

AIR



LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF CHROMIUM (SUPPLEMENT)



**Locating And Estimating
Air Emissions
From Sources of
Chromium
(Supplement)**

Note: The material herein on electroplating, chromic acid anodizing, and cooling towers supersedes the material in the document EPA-450/4-84-007g

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1.0 PURPOSE OF DOCUMENT

The U. S. Environmental Protection Agency (EPA), States, and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, very little information is available on the ambient air concentrations of these substances or on the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents that compile available information on the sources and emissions of these substances. This document was prepared as a supplement to a previous EPA document that addressed chromium emissions, "Locating and Estimating Air Emissions From Sources of Chromium," EPA-450/4-84-007g. The supplement updates technical information and presents new emission data upon which emission factors are based for chromium emissions from cooling towers and chromium electroplating operations. The reader should use both the original document and this supplement to obtain the most complete assessment of emissions from these two sources of chromium emissions. The information in this supplement was obtained by EPA's Emission Standards Division for use in development of National Emission Standards for a Hazardous Air Pollutant (NESHAP) for chromium used in cooling towers and electroplating operations.

The reader is strongly cautioned against using the emissions information contained in the original document or this supplement to develop an exact assessment of emissions from any particular facility. Because of insufficient data, no estimate can be made of the error that could result when these factors are used to calculate emissions from any given facility. It is possible, in some extreme cases, that orders-of-magnitude differences could result between actual and calculated emissions, depending on differences in source configurations, control equipment, and operating practices. Thus, in situations where an accurate assessment of chromium emissions is necessary, source-specific information should be obtained to confirm the existence of particular emitting operations, the types and effectiveness of control measures, and the impact of operating practices. A source test and/or material balance should be considered as the best means to determine air emissions directly from an operation.

2.0 OVERVIEW OF DOCUMENT CONTENTS

This section outlines the information presented in the remaining sections of this report and indicates whether the information is new or whether it is a revision of information presented in the original document.

Section 3.1 presents process descriptions for five kinds of plating/anodizing operations. New information is included for decorative electroplating of plastics, chromic acid anodizing, and trivalent chromium plating. Additional process information is provided to supplement the discussion of hard and decorative electroplating presented in the original document. New emission data are presented for hard and decorative electroplating operations; the results of an engineering mass balance to obtain an emission estimate for chromic acid anodizing are also presented. A significant change from the original document is in the format of the chromium emission factors for hard and decorative plating operations from kilograms per hour per square foot of tank area to milligrams per ampere-hour. Supplemental information has been included on emission control techniques for reduction of chromic acid mist from plating operations. New information is presented on nationwide chromium emission estimates for three types of plating operations: hard, decorative, and chromic acid anodizing.

Section 3.2 presents updated information about the distribution of industrial process cooling towers that use chromium-based water treatment chemicals and presents new information about comfort cooling towers. New information also is presented on emission reduction techniques for chromium emissions from cooling towers. New emission data are presented for cooling towers equipped with low- and high-efficiency drift eliminators. A significant change from the original document is in the format of the chromium emission factor from picograms per joule of thermal energy input to the power plant associated with the cooling tower to percentage of the recirculating chromium that is emitted. New information is presented on nationwide chromium emission estimates for industrial cooling towers in eight industries.

Section 4.0 summarizes the procedures used for source sampling and analysis of chromium in emission streams from electroplating operations and cooling towers.

3.0 CHROMIUM EMISSION SOURCES

3.1 CHROMIUM ELECTROPLATING AND CHROMIC ACID ANODIZING OPERATIONS

3.1.1 Background Information

Plating and anodizing operations range in size from small shops, with one or two tanks that are operated only a few hours per week, to large shops with several tanks that are operated 24 hours per day, 7 days per week. Many plating and anodizing operations are captive shops that perform chromium electroplating or chromic acid anodizing as one operation within or for a manufacturing facility, while others are job shops that provide custom plating or anodizing services for many different clients. Captive and job shops may perform hard or decorative chromium plating or chromic acid anodizing or any combination of these three operations.

The estimated number of electroplating shops nationwide is 1,540 hard chromium plating facilities and 2,790 decorative chromium plating facilities.¹ The estimated number of chromic acid anodizing shops nationwide is 680.² Electroplating and anodizing shops typically are located in or near industrial centers in areas of high population density. States with large numbers of chromium electroplaters include California, Illinois, Massachusetts, Michigan, New York, Ohio, and Pennsylvania.

3.1.1.1 Hard Chromium Electroplating of Metals-- In hard plating, a relatively thick layer of chromium is deposited directly on the base metal (usually steel) to provide a surface with wear resistance, a low coefficient of friction, hardness, and corrosion resistance, or to build up surfaces that have been eroded by use.³ Hard plating is used for items such as hydraulic cylinders and rods, industrial rolls, zinc die castings, plastic molds, engine components, and marine hardware.

Tanks used for hard chromium electroplating usually are constructed of steel and lined with a polyvinyl chloride sheet or plastisol. The anodes, which are insoluble, are made of a lead alloy that contains either tin or antimony. The substrate to be plated, the cathode, is suspended from a plating rack that is connected to the cathode bar of the rectifier. The plating rack may be loaded in the tank manually, by a hoist, or by an automatically controlled hoist system.

The plating tanks typically are equipped with some type of heat exchanger. Mechanical agitators or compressed air supplied through pipes on the tank bottom provide uniformity of bath temperature and composition. Chromium electroplating requires constant control of the plating bath temperature, current density, plating time, and bath composition.

Hexavalent chromium plating baths are the most widely used baths to deposit chromium on metal. Hexavalent chromium baths are composed of chromic acid, sulfuric acid, and water. The chromic acid is the source of the hexavalent chromium that reacts and deposits on the metal and that is emitted to the atmosphere. The sulfuric acid in the bath catalyzes the chromium deposition reactions. Typical operating parameters are given in Table 1.⁴

The evolution of hydrogen gas from chemical reactions at the cathode consumes 80 to 90 percent of the power supplied to the plating bath, leaving the remaining 10 to 20 percent for the deposition reaction. When the hydrogen gas evolves, it entrains chromic acid and causes misting at the surface of the plating bath.

3.1.1.2 Decorative Chromium Electroplating of Metals. In decorative plating, the base material (e.g., brass, steel, aluminum, or plastic) generally is plated with a layer of nickel followed by a relatively thin layer of chromium to provide a bright surface with wear and tarnish resistance. Decorative plating is used for items such as automotive trim, metal furniture, bicycles, hand tools, and plumbing fixtures. The purpose of decorative chromium plating is to achieve a combination of the following surface properties:

1. Blue-white color;
2. High reflectivity;
3. Tarnish resistance;
4. Corrosion resistance;
5. Wear resistance; and
6. Scratch resistance.⁵

Decorative electroplating baths operate on the same principle as that described for the hard chromium plating process: the metal substrate is immersed in a plating solution, and direct current is passed from the anode through the

TABLE 1. TYPICAL OPERATING PARAMETERS FOR HARD CHROMIUM
ELECTROPLATING

Plating thickness, μm (mil)	1.3-762 (0.05-30)
Plating time, min ^a	20-2,160
Chromic acid concentration, g/l (oz/gal) ^b	225-375 (30-50)
Temperature of solution, °C (°F)	49-66 (120-150)
Voltage, volts	c
Current, amperes (A)	d
Current density, A/m ² (A/ft ²) ^e	1,600-6,500 (150-600)

^a min. = minutes.

^b g/l = grams per liter, oz/gal = ounces per gallon.

^c Depends on the distance between the anodes and the items being plated.

^d Depends on the amount of surface area plated.

^e A/m² = amperes per square meter, A/ft² = amperes per square foot.

plating solution causing the desired metal (copper, nickel, chromium) to deposit out of the solution onto the metal substrate (cathode).

Decorative chromium plating requires shorter plating times and operates at lower current densities than does hard chromium plating to achieve the desired properties of the chromium plate. Some decorative chromium plating operations use fluoride catalysts instead of sulfuric acid because fluoride catalysts, such as fluosilicate or fluoborate, have been found to produce higher bath efficiencies.⁶ Typical operating parameters are shown in Table 2.⁷

3.1.1.3 Decorative Chromium Electroplating of Plastics

Most plastics that are electroplated with chromium are formed from the polymer composed of acrylonitrile, butadiene, and styrene (ABS). The process for chromium electroplating of ABS plastics consists of the following steps:⁸

1. Chromic acid/sulfuric acid etch;
2. Dilute hydrochloric acid dip;
3. Colloidal palladium activation;
4. Dilute hydrochloric acid dip;
5. Electroless nickel plating or copper plating; and
6. Chromium electroplating cycle.

After each process step, the plastic is rinsed with water to prevent carry-over of solution from one bath to another. The chromic acid/sulfuric acid etch solution (Table 3) renders the ABS surface hydrophilic and modifies the surface to provide adhesion for the metal coating.⁹ The dilute hydrochloric acid dips are used to clean the surface and remove palladium metal from the plating rack, which is insulated with a coating of polyvinyl chloride. The colloidal palladium activation solution deposits a thin layer of metallic palladium over the plastic surface.¹⁰ The metallic palladium induces the deposition of copper or nickel, which will not deposit directly onto plastic. The electroless nickel and copper plate are applied to impart electrical conductivity to the part; otherwise, the insulating surface of the plastic could not be electroplated with chromium. The electroless nickel plating or copper electroplating baths develop a film on the plastic about 1.0 micrometer (μm) (3.9×10^{-5} inch [in.]) thick. The plating time for electroless nickel

TABLE 2. TYPICAL OPERATING PARAMETERS FOR DECORATIVE CHROMIUM PLATING

Plating thickness, μm (mil)	0.003-2.5 (0.0001-0.1)
Plating time, min	0.5-5
Chromic acid concentration, g/l (oz/gal)	225-375 (30-50)
Temperature of solution, $^{\circ}\text{C}$ ($^{\circ}\text{F}$)	38-46 (100-115)
Voltage, volts	a
Current, A	b
Current density, A/m^2 (A/ft^2)	540-2,400 (50-220)

^a Depends on the distance between the anodes and the items being plated.

