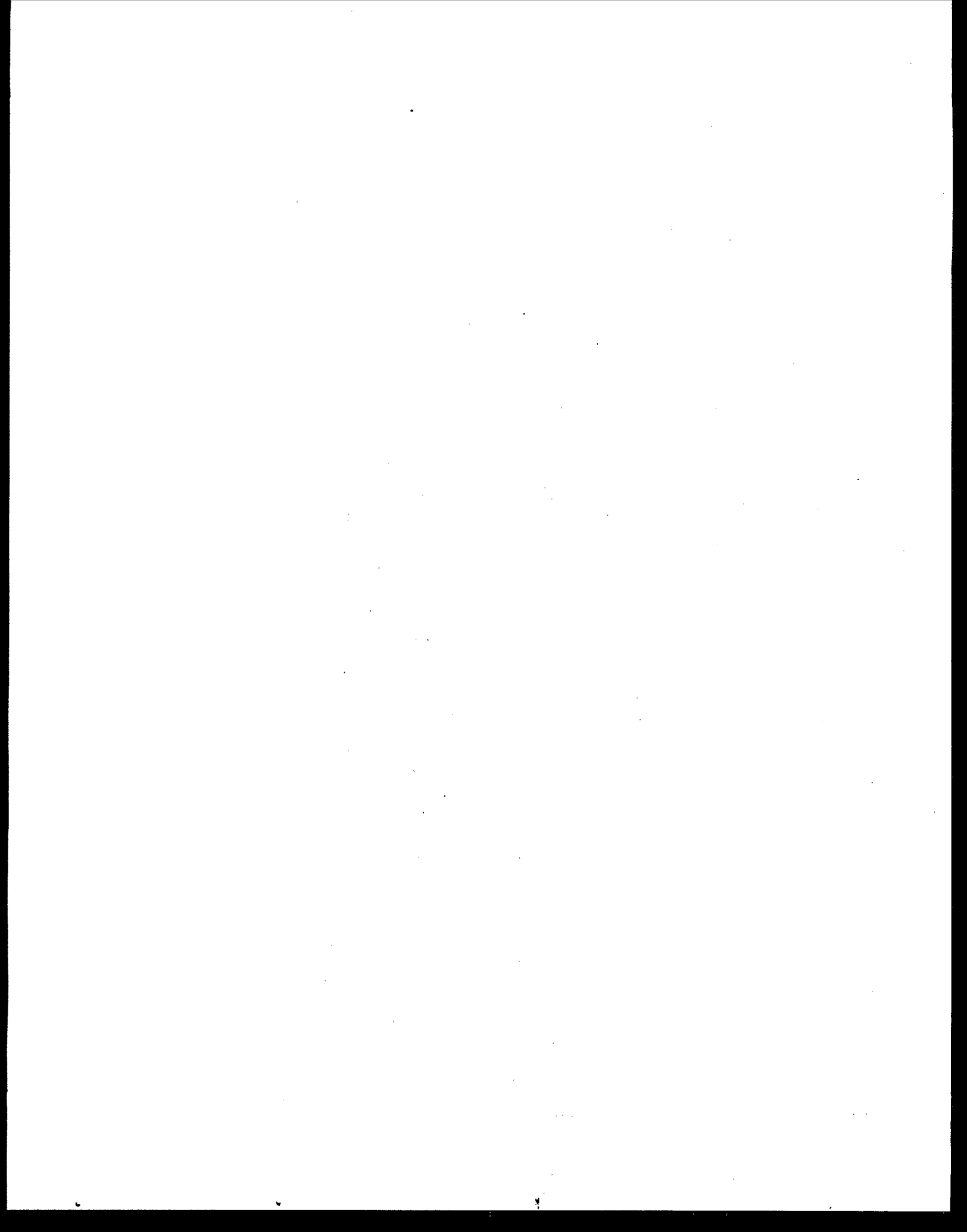




Title III Section 313 Release Reporting Guidance

*Estimating Chemical Releases From
Electroplating Operations*



Estimating Chemical Releases From Electroplating Operations

Facilities engaged in electroplating operations may be required to report annually any releases to the environment of certain chemicals regulated under Section 313, Title III, of the Superfund Amendments and Reauthorization Act (SARA) of 1986. If your facility is classified under SIC codes 20 through 39 (electroplating facilities generally fall under SIC code 3471) and has 10 or more full-time employees, for calendar year 1987 you must report all environmental releases of any Section 313-listed chemical or chemical category manufactured or processed by your facility in an amount exceeding 75,000 pounds per year or otherwise used in an amount exceeding 10,000 pounds per year. For calendar years 1988 and 1989 (and beyond), the threshold reporting quantity for manufactured or processed chemicals drops to 50,000 and 25,000 pounds per year, respectively.

This document has been developed to assist those who perform electroplating operations in the completion of Part III (Chemical Specific Information) of the Toxic Chemical Release Inventory Reporting Form. Included herein is general information on toxic chemicals used and process wastes generated, along with several examples to demonstrate the types of data needed and various methodologies available for estimating releases. If your facility performs other operations in addition to electroplating, you must also include any releases of toxic chemicals from these operations.

Step One

Determine if your facility processes or uses any of the chemicals subject to reporting under Section 313.

A suggested approach for determination of the chemicals your facility uses that could be subject to reporting requirements is to make a detailed review of the chemicals and materials you have purchased. If you do not know the specific ingredients of a chemical formulation, consult your suppliers for this information. If they will not provide this information, you must follow the steps outlined to handle this eventuality in the instructions provided with the Toxic Chemical Release Inventory Reporting Form.

