it is difficult to apply a single emission factor for a single pollutant to a general process such as "electroplating." Therefore, use of these factors should be approached with extreme caution. Although this fills a void with published emission factors for NOX and VOCs, these are best approached using calculational methods such as mass balance or by the use of vapor pressures. In addition, these factors, particularly VOC may be out of date as cleaning and degreasing methods have changed and the VOC emissions have been reduced. Other sources of VOC factors are available in the literature including US EPA AP-42 Chapter 4, Emission Factors for Evaporation Loss Sources.

In addition, when VOCs are used, equipment and Best Management Practices (BMPs) have improved since the time of the VOC emission studies used in development of emission factors. Briefly, these include withdrawal speed of the parts, mechanical transports, and equipment design such as increase freeboard in a degreaser, and lower condenser temperatures.

Other Emission Estimation Techniques

Other emission estimation techniques exist and are in frequent use. However, discussion and analysis of these techniques go beyond the scope of this paper and the focus on available emission factors. Other references cover these techniques. In summary, these techniques include the use of vapor pressures to estimate emissions including, mass balance approaches to emissions estimation and modeling to estimate emissions. [6]

Data Gaps and Priority Recommendations

Even with the availability of US EPA AP-42 emission factors and more recent work performed by the SCAQMD and others, emission factors for many metal finishing related processes are not available and published. The priority processes according to overall hazard, potential to emit, and widespread use in many facilities are included in AP-42 and the SCAQMD work There is, however, a need to expand the available emission factors. An initial list of priorities and recommendations include:

1. Further breakdown of emission factors with consideration and accounting for important variables as defined earlier in this paper. These variables include temperature, agitation, concentration, current density, surface tension and viscosity, etc. The work presented in previous AESF Week

[5] US EPA Chief Website

[6] JR Lord and P Gallerani, Proc. AESF/EPA Conference for Environmental Excellence., p. 243, 1996

conferences[7], with the work described under reference number 4 are well documented and accounted for agitation as a variable. More of these studies need to be undertaken.

2. Stripping Processes – Actual emission factors are lacking for most stripping processes. Although emissions are primarily estimated through the use of vapor pressures, side reactions occur.[8] For example, strong solutions of nitric acid react with nickel and some other metals to release N_2O_4, which is a hazardous gas. According to Durney in the Electroplating Engineering Handbook, stripping of nickel results in a medium-high gassing rate. [9]

3. More robust emission factors as started by SCAQMD. The documentation and approach taken are sound, but more data at more facilities is necessary to develop emission factors to be used industry-wide.

4. Pickling and chemical milling – Emission estimates are primarily achieved through acid vapor pressure. However, these are relatively high gassing processes coupled with high acid concentrations, and the presence of such mixtures as nitric acid, sulfuric acid and hydrofluoric acid lead us to recommend the development of emission factors/emission estimating tools for these processes.

We recommend gathering available emission test reports from state regulatory agencies, and wiling facilities, perhaps coupled with NMFRC or a like entity to conduct a survey and/or organize a data gathering effort. From these efforts, further data gap analysis can be conducted and efforts to further develop usable and robust emission factors that can benefit the industry can be undertaken.

[7] Dean High, Proc. AESF/EPA Conference for Environmental Excellence, 2000 and 2001
[8] J. Lord, personal communication.
[9] Lawrence J. Durney, Electroplating Engineering Handbook, Van Nostrand Reinhold, New York, pp. 646-650.