^b Depends on the amount of surface area being plated.

TABLE 3. CHROMIC ACID/SULFURIC ACID ETCH SOLUTION

Concentrated sulfuric acid, g/l (oz/gal)	172 (23)
Chromic acid, g/l (oz/gal)	430 (57)
Temperature, $^{\circ}\text{C}$ ($^{\circ}\text{F}$)	60-65 (140-149)
Immersion time, min	3-10

plating and electroless copper plating ranges from 10 to 15 minutes and 15 to 30 minutes, respectively, at temperatures ranging from 25° to 35°C (77° to 95°F). The components of the plating baths include the metal salt (nickel or copper), a reducing agent, a complexing agent, a stabilizer, and a pH buffer system.¹¹ The electroplating of plastics follows the same cycle as that described for decorative chromium electroplating.¹²

3.1.1.4 Chromic Acid Anodizing. Chromic acid anodizing is used primarily on aircraft parts and architectural structures that are subject to high stress and corrosion. Chromic acid anodizing is used to provide an oxide layer on aluminum that imparts the following properties:

1. Corrosion protection;
2. Electrical insulation;
3. Ease of coloring; and
4. Improved dielectric strength.¹³

Figure 1 presents a flow diagram for a typical chromic acid anodizing process.

There are four primary differences between the equipment used for chromium electroplating and that used for chromic acid anodizing: (a) chromic acid anodizing requires the rectifier to be fitted with a rheostat or other control mechanism to permit starting at about 5 V, (b) the tank is the cathode in the electrical circuit, (c) the aluminum substrate acts as the anode, and (d) sidewall shields typically are used instead of a liner in the tank to minimize short circuits and to decrease the effective cathode area.¹⁴ Types of shield materials used are herculite glass, wire safety glass, neoprene, and vinyl chloride polymers.¹⁵

The following pretreatment steps typically are used to clean the aluminum before anodizing:

1. Alkaline soak;
2. Desmut;
3. Etching; and
4. Vapor degreasing.

The pretreatment steps used for a particular aluminum substrate depend upon the amount of smut and the composition of the aluminum. The aluminum substrate is rinsed between pretreatment

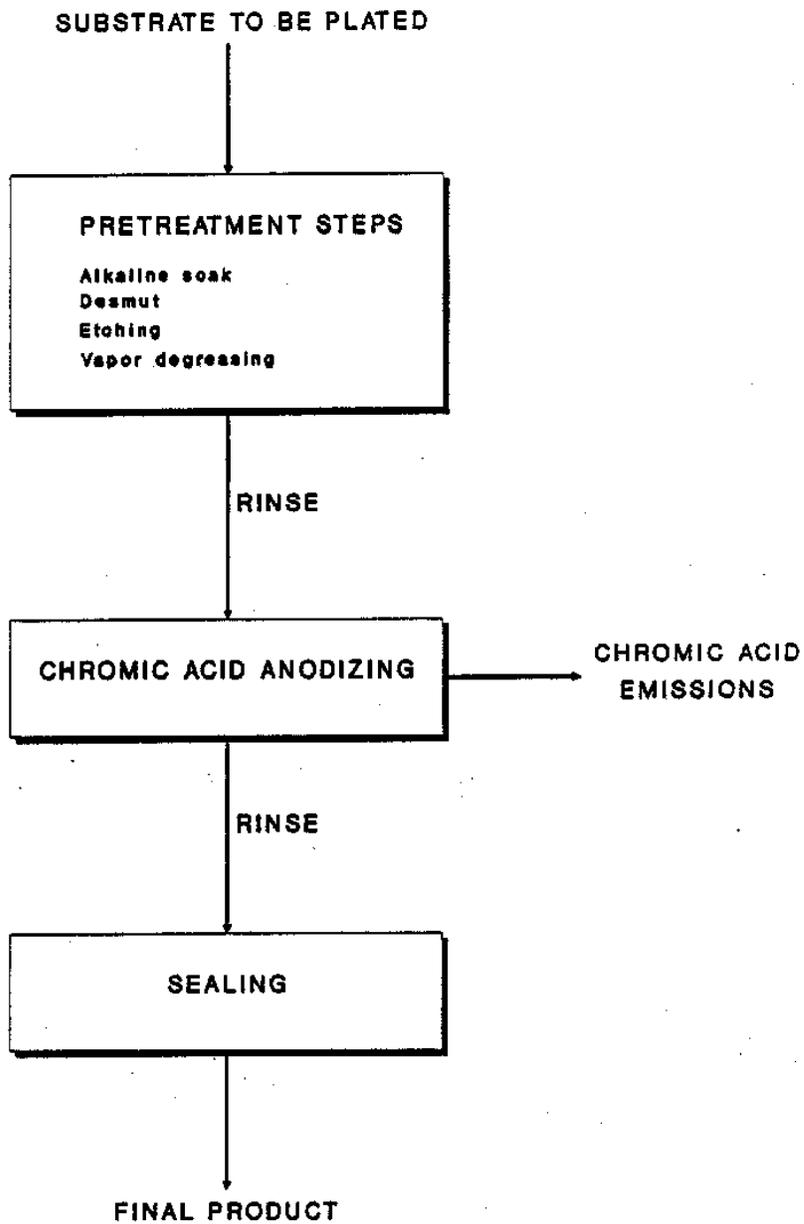


Figure 1. Flow diagram for a typical chromic acid anodizing process.

steps to remove cleaners.

The alkaline soak is the primary preparatory step in cleaning the aluminum; its purpose is to dislodge soil from the aluminum surface. The solutions for alkaline cleaning are typically made up of compounds such as sodium carbonate, sodium phosphate, and sodium hydroxide and usually contain a small amount of silicate to prevent metal attack.¹⁶ The alkaline soak consists of immersing the metal in the alkaline solution that is mildly agitated with air.

The purpose of desmutting is to remove soil or grease films that cleaners and etchants leave behind. Desmutting baths typically consist of a cold nitric acid solution mixed with water at a concentration ranging from 5 to 50 percent acid by volume. The nitric acid bath also is used either as a bleaching treatment to remove dyes from faulty coatings or as part of the technique of producing multicolor coatings.¹⁷ Other desmutting treatments use combinations of chromic, phosphoric, and sulfuric acids depending upon the amount of smut to be removed or the aluminum composition.

When a dull finish is desired, the aluminum is etched before anodizing. Etching baths consist of a dilute solution of soda ash, caustic soda, or nitric acid.¹⁸ The degree of etching desired and the composition of the aluminum being treated determine the concentration of the etch solution, temperature of the bath, and duration of the etch.

The vapor degreasing step for aluminum is the same as the vapor degreasing step for metals that are chromium plated.

Typical operating parameters for chromic acid anodizing baths are presented in Table 4.^{19,20} The voltage is applied step-wise (5 V per minute) from 0 to 40 V and maintained at 40 V for the remainder of the anodizing time. A low starting voltage (i.e., 5 V) minimizes current surge that may cause "burning" at contact points between the rack and the aluminum part. The process is effective over a wide range of voltages, temperatures, and anodizing times. All other factors being equal, high voltages tend to produce bright transparent films, and lower voltages tend to produce opaque films.²¹ Raising the bath temperature increases current density to produce thicker films in a given time period. Temperatures up to 49°C (120°F) typically are used

TABLE 4. TYPICAL OPERATING PARAMETERS FOR CHROMIC ACID ANODIZING

Chromic acid concentration, g/l (oz/gal)	50-100 (6.67-13.3)
Temperature, °C (°F)	32-35 (90-95)
Plating time, min	30-60
pH	0.5-0.85
Current density, A/m ² (A/ft ²)	1,550-7,750 (144-720)
Voltage (step-wise), volts	30-40
Film thickness, μm (mil)	0.5-1.27 (0.02-0.05)

to produce films that are to be colored by dyeing.²² The amount of current varies depending on the size of the aluminum parts; however, the current density typically ranges from 1,550 to 7,750 A/m² (144 to 720 A/ft²).

The postanodizing steps include sealing and air drying. Sealing causes hydration of the aluminum oxide and fills the pores in the aluminum surface. As a result, the elasticity of the oxide film increases but the hardness and wear resistance decrease.²³ Sealing is performed by immersing aluminum in a water bath at 88° to 99°C (190° to 210°F) for a minimum of 15 minutes.²⁴ Chromic acid or other chromates may be added to the solution to help improve corrosion resistance. The aluminum is allowed to air dry after it is sealed.

3.1.1.5 Trivalent Chromium Plating Trivalent chromium electroplating baths have been developed primarily to replace decorative hexavalent chromium plating baths. Development of a trivalent bath has proven to be difficult because trivalent chromium solvates in water to form complex stable ions that do not readily release chromium. The trivalent chromium baths that have been developed are proprietary baths.