The list presented here includes chemicals typically used in electroplating operations that are subject to reporting under Section 313. This list does not necessarily include all of the chemicals your facility uses that are subject to reporting, and it may include many chemicals that you do not use. You should also determine whether any of the listed chemicals are created during processing at your facility.

Degreasing solvents: Perchloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, and others

Alkaline cleaning agents: Sodium hydroxide

Acid cleaning and pickling agents: Sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, chromic acid

Chelating agents: Thiourea, nitrilotriacetic acid (NTA), ethyleneimine (aziridine)

Components of plating and other process baths: Cadmium compounds, chromium compounds, sodium hydroxide, cobalt compounds, copper compounds, lead compounds, nickel compounds, silver compounds, zinc compounds, cyanide compounds, sulfuric acid, sodium sulfate, phosphoric acid, ammonia, arsenic compounds, selenium compounds, various aldehydes

Step Two

Determine if your facility surpassed the threshold quantities established for reporting of listed chemicals last year.

You must submit a separate Toxic Chemical Release Inventory Reporting Form for each listed chemical that is "manufactured," "processed," or "otherwise used" at your facility in excess of the threshold quantities presented earlier. Manufacture includes materials produced as byproducts or impurities. Toxic compounds that are incorporated into your products (for example, metals that are plated onto metal articles) would be considered "processed" because they become part of the marketed finished product. Degreasing solvents, cleaning agents, and other chemicals that do not become part of the finished product would be considered "otherwise used."

The amount of a chemical processed or otherwise used at your facility represents the amount purchased during the year, adjusted for beginning and ending inventories. To ascertain the amount of chemical in a mixed formulation, multiply the amount of the

mixture (in pounds) by the concentration of the chemical (weight percent) to obtain the amount of chemical processed.

Example: Determining whether 1,1,1-trichloroethane was used in sufficient quantity to require reporting under Section 313.