There are two types of trivalent chromium processes on the market: single-cell and double-cell processes. The major differences in the two processes are that (1) the double-cell process solution contains minimal-to-no chlorides whereas the single-cell process contains a high concentration of chlorides; and (2) the double-cell process utilizes lead anodes that are placed in anode boxes that contain a dilute sulfuric acid solution and are lined with a permeable membrane whereas the single-cell process utilizes carbon or graphite anodes that are placed in direct contact with the plating solution.²⁵

The advantages of the trivalent chromium processes over the hexavalent chromium process are (1) fewer environmental concerns, (2) higher productivity, and (3) lower operating costs. In the trivalent chromium process, hexavalent chromium is a plating bath contaminant. Therefore, the bath does not contain any appreciable amount of hexavalent chromium which is more toxic than trivalent chromium. The total chromium concentration of trivalent chromium solutions is approximately one-fifth that of hexavalent chromium solutions.²⁶ As a result of the chemistry of the trivalent chromium electrolyte, misting does not occur during plating, as it does during hexavalent chromium plating. Use of trivalent chromium also reduces waste disposal problems and costs. Waste treatment of hexavalent chromium is a two-stage process. The hexavalent chromium is first reduced to the trivalent chromium ion; then it can be precipitated as chromium

hydroxide. Trivalent chromium plating solution wastewaters are already in the reduced trivalent state and require only the chromium hydroxide precipitation step.

Productivity is increased when trivalent chromium processes are used because less stripping and replating of parts is required and more parts can be placed on a rack, and more racks can be placed on a workbar.²⁷

The cost of trivalent chromium is less than hexavalent chromium because of the lower wastewater treatment costs and lower operating costs due to a reduction in rejects and high productivity.

The disadvantages of the trivalent chromium process are that the process is more sensitive to contamination than the hexavalent chromium process and the trivalent chromium process cannot plate the full range of plate thicknesses that the hexavalent chromium process does.²⁸ Because it is sensitive to contamination, the trivalent chromium process requires more thorough rinsing and tighter laboratory control than the hexavalent chromium process. Trivalent chromium baths can plate thicknesses ranging up to 0.13 to 25 micrometers (μm) (0.005 to 1.0 mils) thick.²⁸ The hexavalent chromium process is able to plate up to 762 μm (30 mils) thick. Therefore, trivalent chromium solutions cannot be used for most hard chromium plating applications.

The plating efficiency of a trivalent chromium bath, approximately 20 to 25 percent, is slightly higher than that of a hexavalent chromium plating bath.²⁹ The color, hardness, and corrosion resistance of trivalent chromium deposits are comparable to those of hexavalent chromium deposits.³⁰ However, the composition of the trivalent chromium deposit is significantly different than that of the hexavalent chromium deposit. Table 5 presents the composition of trivalent and hexavalent chromium deposits.³¹

3.1.2 Uncontrolled Chromium Emissions

Emissions of chromic acid mist from the electrodeposition of chromium from chromic acid plating baths occur because of the inefficiency of the hexavalent chromium plating process; only about 10 to 20 percent of the current applied actually is used to deposit

TABLE 5. HEXAVALENT AND TRIVALENT CHROMIUM DEPOSIT COMPOSITIONS

Chromium deposit	Carbon, % wt	Oxygen, % wt	Chromium, % wt
Hexavalent	0.0	0.4	99+
Trivalent	2.9	1.6	95+

chromium on the item plated. Eighty to ninety percent of the current applied is consumed by the evolution of hydrogen gas at the cathode with the resultant liberation of gas bubbles. Additional bubbles are formed at the anode due to the evolution of oxygen. As the bubbles burst at the surface of the plating solution, a fine mist of chromic acid droplets is formed.

3.1.2.1 Hard Chromium and Decorative Electroplating Operations. Uncontrolled emission data for eight hard chromium plating operations and two decorative chromium plating operations are presented in Table 6. These data were obtained from nine EPA tests and one non-EPA test. Table 7 presents tank parameters and process operating parameters monitored during each of the 10 tests. The process parameters monitored during testing include current supplied to the plating baths, voltage, and chromic acid concentration and temperature of the plating baths. The chromic acid concentration and temperature did not vary significantly within each type operation for the emission tests and appeared to be representative of typical operating values for conventional hard and decorative chromium plating operations. The amount of current supplied during testing varied considerable because of the different types and quantities of parts plated.

Based on the existing test data, an uncontrolled emission factor of 10 milligrams of hexavalent chromium per ampere-hour (mg/Ah) (0.15 grain per ampere-hour [gr/Ah]) is considered to be representative of uncontrolled emissions from a hard chromium electroplating operation, and an uncontrolled hexavalent chromium emission factor of 2.0 mg/Ah (0.031 gr/Ah) is considered representative of uncontrolled emissions from a decorative chromium electroplating operation.

3.1.2.2 Chromic Acid Anodizing Operations. Uncontrolled emission data for chromic acid anodizing operations were not obtained through an EPA source test at an anodizing facility. Instead, an estimate of the amount of hexavalent chromium emissions was made by performing a mass balance on a scrubber used to control emissions from a chromic acid anodizing operation. Outlet scrubber water grab samples were analyzed to determine the amount of hexavalent chromium in the sample, and a mass balance was performed on the scrubber to determine the inlet hexavalent chromium emission rate. The

TABLE 6. UNCONTROLLED EMISSION DATA^a

Plant	Process conditions			Actual gas flow rate, m ³ /min (ft ³ /min)	Mass emission rate, kg/h (lb/h)		Process Cr ⁺⁶ emission rate, mg/A•h (gr/A•h)
	No. of tanks	Total tank surface area, m ² (ft ²)	Ampere- hours		Total Cr	Cr ⁺⁶	
<u>Hard chromium plating</u>							
Plant A ^b ³²	1	5.2 (56)	20,458	177 (6,260)	0.08 (0.17)	0.08 (0.17)	9.0 (0.14)
Plant B ^b ³³	4	8.5 (92)	54,667	300 (10,400)	0.024 (0.052)	0.011 (0.025)	2.2 (0.03) ^c
Plant C ^d ³⁴	1	5.8 (63)	13,983	226 (7,970)	0.029 (0.064)	0.026 (0.057)	4.0 (0.06)
Plant D ^b ³⁵	1	5.6 (56)	2,480	242 (6,260)	0.009 (0.167)	e (0.168)	3.5 (0.05) ^c
Plant E ^f ³⁶	2	9.2 (72.5)	8,524	298 (18,100)	0.100 (0.10)	0.102 (0.10)	22.5 (0.35)
Plant F ^b ³⁷	3	6.7 (20)	8,790	512 (4,540)	0.045	0.045 (0.183)	15.5 (0.24)
Plant G ^b ³⁸	2	2.5 (26.5)	14,400	153 (5,390)	0.008 (0.018)	0.0152 (0.0333)	3.2 (0.05)
Plant H ^{g,h} ³⁹	4	8.5 (92)	20,050	330 (11,600)	0.050 (0.011)	0.039 (0.09)	<u>4.6 (0.07)</u> 9.8 (0.15)
Average							
<u>Decorative chromium plating</u>							
Plant I ⁱ ⁴⁰	1	2.8 (30.3)	6,500	130 (4,700)	i	0.0036 (0.0080)	1.4 (0.02)
Plant J ^c ⁴¹	1	22.3 (240)	96,840	990 (35,000)	0.0561 (0.124)	0.0658 (0.145)	<u>2.0 (0.03)</u>
Average							
							<u>1.7 (0.03)</u>

^a All tests were performed by EPA except for the Plant D test which was performed by the Naval Energy and Environmental Support Activity, Port Hueneme, California.

^b Ampere-hour and mass emission rate values are based on an average of three test runs.

^c Not included in average value because data are based on total chromium.

^d Ampere-hour and mass emission rate values are based on an average of four test runs.

^e Hexavalent chromium emissions were not reported.

^f Ampere-hour and mass emission rate values are based on an average of 12 test runs.

^g Ampere-hour and mass emission rate values are based on an average of six test runs.

^h Preliminary test data.

ⁱ Total chromium emissions were not determined

TABLE 7. TANK PARAMETERS AND PROCESS OPERATING PARAMETERS MONITORED DURING CHROMIUM PLATING TESTS

Plant	Tank parameters		Average process parameters monitored				
	No. of tank(s)	Total tank surface area, m ² (ft ²) ^a	Total tank capacity, l (gal) ^b	Current, amperes	Voltage, volts	Chromic acid concentration, g/l (oz/gal)	Bath temp., °C (°F)
<u>Hard chromium plating</u>							
Plant A ³²	1	5.2 (56)	15,820 (4,180)	8,837	7.4	210 (28)	52 (125)
Plant B ³³	4	8.5 (92)	36,100 (9,540)	11,150	8.7	250 (33)	54 (145)
Plant C ³⁴	1	5.9 (63)	10,710 (2,830)	6,223	9.0	255 (34)	50 (130)
Plant D ³⁵	1	5.6 (60)	7,190 (1,900)	2,483	6.6	210 (28)	60 (125)
Plant E ³⁶	2	9.2 (99)	11,210 (2,962)	5,215	6.8	240 (33)	59 (130)
Plant F ³⁷	3	6.7 (72.5)	23,070 (6,094)	1,149	6.1	250 (33)	49 (133)
Plant G ³⁸	2	2.5 (26)	4,130 (1,090)	1,614	12.3	210 (28)	62 (131)
Plant H ³⁹	4	8.5 (92)	36,100 (9,540)	2,860	7.9	250 (33)	54 (140)
<u>Decorative chromium plating</u>							
Plant I ⁴⁰	1	2.8 (30)	3,860 (1,020)	2,700	5.1	280 (37)	48 (119)
Plant J ⁴¹	1	22.3 (240)	61,170 (16,160)	21,317	22.4	173 (33)	49 (130)

^a m² = square meters, ft² = square foot.

^b l = liters, gal = gallons.

results of this mass balance indicate that an uncontrolled of emission factor of 6.0×10^{-4} kilogram of hexavalent chromium per hour per square meter of tank surface area (1.2×10^{-4} pound per hour per square foot of tank surface area) is appropriate to characterize emissions from chromic acid anodizing.⁴²

3.1.3 Emission Reduction Techniques

The principal techniques used to control emissions of chromic acid mist from decorative and hard chromium plating and chromic acid anodizing operations include add-on control devices and chemical fume suppressants. The control devices most frequently used are mist eliminators and wet scrubbers that are operated at relatively low pressure drops. Because of the corrosive properties of chromic acid, control devices typically are made of polyvinyl chloride (PVC) or fiberglass.

Chemical fume suppressants are added to decorative chromium plating and chromic acid anodizing baths to reduce chromic acid mist. Although chemical agents alone are effective control techniques, many plants use them in conjunction with a control device.

Chevron-blade and mesh-pad mist eliminators are the types of mist eliminators most frequently used to control chromic acid mist. The most important mechanism by which mist eliminators remove chromic acid droplets from gas streams is the inertial impaction of droplets onto a stationary set of blades or a mesh pad. Mist eliminators typically are operated as dry units that are periodically washed down with water to clean the impaction media.

The wet scrubbers typically used to control emissions of chromic acid mist from chromium plating and chromic acid anodizing operations are single and double packed-bed scrubbers. Other scrubber types used less frequently include fan-separator packed-bed and centrifugal-flow scrubbers. The mechanism by which scrubbers remove chromic acid droplets from the gas streams is wetting the gas stream to increase the particles mass followed by impingement on a packed bed. Once-through water or recirculated water typically is used as the scrubbing liquid because chromic acid is highly soluble in water.

Chemical fume suppressants are surface-active compounds that are added directly to chromium plating and chromic acid anodizing baths

to reduce or control misting. Fume suppressants are classified as temporary or as permanent. Temporary fume suppressants are depleted mainly by the decomposition of the fume suppressant and dragout of the plating solution, and permanent fume suppressant are depleted mainly by dragout of the plating solution. Fume suppressants, which are manufactured in liquid, powder, or tablet form, include wetting agents that reduce misting by lowering the surface tension of the plating or anodizing bath, foam blankets that entrap chromic acid mist at the surface of the plating solution, or combinations of both a wetting agent and foam blanket.

The performance capabilities of the control devices used to control chromic acid mist are presented in Table 8. The air pollution control devices tested include four mist eliminators, three packed-bed scrubbers, and one packed-bed scrubber in conjunction with a mist eliminator used to control emissions from hard chromium plating operations. In addition, one emission test was conducted at a decorative chromium plating facility to determine the performance of chemical fume suppressants in controlling chromic acid mist.

The average hexavalent chromium removal efficiency of mist eliminators was 98 percent for mist eliminators with double sets of blades, 90 percent for mist eliminators with single sets of blades, and 94 percent for mesh pad units. The average hexavalent chromium removal efficiency of scrubbers was 97 percent efficient. The hexavalent chromium removal efficiency of the scrubber in conjunction with the mist eliminator was 95 percent.

For decorative chromium plating operations, the performance efficiency of both chemical fume suppressants tested (a foam blanket and a combination of a foam blanket and wetting agent) was greater than 99 percent. This performance efficiency is achievable as long as vendor recommendations on the makeup and use of the fume suppressants are followed rigorously.

3.1.4 Nationwide Emission Estimates

Table 9 presents the estimated number of operations and the nationwide annual emission rate for each type of operation. The nationwide emission rate for hard chromium electroplating operations was based on the assumption that 30 percent of operations are

TABLE 8. PERFORMANCE LEVELS OF INDIVIDUAL CONTROL DEVICES

Plant	Control device	Average removal efficiency for Cr ⁺⁶ , percent
<u>Hard chromium plating</u>		
Plant A ³²	ME-DSB ^a	98 ^b
Plant G ³⁸	ME-SSB ^c	91 ^b
Plant C ³⁴	ME-SSB ^d	88 ^e
Plant D ³⁵	ME-MP ^f	94 ^{b,g}
Plant B ³³	DPBS ^h	96 ^{b,g}
Plant E ³⁶	SPBS ⁱ	99 ^j
Plant F ³⁷	DPBS ^h	96 ^b
Plant H ³⁹	PBS+ME-DSB ^k	95 ^{l,m}
<u>Decorative chromium plating</u>		
Plant I ⁴⁰	Foam blanket	>99 ^b
Plant I ⁴⁰	Wetting agent/foam blanket	>99 ^b

^a Mist eliminator with double set of overlapping-type blades.

^b Removal efficiency based on an average of three test runs.

^c Mist eliminator with single set of overlapping-type blades.

^d Mist eliminator with single set of wave-type blades.

^e Removal efficiency based on average of four test runs.

^f Mesh pad mist eliminator.

^g Based on total chromium emission data.

^h Double packed-bed scrubber.

ⁱ Single packed-bed scrubber.

^j Remocla efficiency based on an average of 12 test runs.

^k Double packed-bed scrubber in conjunction with a mist eliminator containing a double set of wave-type blades.

^l Preliminary test data.

^m Removal efficiency based on an average of six test runs.

TABLE 9. NATIONWIDE NUMBER OF OPERATIONS AND ESTIMATED HEXAVALENT CHROMIUM EMISSIONS FROM CHROMIUM ELECTROPLATING AND CHROMIC ACID ANODIZING OPERATIONS

Operation	No. of plants nationwide	Nationwide Cr ⁺⁶ emissions, Mg/yr (tons/yr)
Hard chromium plating ¹	1,540	146 (161)
Decorative chromium plating ¹	12,790	10 (11)
Chromic acid anodizing ²	680	3.5 (3.8)

uncontrolled, 30 percent of operations are controlled by mist eliminators with single sets of blades (90 percent efficient), and 40 percent are controlled by single packed-bed scrubbers (97 percent efficient). The nationwide emission rate for decorative chromium electroplating operations was based on the assumption that 15 percent of operations are uncontrolled, and 85 percent are controlled by chemical fume suppressants or single packed-bed scrubbers (97 percent efficient). The nationwide annual emission rate for chromic acid anodizing operations was based on the assumption that 40 percent of operations are uncontrolled, 10 percent are controlled by mist eliminators with single sets of blades (90 percent efficient) and 50 percent are controlled by chemical fume suppressants or single packed-bed scrubbers (97 percent efficient).

The assumptions regarding the existing control levels for each type operation were derived from data obtained during the development of the NESHAP for chromium electroplating operations. In estimating nationwide annual chromium emissions, the efficiency of chemical fume suppressants used in decorative chromium and chromic acid anodizing operations was assumed to be 97 percent rather than 99 percent as demonstrated by test data (see Table 8). The 97 percent figure is conservative and accounts for the fact that platers may not rigorously follow vendor recommendations on the use of fume suppressants in the absence of monitoring or recordkeeping requirements.

3.2 COOLING TOWERS

3.2.1 Background Information

Cooling towers are devices that cool warm water by contacting it with ambient air that is drawn or forced through the tower. This cool water is then used to remove heat from a process or an HVAC chiller before returning to the cooling tower. Chemicals are added to this recirculating water to inhibit heat exchanger corrosion. One of the many classes of corrosion inhibitors used is chromium based. Air emissions of chromium occur when water droplets (and the chemicals they contain) entrained in the air stream that is drawn through the tower are emitted to the atmosphere. These droplet emissions are referred to as "drift." All cooling towers that are used to remove heat from an industrial process or chemical reaction are referred to as industrial process cooling towers (IPCT's). Towers

that are used to cool heating ventilation and air conditioning (HVAC) and refrigeration systems are referred to as comfort cooling towers (CCT's).

3.2.1.1 Industrial Process Cooling Towers. Major users of IPCT's that also use chromium-based water treatment chemicals are chemical manufacturing plants, petroleum refineries, and primary metals facilities. Several miscellaneous manufacturing industries (textiles, tobacco products, tire and rubber products, and glass products), and utilities use chromium-based water treatment chemicals to a lesser degree. It is estimated that IPCT's are used at approximately 190 petroleum refineries, 1,800 chemical manufacturing plants, 240 primary metals plants, and 730 plants in the miscellaneous industries.⁴³ In addition, the percentage of cooling towers using chromium-based water treatment chemicals in each industry is estimated as 70 percent at petroleum refineries, 40 percent at chemical manufacturing plants, 20 percent at primary metals facilities, 15 percent at plants in the tire and rubber industry, and 5 percent at plants in the other miscellaneous industries.⁴³ In the utilities industry, it was reported that chromium-based water treatment chemicals are used at two electric power plants.⁴⁴ When combined with data from plant responses to EPA information requests in each of these industries, these estimates result in a total of about 2,850 IPCT's using chromium-based water treatment chemicals: 475 at petroleum refineries, 2,040 at chemical plants, 224 at primary metals plants, 110 at miscellaneous plants and 6 at utilities. The nationwide baseline Cr⁺⁶ emissions from these towers are estimated to be 85 megagrams per year (Mg/yr) (94 tons per year [tons/yr]).⁴³

3.2.1.2 Comfort Cooling Towers. Comfort cooling towers are used in all States in the U.S., primarily in urban areas. Major users of CCT's with HVAC systems include hospitals, hotels, educational facilities, office buildings, and shopping malls. Refrigeration systems that may operate with CCT's include ice skating rinks, cold storage (food) warehouses, and other commercial operations. The EPA estimates that the nationwide population of CCT's is 250,000 units and that 15 percent of CCT's (about 37,500) use chromium-based water treatment chemicals. These CCT's are estimated to emit between 7.2 and 206 Mg/yr (8 to 227 tons/yr) of

chromium.⁴⁵ Chromium use in CCT's appears to be distributed randomly across the country.⁴⁵

In the development of the proposed rule under the Toxic Substances Control Act (TSCA) (see 52 FR 10206) for comfort cooling towers, EPA developed model tower parameters and estimates of chromium emissions per model tower to represent the population of CCT's in the U.S. Table 10 presents the model parameters and baseline emission estimates.⁴⁵ These data were used in conjunction with census information and assumptions about the distribution of CCT's by State to develop statewide, nationwide, and per capita estimates of Cr⁺⁶ emissions from CCT's as shown in Table 11. Emissions from Industrial Process Cooling Towers-Background Information for Proposed Standards. Draft. Prepared for U. S. Environmental Protection Agency. Research Triangle Park, North Carolina. May 1988.⁴⁵

The emission estimates in Table 10 and Table 11 are expressed as a range because of the uncertainty associated with emission data collected by the Agency from CCT tests. Because the emission factors developed to estimate Cr⁺⁶ emissions from cooling towers are independent of tower operating parameters (recirculation rate, chromate concentration, cooling range), the factors are applicable to both CCT's and IPCT's. Section 3.2.3.1 of this document discusses specific emission factors to use for estimating Cr⁺⁶ emissions from CCT's on a case by case basis. [Note: The proposed TSCA rule would prohibit the use of chromium-based chemicals in CCT's. If promulgated, this rule would have the effect of reducing Cr⁺⁶ emissions from CCT's to zero.]