An electroplater purchased 95 percent 1,1,1-trichloroethane for use in a vapor degreaser. In 1987, 3,000 pounds of this material was in storage at the beginning of the year, 18,000 pounds was purchased, and 6,000 pounds was in storage at the end of the year. The quantity of 1,1,1-trichloroethane used by the facility equals:

$$\begin{aligned} &(3,000 \text{ lb} \times 0.95) \text{ (beginning inventory)} + \\ &(18,000 \text{ lb} \times 0.95) \text{ (purchased)} - \\ &(6,000 \text{ lb} \times 0.95) \text{ (ending inventory)} \\ &= 14,250 \text{ lb} \end{aligned}$$

A listed chemical may be a component of several formulations you purchase, so you may need to ask your supplier for information on the concentration (percentage) of the chemical in each. For chemical categories, your reporting obligations are determined by the total amounts of all chemicals in the category. For example, in a copper plating bath, three cyanide-containing compounds are used: CuCN, NaCN, and KCN. The quantity of cyanide compounds used equals the sum of the quantities of CuCN, NaCN, and KCN used. For a substance such as CuCN, the amount used must be considered in determining whether the threshold is met for both copper- and cyanide-containing compounds.

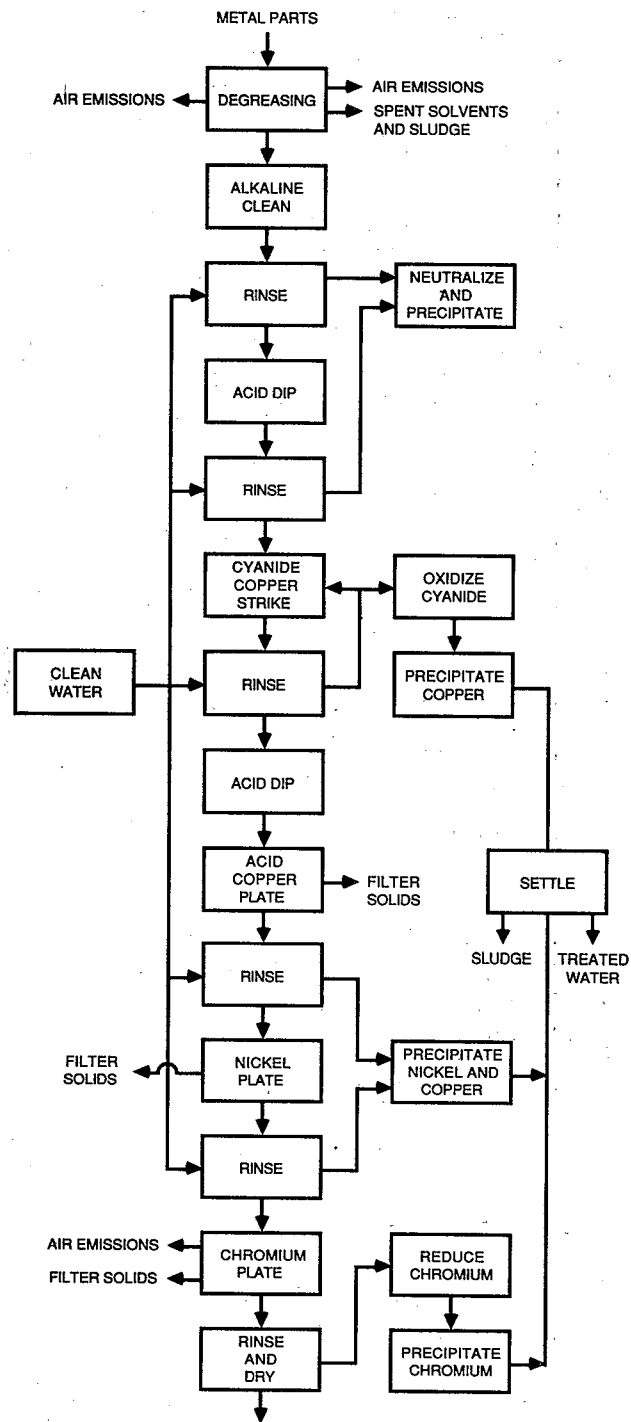
You must complete a report for each chemical for which a threshold is exceeded. The thresholds apply separately; therefore, if you both process and use a chemical and either threshold is exceeded, you must report for both activities. If neither threshold is exceeded, no report is needed.