3.2.1.3 Cooling Tower Fundamentals. Schematics of typical cooling tower designs are shown in Figure 2.⁴⁶ The major cooling tower components include the fan(s), fill material, water distribution deck or header, drift eliminator, structural frame, and cold water basin. Other components that affect tower operation include the pumps and pipes necessary to circulate the cooling water through the cooling tower and heat exchanger loops.

Most IPCT's are designed with induced-draft airflow, but many have forced-draft airflow, and some (especially in the utilities industry) have natural-draft airflow. Induced draft is provided by a propeller-type axial fan located in the stack at the top of the tower. Forced-draft towers are usually smaller than induced-draft towers and have either centrifugal fans located at the base of the tower, which is constructed as a plenum to provide positive-pressure

TABLE 10. MODEL COMFORT COOLING TOWERS AND HOURLY BASELINE Cr⁺⁶ EMISSIONS

Model tower	Model building size m ² (ft ²)	Model tower cooling requirements		Flow rates, l/min (gal/min)			Chromium emissions per tower, mg/h (lb/1,000 h)
		W (Btu/h)	Tons	Recirculation rate	Evaporation rate	Blowdown rate	
1	673 (7,240)	95,400 (325,800)	27	246 (65)	2.08 (0.55)	0.53 (0.14)	19.9 (0.044)
2	1,460 (15,720)	207,100 (707,400)	59	534 (141)	4.54 (1.20)	1.14 (0.30)	43.2 (0.095)
3	3,405 (36,650)	482,900 (1,649,000)	137	1,250 (330)	10.6 (2.80)	2.65 (0.70)	101 (0.222)
4	6,224 (66,990)	882,900 (3,015,000)	251	2,280 (602)	19.4 (5.12)	4.85 (1.28)	184 (0.406)
5	12,338 (132,800)	1,750,000 (5,976,000)	498	4,520 (1,194)	38.4 (10.15)	9.61 (2.54)	365 (0.804)
6	37,626 (405,000)	5,338,000 (18,230,000)	1,520	13,800 (3,642)	117.0 (30.96)	29.3 (7.74)	1,110 (2.45)

Assumptions:

Wet bulb temperature = 23.9 °C (75°F)

Hot water temperature = 29.4°C (85°F)

Cooling range = 5.6°C (10°F)

Cooling requirements = 142 W/m² floorspace (45 Btu/ft²/h)

Cycles of concentration = 5

Latent heat/total heat = 0.8

Chromate concentration = 10 ppm

Chromium emission factor = 0.0003 mg Cr⁺⁶/(ppm Cr⁺⁹)(liter H₂O)

(2.504 x 10⁻⁹ lb Cr⁺⁶/ppm Cr⁺⁶/gal H₂O)

TABLE 11. LOWER- AND UPPER-BOUND ESTIMATES OF Cr⁺⁶ EMISSIONS PER STATE AND ANNUAL Cr⁺⁶ EMISSIONS PER PERSON

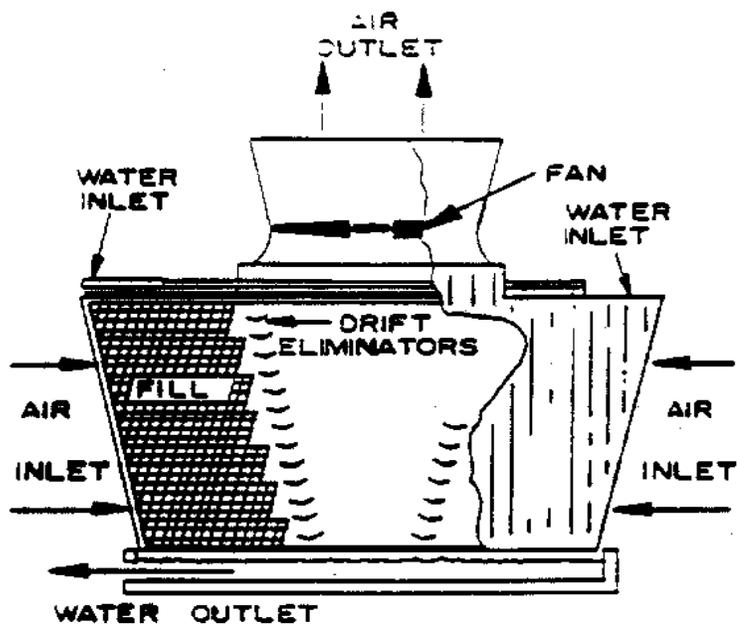
State	Utilization, percent	Cr ⁺⁶ emissions, kg/yr						Total Cr ⁺⁶ emissions, kg/yr	Annual Cr ⁺⁶ emissions, per person, kgx10,000/yr
		Model No.							
		1	2	3	4	5	6		
ALABAMA	59	1.09 -30.91	0.6 -302	15.2 -432	22.8 -647	33.9 -962	77.9 -2,212	161 - 4,585	4.01 - 113.8
ALASKA*	0	0.00 - 0.0	0.0 -0	0.0 -0	0.0 -0	0.0 -0	0.0 -0	0 - 0	0.0 -0.0
ARIZONA	55	0.76 -21.5	7.4 -210	10.6 -300	15.9 -450	23.6 -670	43.2 -1,540	112 - 3,192	3.74 - 106.1
ARKANSAS	56	0.61 -17.5	6.0 -171	8.6 -244	12.9 -366	19.1 -544	44.0 -1,250	91 - 2,592	3.80 - 108.0
CALIFORNIA	54	6.13 - 174.0	59.9 -1,700	85.6 -2,430	128.3 -3,644	190.8 -5,417	438.8 - 12,458	909 -25,823	3.67 - 104.1
COLORADO	29	0.41 -11.7	4.0 -114	5.8 -164	8.6 -245	12.8 -365	29.5 -839	61 - 1,739	1.97 -55.9
CONNECTICUT	33	0.47 -13.4	4.6 -131	6.6 -187	9.9 -281	14.7 -418	33.8 -961	70 - 1,992	2.24 -63.6
DELAWARE	33	0.09 - 2.6	0.9 - 26	1.3 - 37	1.9 - 55	2.9 - 81	6.6 -187	14 - 388	2.24 -63.6
FLORIDA	89	4.32 - 122.5	42.2 -1,197	60.3 -1,712	90.4 -2,567	134.4 -3,816	309.1 -8,776	641 -18,191	6.04 - 171.6
GEORGIA	59	1.54 -43.8	15.1 -428	21.5 -611	32.3 -917	48.0 -1,363	110.4 -3,134	229 - 6,496	4.01 - 113.8
HAWAII	100	0.47 -13.2	4.6 -129	6.5 -185	9.8 -278	14.5 -413	33.4 -949	69 - 1,967	6.79 - 192.8
IDAHO	21	0.10 - 2.8	1.0 - 27	1.4 - 39	2.1 - 58	3.1 - 87	7.0 -199	15 - 413	1.43 -40.5
ILLINOIS	42	2.21 -62.7	21.6 -613	30.9 -876	46.3 -1,314	68.8 -1,954	158.2 -4,493	328 - 9,313	2.85 -81.0
INDIANA	42	1.07 -30.4	10.5 -297	15.0 -425	22.4 -636	33.3 -946	76.6 -2,176	159 - 4,511	2.85 -81.0
IOWA	38	0.51 -14.5	5.0 -142	7.1 -203	10.7 -304	15.9 -452	36.6 -1,039	76 - 2,154	2.58 -73.3
KANSAS	42	0.46 -13.1	4.5 -128	6.5 -184	9.7 -275	14.4 -409	33.2 -942	69 - 1,952	2.85 -81.0
KENTUCKY	42	0.73 -20.7	7.1 -202	10.2 -289	15.3 -433	22.7 -644	52.2 -1,481	108 - 3,069	2.85 -81.0
LOUISIANA	65	1.30 -36.8	12.7 -360	18.1 -514	27.2 -771	40.4 -1,146	92.9 -2,636	192 - 5,465	4.41 - 125.3
MAINE	21	0.11 - 3.2	1.1 - 31	1.6 - 45	2.4 - 67	3.5 - 99	8.0 -229	17 - 474	1.43 -40.5
MARYLAND	46	0.91 -25.9	8.9 -253	12.7 -361	19.1 -542	28.4 -806	65.3 -1,853	135 - 3,841	3.12 -88.7
MASSACHUSETTS	33	0.87 -24.8	8.5 -242	12.2 -346	18.3 -519	27.2 -772	62.5 -1,774	130 - 3,678	2.24 -63.6
MICHIGAN	33	1.42 -40.3	13.9 -394	19.8 -563	29.7 -844	44.2 -1,255	101.6 -2,886	211 - 5,981	2.24 -63.6
MINNESOTA	29	0.55 -15.7	5.4 -153	7.7 -219	11.6 -328	17.2 -488	39.5 -1,122	82 - 2,326	1.97 -55.9
MISSISSIPPI	59	0.70 -19.9	6.9 -195	9.8 -278	14.7 -417	21.9 -621	50.3 -1,427	104 - 2,958	4.01 - 113.8
MISSOURI	42	0.96 -27.3	9.4 -26	713.4 -382	20.2 -573	30.0 -851	68.9 -1,957	143 - 4,057	2.85 -81.0
MONTANA	25	0.09 - 2.7	0.9 - 26	1.3 - 37	2.0 - 56	2.9 - 84	6.8 -192	14 - 398	1.70 -48.2
NEBRASKA	38	0.28 - 7.9	2.7 - 77	3.9 -110	5.8 -165	8.7 -246	19.9 -566	41 - 1,172	2.58 -73.3
NEVADA	39	0.16 - 4.5	1.6 - 44	2.2 - 63	3.3 - 95	5.0 -141	11.4 -323	18 - 511	1.83 -52.1
NEW HAMPSHIRE	27	0.12 - 3.4	1.2 - 34	1.7 - 48	2.5 - 72	3.8 -107	8.7 -246	212 - 6,034	2.85 -81.0
NEW JERSEY	42	1.43 -40.6	14.0 -397	20.0 -568	30.0 -851	44.6 -1,266	102.5 -2,911	212 - 6,034	2.85 - 81.0

TABLE 11. (Continued)

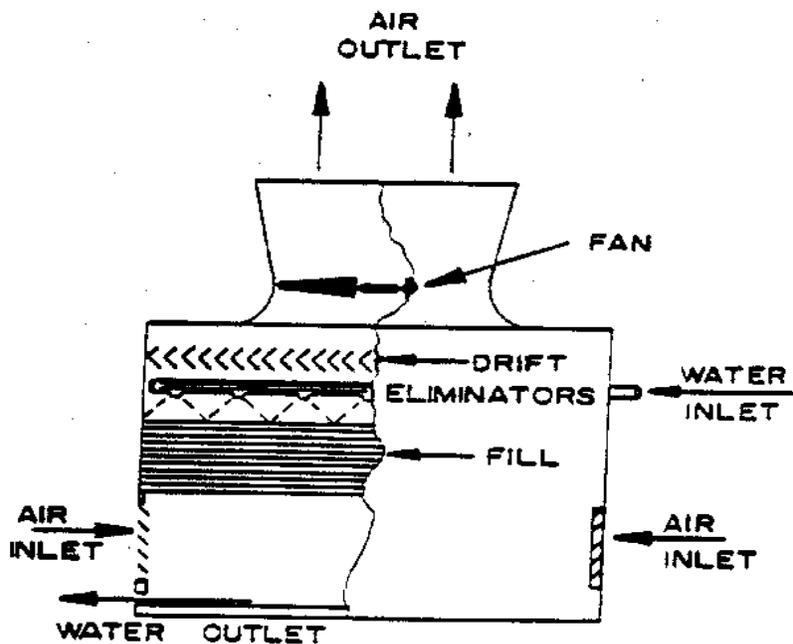
State	Utilization, percent	Cr ⁺⁶ emissions, kg/yr						Total Cr ⁺⁶ emissions, kg/yr	Annual Cr ⁺⁶ emissions, per person, kgx10,000/yr
		Model No.							
		1	2	3	4	5	6		
NEW MEXICO	39	0.25 - 7.0	2.4 - 69	3.5 - 98	5.2 -147	7.7 -219	17.8 -504	37 -1,045	2.65 -75.2
NEW YORK	33	2.63 -74.6	25.7 -729	36.7 -1,042	55.0 -1,562	81.8 -2,3231	88.1 -5,342	390 -11,072	2.24 -63.6
NORTH CAROLINA	53	1.48 -42.1	14.5 -411	20.7 -588	31.0 -881	46.1 -1,310	106.1 -3,013	220 - 6,244	3.60 - 102.2
NORTH DAKOTA	25	0.08 - 2.2	0.7 - 21	1.1 - 30	1.6 - 45	2.4 - 67	5.5 -155	11 - 322	1.70 -48.2
OHIO	39	1.93 -54.7	18.8 -535	26.9 -764	40.4 -1,146	60.0 -1,704	138.0 -3,918	286 - 8,122	2.65 -75.2
OKLAHOMA	54	0.78 -22.2	7.7 -217	10.9 -311	16.4 -466	24.4 -692	56.1 -1,592	116 - 3,301	3.67 - 104.1
OREGON	23	0.29 - 8.4	2.9 - 82	4.1 -117	6.2 -175	9.2 -261	21.2 -599	44 - 1,242	1.56 -44.3
PENNSYLVANIA	39	2.11 -59.8	20.6 -584	29.4 -835	44.1 -1,252	65.6 -1,862	150.8 -4,281	313 - 8,874	2.65 -75.2
RHODE ISLAND	33	0.14 - 4.1	1.4 - 40	2.0 - 57	3.0 - 86	4.5 -127	10.3 -293	21 - 606	2.24 -63.6
SOUTH CAROLINA	59	0.89 -25.1	8.7 -246	12.4 -351	18.5 -527	27.6 -783	63.4 -1,800	131 - 3,732	4.01 - 113.8
SOUTH DAKOTA	33	0.11 - 3.0	1.0 - 29	1.5 - 42	2.2 - 63	3.3 - 93	7.6 -215	16 - 445	2.24 -63.6
TENNESSEE	50	1.10 -31.1	10.7 -304	15.3 -435	22.9 -652	34.1 -969	78.5 -2,228	163 - 4,618	3.40 -96.4
TEXAS	63	4.35 - 123.6	42.5 -1,208	60.8 -1,726	91.2 -2,588	135.5 -3,848	311.7 -8,850	646 -18,343	4.28 - 121.5
UTAH	31	0.22 - 6.4	2.2 - 62	3.1 - 89	4.7 -133	7.0 -198	16.0 -456	33 - 944	2.11 -59.8
VERMONT	25	0.06 - 1.7	0.6 - 17	0.8 - 24	1.3 - 36	1.9 - 54	4.3 -123	9 - 255	1.70 -48.2
VIRGINIA	42	1.07 -30.51	0.5 -298	15.0 -426	22.5 -639	33.4 -950	76.9 -2,184	159 - 4,527	2.85 -81.0
WASHINGTON	20	0.39 -11.2	3.9 -109	5.5 -156	8.3 -235	12.3 -349	28.2 -802	59 - 1,662	1.36 -38.6
WEST VIRGINIA	42	0.38 -10.9	3.8 -107	5.4 -152	8.0 -229	12.0 -340	27.5 -781	57 - 1,620	2.85 -81.0
WISCONSIN	31	0.68 -19.4	6.7 -190	9.5 -271	14.3 -407	21.3 -604	49.0 -1,390	101 - 2,881	2.11 -59.8
WYOMING	25	0.06 - 1.7	0.6 - 16	0.8 - 23	1.2 - 35	1.8 - 52	4.2 -120	9 - 248	1.70 -48.2
WASHINGTON, DC	50	0.14 - 3.9	1.4 - 39	1.9 - 55	2.9 - 83	4.3 -123	10.0 -283	21 - 586	3.40 -96.4
TOTAL FOR U.S. ^b		49 - 1,392	479 - 13,602	685 - 19,445	1,027 - 29,156	1,527 - 43,349	3,511 - 99,689	7,277 - 206,633	

^a Alaska was assumed to have no CCT's because, on average, there are no days when the mean temperature exceeds 60°F.

^b The population of Alaska was subtracted from the national population prior to the calculation of the national annual Cr⁺⁶ emissions per person.



MECHANICAL DRAFT
CROSS-FLOW TOWER



MECHANICAL DRAFT
COUNTER-FLOW TOWER

Figure 2. Internals of crossflow and counterflow cooling towers (reprinted from Reference No. 48).

airflow through the fill material, or axial fans located on the side of the tower. Natural-draft airflow relies on air currents created by temperature differences between the air in the tower and the atmosphere. When the cooling demands are minimal and the air temperature is low enough, water can be circulated through the tower and cooled sufficiently without using the fans. In these instances, a natural draft is created in the cooling tower.

The direction of the airflow through a mechanical draft tower is either crossflow or counterflow. Crossflow refers to horizontal airflow through the fill, and counterflow refers to upward vertical airflow. Fill material is used to maintain an even distribution of water across the horizontal plane of the tower and to create as much water surface as practical to enhance evaporation and sensible heat transfer.

3.2.2 POTENTIAL EMISSION REDUCTION TECHNIQUES

Techniques to control chromium emissions from cooling towers involve two different strategies: modification of chromium addition to the recirculating water, and improved reduction of drift. The first technique involves reducing the concentration of chromium in the water treatment program, thereby reducing the concentration of chromium in the drift emitted. The second technique involves retrofitting towers with HEDE's to reduce drift emissions to the lowest possible rate.

3.2.2.1 Alternative Water Treatment Programs Responses to 28 EPA information requests and a survey of the Chemical Manufacturers Association indicate that the average chromate concentration for those IPCT's using chromium-based corrosion inhibitors is 13 ppm.^{43,47} One potential chromium emission reduction technique involves alternative water treatment programs such as programs with lower chromate levels, or nonchromate treatments.

A low-chromate treatment program would reduce Cr⁺⁶ emissions from IPCT's by limiting the chromate concentration in cooling water. Water treatment programs are available that maintain average chromate concentrations of 0.5 to 4 ppm in the recirculating water, but these programs have not always been successful in industrial applications. Low-chromate programs that have provided acceptable results in a number of cases maintain chromate concentrations in the range of 4 to 6 ppm.