Step Three

Identify points of release for the chemical(s) subject to reporting.

An effective means of evaluating points of release for listed toxic chemicals is to draw a process flow diagram identifying the operations performed at your facility. The figure on the right is an example flow diagram for electroplating (chromium plating of zinc die castings). Because each facility is unique, you are strongly urged to develop a flow diagram for your particular operations that details the input of materials and chemicals and the waste sources resulting from the operation of each unit.

The largest source of toxic releases at electroplating facilities will occur in the wastewater. Wastewater is generated from a variety of sources, including the rinsing of parts between process baths during metal cleaning, plating, and post-plating operations; the dumping of exhausted or spent process baths; and the rinsing required during auxiliary operations such as rack stripping. Wastewater usually is centrally collected and treated before discharge; thus, all of these sources are aggregated into one release point. Solid waste is generated primarily from the treatment of wastewater. Other sources include filter solids from plating baths, anode wastes, spent degreaser solvent and sludge, and precipitates from electroless nickel bath regeneration. Two notable air releases are solvents from metal-degreasing operations and mists evolved from electrolytic cleaning solutions and cyanide and chromium plating solutions.



Example Flow Diagram of Chromium Plating of Decorative Zinc Die Castings

Step Four

Estimate releases of toxic chemicals.

After all of the toxic chemicals and waste sources have been identified, you can estimate the releases of the individual chemicals. Section 313 requires that releases to air, water, and land and transfers to offsite facilities be reported for each toxic chemical meeting the threshold reporting values. The usual approach entails first estimating releases from waste sources at your facility (that is, wastewater, air release points, and solid waste) and then, based on the disposal method used, determining whether releases from a particular waste source are to air, water, land, or an offsite disposal facility.

In general, there are four types of release estimation techniques:

- **Direct measurement**
- **Mass balance**
- **Engineering calculations**
- **Emission factors**

Descriptions of these techniques are provided in the EPA general Section 313 guidance document, *Estimating Releases and Waste-Treatment Efficiencies for the Toxic Chemical Release Inventory Form*.

Provisions of the Clean Air Act, Clean Water Act, Resource Conservation and Recovery Act, and other regulations require monitoring of certain waste streams. If available, data gathered for these purposes can be used to estimate releases. When only a small amount of direct measurement data is available, you must decide if another estimation technique would give a more accurate estimate. Mass balance techniques and engineering assumptions and calculations can be used in a variety of situations to estimate toxic releases. These methods of estimation rely heavily on process operating

parameters; thus, the techniques developed are very site-specific. Emission factors are available for some industries in publications referenced in the general Section 313 guidance document. Also, emission factors for your particular facility can be developed in-house by performing detailed measurements of wastes at different production levels.

Toxic Releases Via Wastewater

The U.S. Environmental Protection Agency has set effluent limitations on electroplating wastewater discharges to publicly owned treatment works (POTWs) and into navigable waters. Your facility is therefore probably required by a local pretreatment permit or an NPDES permit to monitor discharge wastewater for toxic metals, cyanide, and various toxic organic compounds. The data generated from this monitoring can be used to estimate releases of these compounds. The following example demonstrates a wastewater release estimation based on direct measurement.

Example: Using direct measurement to estimate releases of cyanide via wastewater.

An electroplating facility discharges its pretreated wastewater to a POTW. The municipality operating the POTW requires the electroplater to monitor this discharge once per month for various parameters, including total cyanide. The mass loading (pounds per day) of cyanide in the discharge is calculated for each sampling day by multiplying the daily flow by the measured cyanide concentration and unit conversion factors:

Amount of cyanide released to wastewater =

$$\begin{aligned} & \text{cyanide concentration (mg/liter)} \times \\ & \text{wastewater flow (gal/day)} \times \\ & 3.78 \text{ liters/1 gal} \times \\ & 1 \text{ lb/453,000 mg} \end{aligned}$$

Cyanide and flow data from the days when cyanide was monitored during 1987 and the calculated mass loadings of cyanide are presented below:

Day	Wastewater flow, gal/day	CN conc., mg/liter	CN mass loading, lb/day
Jan. 8	21,500	1.5	0.27
Feb. 12	20,500	0.8	0.14
Mar. 10	20,800	0.6	0.10
Apr. 15	22,000	0.5	0.09
May 9	23,500	0.7	0.14
June 13	21,300	1.9	0.34
July 11	25,900	2.1	0.44
Aug. 10	21,500	1.0	0.18
Sep. 8	24,600	0.9	0.18
Oct. 12	25,000	0.8	0.17
Nov. 10	20,100	0.6	0.10
Dec. 8	20,700	0.2	0.03

The average daily cyanide discharge based on these monitoring data is 0.18 pound per day. Assuming the plant operates 250 days per year, the total quantity of cyanide released via wastewater to the POTW equals:

$$0.18 \text{ lb/day} \times 250 \text{ days/year} \\ = 45 \text{ lb}$$

Monitoring data may not be available for some of the toxic chemicals present in your wastewater. In this case, you must use another estimation method. The following example demonstrates the use of a mass balance combined with an engineering calculation.

Example: Using a mass balance combined with an engineering calculation to estimate releases of nitrilotriacetic acid (NTA) via wastewater.

A facility used 12,970 pounds of NTA in its electroless plating operation during

1987. Because it does not become part of the product, all of the NTA used becomes part of the facility's waste and is either destroyed during waste treatment or released from the facility. To estimate releases of NTA, one needs the answers to two questions:

- How much NTA is destroyed during treatment?
- In what form(s) is NTA released from the facility (wastewater, solid waste, air emissions)?

At this facility, NTA enters the wastewater stream as a chelate-metal complex during the rinsing of metal parts from the plating bath. This wastewater stream goes through a pH adjustment/clarification system where lime is added to precipitate metals. Typically, chelating agents will not be destroyed in this process, nor will they precipitate along with the metals. On the contrary, the purpose of chelating agents is to keep the metal ions in solution in the plating bath. An engineering assumption can therefore be made that all of the NTA entering waste treatment leaves in the wastewater discharge. Given that the wastewater is discharged to a POTW, the plant in this example could report wastewater releases of 13,000 pounds of NTA.

If your facility uses a listed mineral acid or base, but this acid or base is effectively neutralized in use or during wastewater treatment (to pH 6 to 9, as required by most effluent standards), no release quantities should be reported. If the acid or base is transformed into a reportable substance, however, you must estimate the quantity of this substance manufactured to determine if the "manufactured" threshold value has been reached. For example, sulfuric acid neutralized by sodium hydroxide yields sodium sulfate, which is a listed chemical.

Toxic Releases Via Solid Waste

Some solid wastes at electroplating facilities are listed as hazardous under RCRA regulations. Others may be deemed hazardous based on the extraction procedure toxicity characteristic (EP toxicity). Generation, transportation, and disposal of certain solid wastes from electroplating may therefore be regulated under RCRA. The RCRA manifesting procedure for hazardous waste shipped offsite requires documentation of quantities shipped. Detailed chemical and physical analyses may be performed on the wastes by treatment, storage, and disposal facilities. The electroplater also may perform analyses on the waste. Release estimates for some compounds can therefore be made by direct measurement.

Example: Using direct measurement to estimate releases of toxic metals via solid waste.

Wastewater treatment sludge from an electroplating operation is shipped to an offsite secure chemical landfill for disposal. Shipping manifests for the past year contain detailed information on the quantity of sludge sent to the landfill. Shipments of sludge were made on a monthly basis. The landfill performed detailed chemical analysis for nickel on representative portions of each shipment before final disposal. As shown in the following table, the information from the manifests and landfill can be combined to estimate releases of toxic metals and cyanide in the wastewater treatment sludge.