Because of NPDES chromium restrictions and other regulations, nonchromium treatments are now more widely used than chromium treatments. The most common nonchromium treatment program is phosphate based, but others include molybdates, zinc, and all-organic treatments (primarily organo-phosphorus compounds). However, these alternative programs may not perform corrosion inhibition functions as well or as cheaply as chromates depending on the individual cooling tower system. The performance of any treatment program is dependent on water quality parameters (pH, alkalinity, hardness, and conductivity) and operating conditions (water temperature, flow velocity, inhibitor concentration, and the presence of contaminants such as H₂S, SO₂, NH₃, and NO₂) that are specific to each cooling system.

3.2.2.2 High-Efficiency Drift Eliminator (HEDE) Retrofits
Water droplets entrained in the air and the dissolved and suspended solids contained in the droplets that are emitted from cooling towers are referred to as drift. Drift eliminators can be installed at the exit of the fill sections to reduce the amount of drift in the exiting airflow. Historically, the purpose of drift reduction has been to alleviate the nuisance deposition of water drift and its dissolved solids on nearby buildings or on personal property such as automobiles. More recently, the concern has focused on the environmental impact caused by the compounds contained in the drift and, thus, on the deposition of these compounds. Drift eliminators are designed with pressure drops lower than those of other air pollution control equipment and rely primarily upon the impaction of water droplets on drift eliminator surfaces to reduce the concentration of drift from the exit air of cooling towers. The drift eliminator blades are configured to force directional changes in the airflow such that the momentum of the water droplets causes them to impinge onto the blade surfaces. The number of directional airflow changes, the spacing between the blade surfaces, the angle of directional change, and the capability to return the collected water to a quiescent area of the plenum are the major design features (parameters) in drift eliminators that affect efficiency. Drift eliminators are constructed of wood, PVC, metal, asbestos-cement, polystyrene, or cellulose. The material most often specified is PVC.

Figure 3 presents schematics of the three major drift eliminator designs: herringbone (blade-type), waveform, and cellular (or honeycomb). Low-efficiency drift eliminators (LEDE's) include herringbone, some waveform (sinusoidal), and some cellular designs. Herringbone designs are constructed to create two or three major directional changes in the airflow. The blades are sloped in opposing directions in a manner that provides drainage of the accumulated drift into the fill area. The blades typically are constructed of wood, but other materials (e.g., metal and asbestos cement board) also are used. Waveform drift eliminators are configured in a sinusoidal wave pattern such that two major directional changes in the airflow are created. The sinusoidal blades are constructed of asbestos cement board or PVC material. Cellular drift eliminators are configured with thinner blades in a honeycomb pattern. The airflow passages in the cellular drift eliminators, which are narrower than those of other designs, reduce the distance a droplet must travel across the stream to impact on the surface. Drainage of the collected water to prevent reentrainment is not a design criteria of LEDE's.

High-efficiency drift eliminators include a few of both cellular and sinusoidal designs. The cellular HEDE's that achieve the higher efficiencies are designed with complex configurations that contain numerous, closely constructed airflow passages. Thin materials of construction are used to reduce the area of blockage to the airflow and minimize the pressure drop that is created by the eliminator. For sinusoidal drift eliminators, the blades are placed closer together in high-efficiency designs than in low-efficiency designs, and the exit is configured with a tip for draining captured water that normally is partially reentrained in the airflow. Typically, drainage of water into a quiescent area of the tower is a major design consideration of HEDE's. A few drift eliminators installed in towers built in recent years are more likely to be higher efficiency waveform or cellular units, but the vast majority of older towers still have lower efficiency herringbone and waveform eliminators.

The performance of a drift eliminator is affected primarily by the droplet or particle size and the airflow velocities through the drift eliminator. Small droplets are created both from evaporation of

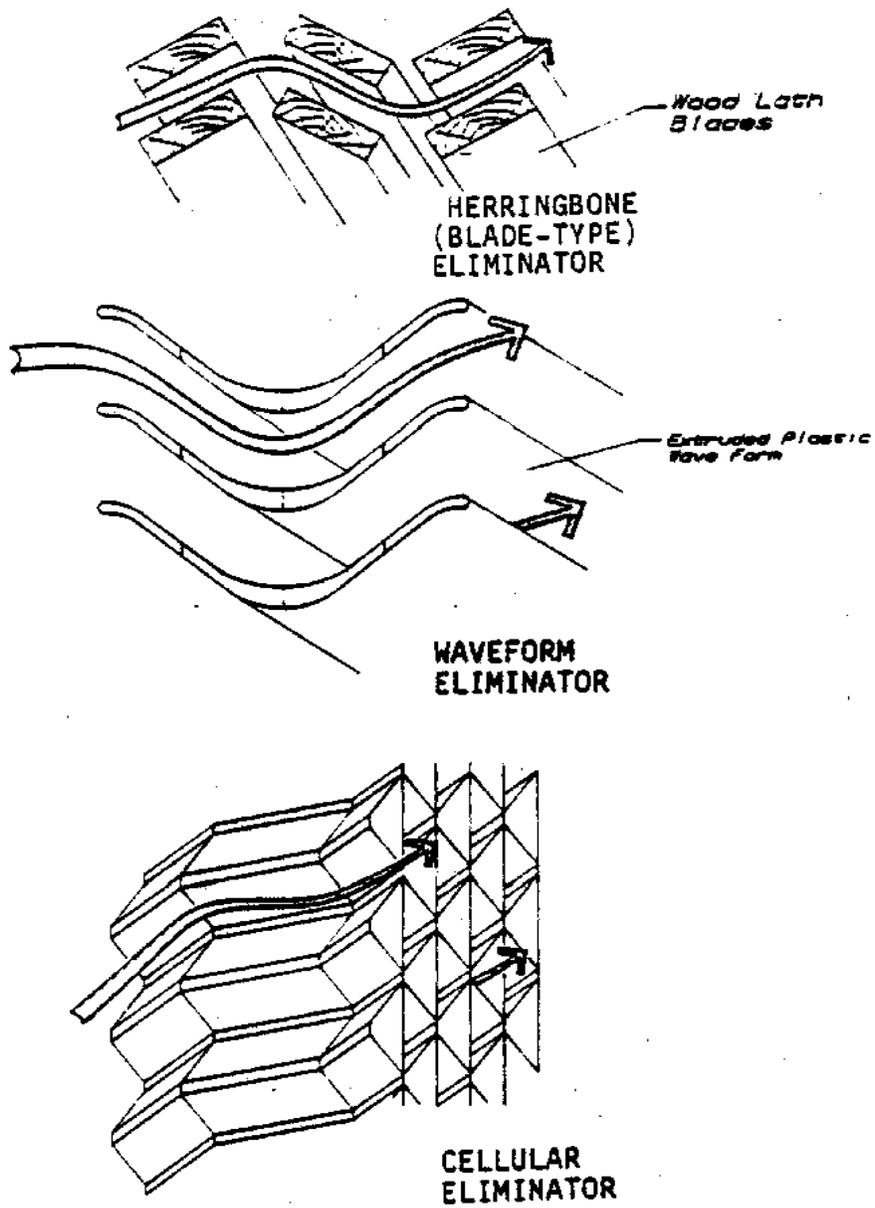


Figure 3. Designs of various drift eliminators (reprinted from Reference No. 50).

larger droplets and the physical breakage of larger droplets into small droplets. Parameters that affect the rate of evaporation and the size of droplets created include the water distribution system, the type of fill, the type of tower, the meteorological conditions, and the temperature of the recirculating water.

A drift eliminator manufacturer indicates that HEDE's can remove 80 to 90 percent or more of the drift discharged from low-efficiency herringbone drift eliminators.^{48,49} These drift eliminator efficiencies, however, are based on data collected with a test method that has not been submitted to EPA for approval.

3.2.3 Cooling Tower Emissions

Three series of emission tests were conducted by EPA on IPCT's equipped with low- and high-efficiency drift eliminators. The results of these tests are presented in the next section.

3.2.3.1 Drift and Chromium Emissions. The drift rate (rate of water lost as drift) is often expressed as the percentage of the recirculating water flow rate that is emitted. Likewise, the chromium emission rate can be expressed as a percentage of the recirculating chromium rate. However, the chromium emission rate from towers should not be confused with the drift rate. Based on test results, a drift eliminator manufacturer claims that the achievable drift rates range from 0.001 to 0.02 percent of the recirculating water. The approximate dividing line between drift rates for higher and lower efficiency drift eliminators is 0.008 percent. Those achieving a lower percentage are "higher efficiency," and those that cannot achieve 0.008 percent are "lower efficiency."⁴⁸⁻⁵⁰

One way to estimate drift is to measure emission rate of a salt, like chromium, and assume that the percentage of water emitted as drift is the same as the percentage of the recirculating chromium emitted. However, a claimed drift rate may or may not be related to the chromium emission rate depending on the way the drift rate was measured. Also, it is important to note that drift rate measurement results are highly dependent on the measurement method; therefore, achievable drift rate claims may not be comparable if they are based on different measurement methods.

The EPA-sponsored emission tests of IPCT's at three facilities used an EPA-developed isokinetic test method. Emission factors relating the chromium emission rate to the chromium recirculation rate were developed from each of these emission tests. The average baseline (LEDE) and controlled (HEDE) Cr⁺⁶ emission factors for each test site are presented in Table 12. The emission factors express the chromium emission rate as a percentage of the chromium recirculating rate. The percentage is equivalent to milligrams of chromium emitted per milligram of chromium recirculating in the tower multiplied by 100. It is important to note that the most comprehensive emission tests were conducted at Plant B. At this plant two towers of similar design located side-by-side were tested simultaneously under the same meteorological conditions. One tower was equipped with an LEDE and the other was equipped with an HEDE. Thus, the tests at Plant B provide the best available data on the relative performance of LEDE's and HEDE's. The EPA Method 13-type testing at Plant B indicated a Cr⁺⁶ emission factor of 0.027 percent of the recirculating Cr⁺⁶ for LEDE's and 0.0087 percent for HEDE's. As discussed in Section 3.2.1.2, these factors can be used for both IPCT's and CCT's.

The EPA Method 13 test data represent the best known estimates of cooling tower emission factors. The current factors are based on the assumption that the ratio of hexavalent to total chromium in the emissions is the same as that in the cooling water. The test program conducted by the Agency has not conclusively identified the speciation of emissions (i.e., Cr⁺⁶ versus Cr⁺³). For purposes of estimating Cr⁺⁶ emissions, the conservative assumption is that all of the chromium is Cr⁺⁶.

3.2.3.2 Sample Calculation of Chromium Emissions. The chromium emission rate for any tower can be estimated by multiplying the emission factor by the recirculating rate of water and the chromium concentration in the recirculating water as shown in Equation (1).

$$E_{Cr} = K \times R \times C_{Cr} \quad (1)$$

where:

E_{Cr} = chromium emission rate, mg Cr/min

K = chromium emission factor, percent of recirculating chromium that is emitted

R = recirculating rate of cooling water, liters/min

TABLE 12. COOLING TOWER EMISSION FACTORS FOR Cr⁺⁶ FROM EPA-SPONSORED TESTS ⁵¹⁻⁵³

Test site	Sampling method ^a	Minimum	Maximum	Average	Standard deviation
<u>Baseline emission factor (low-efficiency drift eliminators)^b</u>					
Plant A ^c	EPA	0.0039	0.068	0.032	0.026
Plant B	EPA	0.0098	0.075	0.027	0.017
Plant B	CTI	0.0072	0.055	0.027	0.017
<u>Controlled emission factor (high-efficiency drift eliminators)^b</u>					
Plant A ^c	EPA	0.0019	0.0068	0.0037	0.0018
Plant B	EPA	0.0032	0.019	0.0087	0.0037
Plant B	CTI	0.0012	0.011	0.0044	0.0030
Plant C	EPA	0.0010	0.013	0.0038	0.0041

^a EPA: EPA modified Method 13 isokinetic train (EPA-sponsored test).

CTI: Cooling Tower Institute isokinetic train (EPA-sponsored test).

^b Chromium emission rate expressed as a percentage of the recirculating chromium that is emitted.

^c Some of the results from this test were suspect because of their extreme variability and, thus, were not used to determine this emission factor.

C_{Cr} = concentration of chromium in the recirculating water, mg Cr/liter = ppm (for an average concentration of 13 ppm chromate [CrO_4], this equals 5.83 ppm Cr)

For example, the following calculation estimates the emissions from a 10,000 gallons per minute (gal/min) IPCT with a recirculating chromate concentration of 10 parts per million (ppm), equipped with a low-efficiency drift eliminator.

$$R = (10,000 \text{ gal/min})(3.785 \text{ liters/gallon}) = 37,850 \text{ liters/minute}$$

$$C_{Cr} = 10 \text{ ppm as } CrO_4 = 4.48 \text{ ppm Cr}$$

K = the emission factor for towers with low-efficiency drift eliminators; use K = 0.027 percent.

$$E_{Cr} = K \times R \times C_{Cr} = (0.027\%)(37,850)(4.48) = (0.00027)(37,850)(4.48) = 45.8 \text{ mg Cr emitted/min}$$

To estimate the emissions from the same IPCT equipped with a high-efficiency drift eliminator, use K = 0.0087.

Therefore:

$$E_{Cr} = K \times R \times C_{Cr} = (0.0087\%)(37,850)(4.48) = (0.000087)(37,850)(4.48) = 14.8 \text{ mg Cr emitted/min}$$

Thus, the emission reduction achieved by a HEDE compared to a LEDE is:

$$\frac{45.8 - 14.8}{45.8} \times 100 = 68 \text{ percent.}$$

The following example calculation estimates the emissions from a 500 gal/min CCT with a recirculating chromate concentration of 10 ppm, equipped with a low-efficiency drift eliminator.

$$R = (500 \text{ gal/min})(3.785 \text{ liters/gal}) = 1,892.5 \text{ liters/min}$$

$$C_{Cr} = 10 \text{ ppm as } CrO_4 = 4.48 \text{ ppm Cr}$$

K = 0.027 percent

$$E_{Cr} = K \times R \times C_{Cr} = (0.027\%)(1,892.5)(4.48) = (0.00027)(1,892.5)(4.48) = 2.3 \text{ mg Cr emitted/min}$$

3.2.4 Nationwide Emission Distribution by Industry

In developing the NESHAP for chromium emissions from IPCT's, EPA has generated industry-by-industry estimates of the total number of cooling towers, the number of towers using chromate treatments, and chromium emissions. Table 13 presents these estimates as currently known. The data show that the industries of greatest concern are chemical manufacturing (43 Mg/yr [47.5 tons/yr]), petroleum refining (31.8 Mg/yr [35.1 tons/yr]), and primary metals production (8.4 Mg/yr [9.3 tons/yr]). Together these industries represent 98.2 percent of nationwide chromium emissions from IPCT's.⁴³ Table 13 also presents nationwide estimates of chromium emissions from CCT's.

TABLE 13. NATIONWIDE COOLING TOWER CHROMIUM EMISSIONS SUMMARY⁴³

Industry	Total No. of cooling towers	No. of cooling using chromate	Cr ⁺⁶ emissions ^a	
			Mg/yr	Tons/yr
Chemical manufacturing	5,096	2,039	43.13	47.54
Petroleum refining	680	476	31.82	35.08
Primary metals	1,118	224	8.39	9.25
Tobacco products	336	16	0.23	0.26
Tire and rubber	267	40	0.18	0.20
Textile finishing	1,018	51	0.08	0.09
Glass manufacturing	58	3	0.01	0.01
Utilities	775	6	0.95	1.05
Subtotal (IPCT only)	9,348	2,855	84.8	93.5
Comfort cooling tower	250,000	37,500	7.2-206	8-227
TOTAL	259,350	40,360	92-291	102-320

^a Based on use of low-efficiency drift eliminators.

SECTION 4.0 SOURCE TEST PROCEDURES

4.1 CHROMIUM ELECTROPLATING

During the standards support study for hexavalent chromium emissions from hard and decorative chromium electroplating facilities, samples to be analyzed for hexavalent and total chromium were obtained in accordance with EPA Method 5 (40 CFR Part 60-Appendix A), also referred to as Modified Method 13-B in test reports. The only modification to the sample collection method was the elimination of the filter and the replacement of H₂O in the impingers with 0.1 Normal sodium hydroxide. Method 5 provides detailed procedures and equipment criteria and other considerations necessary to obtain accurate and representative emission samples.

After collection, the samples were analyzed for hexavalent and total chromium (total chromium is the sum of hexavalent chromium plus other chromium). Concentrations of hexavalent chromium were determined using spectrophotometric analysis while total chromium was determined using inductively coupled argon plasmography (ICAP). At the present time, sample analysis has been performed in accordance with the tentative method "Detection of Hexavalent Chromium from Stationary Sources (December 13, 1984)," and a draft method: "E.P.A. Protocol for Emission Sampling for Both Hexavalent and Total Chromium (February 22, 1985)."

4.2 COOLING TOWERS

During the standards support study for chromium emissions from cooling towers, testing was conducted according to two draft test methods developed from previously conducted methods development testing: "Method ___--Determination of Chromium Emissions from Cooling Towers" and "Method ____--Direct Measurement of Gas Velocity and Volumetric Flowrate Under Cyclonic Flow Conditions (Propeller Anemometer)." The cooling tower method is similar to EPA Method 13 (40 CFR Part 60-Appendix A) with the following exceptions: (1) a Teflon[®] filter is used in place of a paper filter, (2) a propeller anemometer is used in place of the pitot tube for gas velocity and flowrate measurements, (3) the determination of the measurement site does not follow EPA Method 1, and (4) the chemical analysis for total chromium in the emission samples is performed using Neutron Activation Analysis

(NAA), Graphite Furnace Atomic Absorption (GFAA), or ICAP. In conjunction with the emissions testing, representative cooling tower water samples were collected to determine the ratio of hexavalent-to-total chromium in the cooling water; these were analyzed for total chromium by NAA, GFAA, or ICAP and for hexavalent chromium by the diphenylcarbazide colorimetric method (in "EPA Draft Method-Determination of Hexavalent Chromium Emissions from Stationary Sources," December 13, 1984). The ratio was used to calculate the amount of hexavalent chromium in the cooling tower emissions.

Preliminary material balance calculations were performed on the cooling water at several towers to compare the apparent chromium loss in the drift emissions with the emission measurements obtained during the standards support study. Variables used in these calculations included: cooling water flow rates to the towers, riser cells, and/or fan cells; blowdown rates; makeup water flow rates; addition(s) of chemicals to the cooling water; and chemical analysis of the cooling water samples taken during testing.

Two major modifications were made to the draft test method for cooling towers based on problems encountered and knowledge gained during the testing program. Initially, the draft method specified the use of NAA to determine the total chromium content of the impinger train samples and the cooling water samples. Because of the length of time required for sample analysis and the limited availability of commercial NAA services, two additional analytical techniques, GFAA and ICAP, were utilized and were added as options to the draft test method. Unlike NAA, both of these techniques require acid solubilization of the chromium in the sample prior to analysis. In assessing the chromium recovery efficiency for the concentrated impinger samples from the first test, it was discovered that a significant residue remained in the beakers used to concentrate the samples. The concentration procedure was modified to require an acid rinse of the beakers used for sample concentration with the rinse being added to the concentrated sample.

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