Month	Sludge shipped, lb	Nickel conc., ppm	Nickel in sludge, lb
Jan.	6,000	50,600	304
Feb.	5,400	51,900	280
Mar.	4,700	48,500	228
Apr.	5,500	37,000	204
May	6,100	30,000	183
June	6,800	75,000	510
July	7,200	84,000	605
Aug.	6,400	55,500	355
Sep.	5,900	50,000	295
Oct.	4,500	105,500	475
Nov.	5,200	69,000	359
Dec.	5,300	20,000	106

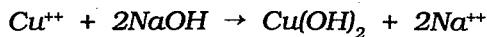
It should be noted that this example only addresses nickel releases in wastewater sludge. Nickel may also be present in other wastes in the facility. Also, the landfill probably would have analytical data for other metals in this sludge that could be used to calculate releases of those compounds.

When direct measurement data are not available, another method of estimating releases is needed. The following example demonstrates the use of an engineering calculation to estimate toxic metal releases via solid waste.

Example: Using an engineering calculation to estimate toxic releases of copper in wastewater treatment sludge.

In an electroplating facility, rinse water from a copper-plating unit is treated separately from other process wastewater. The rinse water is first treated with chlorine to oxidize cyanide. Sodium hydroxide is then added to react with the Cu in the wastewater. The precipitate formed from this reaction is removed as sludge from the facility's central clarification unit.

The reaction of NaOH and Cu⁺⁺ in the rinse water proceeds as follows:



For each mole of Cu present in the rinse water, two moles of NaOH must be added to precipitate the Cu. Purchasing and inventory records indicate that 1,984 pounds of NaOH was used for precipitating Cu last year. The quantity of Cu precipitated (and thus the quantity of Cu released from this source of solid waste) can be estimated by performing the following calculations:

$$\begin{aligned} \text{Molecular weight of Cu} &= 63.5 \text{ lb/lb-mole} \\ \text{Molecular weight of NaOH} &= 40 \text{ lb/lb-mole} \\ \text{Amount of Cu released in sludge} &= \\ &1,984 \text{ lb NaOH} \times \\ &1 \text{ lb-mole NaOH}/40 \text{ lb NaOH} \times \\ &1 \text{ lb-mole Cu}/2 \text{ lb-mole NaOH} \times \\ &63.5 \text{ lb Cu}/1 \text{ lb-mole Cu} \\ &= 1,575 \text{ lb} \end{aligned}$$

The plant in this example could therefore report the release of 1,600 pounds of Cu in the wastewater treatment sludge.

It should be noted that the NaOH in this example only reacted with the Cu present in the wastewater. If other metal ions are present, they may also react with the NaOH, which would make this estimation method ineffective. In some instances, however, this approach can result in a rough approximation of the quantity of releases.

Toxic Releases to Air

Typical emissions to air from electroplating facilities are fugitive in nature and are not monitored. Alternative techniques must therefore be used to estimate air releases. Releases of toxic compounds contained in mists evolved from plating and cleaning baths can be estimated by mass balance (provided

sufficient information is available on the quantity of chemical entering and leaving the process) or engineering calculations. Solvents emitted to air during metal cleaning operations can usually be estimated by mass balance or emission factors as shown in the following example.

Example: Using a mass balance to estimate air emissions of 1,1,1-trichloroethane from a degreasing operation.

In the example presented earlier in this pamphlet, an electroplating facility operating a vapor degreaser used 14,250 pounds of 1,1,1-trichloroethane during the past year. The vapor degreaser contains a built-in local exhaust ventilation system to reduce worker exposure to the solvent. This system collects spray solvent fumes and exhausts them to the atmosphere through the roof of the facility. Spent solvent and sludge that accumulate on the bottom of the degreaser are collected in 55-gallon drums for shipment to an offsite solvent reclaimer. Last year, 13 drums of spent solvent were sent to the reclaimer. Because 1,1,1-trichloroethane is only "used" in the process (i.e., it does not become part of the product) and it is not destroyed during the process or treatment, the entire 14,250 pounds of the solvent is released from the facility either as an air emission or as solid waste. Thus, if the quantity of spent solvent shipped to the reclaimer is known, the quantity emitted to air can be calculated by mass balance, as shown in the following equations:

$$\begin{aligned} \text{Volume of 1,1,1-TCE to reclaimer} &= \\ &13 \text{ drums} \times 55 \text{ gal/drum} \\ &= 715 \text{ gal} \\ \text{Mass of 1,1,1-TCE to reclaimer} &= \\ &715 \text{ gal} \times 11.05 \text{ lb/gal} \\ &= 7,900 \text{ lb} \end{aligned}$$

Amount of 1,1,1-TCE released to air =
14,250 lb (purchased) -
7,900 lb (to reclaimer)
= 6,350 lb

The plant in this example could therefore report the release of 6,400 pounds of 1,1,1-TCE to air and 7,900 pounds shipped offsite as solid waste.

Emission factors for estimating releases of solvents from different types of degreasing units are presented in the EPA publication, *Compilation of Air Pollutant Emission Factors (AP-42)*. To apply these factors properly, you should carefully read the text that accompanies them.

Other Toxic Releases

Electroplating operations produce other wastes from which toxic chemicals may be released. These include:

- **Residues from pollution control devices**
- **Wash water from equipment cleaning**
- **Product rejects**
- **Used equipment**
- **Empty chemical containers**

Releases from these sources may already have been accounted for, depending on the release estimation methods used. These items (and any other of a similar nature) should be included in your development of a process flow diagram.

The contribution of sources of wastes such as cleaning out vessels or discarding containers should be small compared with

process losses. If you do not have data on such sources (or any monitoring data on overall water releases), assume up to 1 percent of vessel content may be lost during each cleaning occurrence. For example, if you discard (to landfill) "empty" drums that have not been cleaned, calculate the release as 1 percent of normal drum content. If the drums are washed before disposal, this may contribute 1 percent of the content to your wastewater loading.

Step Five

Complete the Toxic Chemical Release Inventory Reporting Form.

After estimating the quantity of each chemical released via wastewater, solid waste, and air emissions, you must determine the amount of each chemical released to water, land, or air or transferred to an offsite disposal facility. This determination will be based on the disposal method you use for each of your waste streams. Enter the release estimates for each chemical or chemical category in Part III of the Toxic Chemical Release Inventory Reporting Form. Also enter the code for each treatment method used, the weight percent by which the treatment reduces the chemical in the treated waste stream, and the concentration of the chemical in the influent to treatment (see instructions). Report treatment methods that do not affect the chemical by entering "0" for removal efficiency.

For More Information

**Emergency Planning
and Community
Right-to-Know
Hotline** (800) 535-0202
or
(202) 479-2449
(in Washington, D.C.
and Alaska)

**Small Business
Ombudsman
Hotline** (800) 368-5888
or
(703) 557-1938
(in Washington, D.C.
and Virginia)

The EPA brochure, Title III Section 313 Release Reporting Requirements (EPA 560/4-87-001) presents an overview of the new law. It identifies the types of facilities that come under the provisions of Section 313, the threshold chemical volumes that trigger reporting requirements, and what must be reported. It also contains a complete listing of the chemicals and chemical categories subject to Section 313 reporting. The EPA publication, Estimating Releases and Waste-Treatment Efficiencies for the Toxic Chemical Release Inventory Form (EPA 560/4-88-002), presents more detailed information on general release estimation techniques than is included in this document.

Additional Sources of Information on Releases From Electroplating Operations

U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors, Fourth Edition. AP-42. Research Triangle Park, North Carolina. September 1985.

U.S. Environmental Protection Agency. Development Document for Existing Source Pretreatment Standards for the Electroplating Point Source Category. EPA 440/1-79/003. NTIS PB80-196488. Washington, D. C. August 1979.

U.S. Environmental Protection Agency. Assessment of Industrial Hazardous Waste Practices - Electroplating and Metal Finishing Industries - Job Shops. NTIS PB-264349. Washington, D. C. September 1976.



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