

## Appendix E: Concept Paper for Changes to Rule 11-10: Cooling Towers

### Rules to Be Amended or Drafted

Regulation of organic gases and toxic air contaminants from cooling towers at refineries requires amendment to Air District Regulation 11, Rule 10, *Hexavalent Chromium Emissions from Cooling Towers* which will be renamed *Toxic and Organic Emissions from Cooling Towers*.

### Goals

The goal of this rulemaking is to achieve technically feasible and cost-effective total hydrocarbon (THC) and hazardous air pollutants emission reductions from cooling towers at Bay Area refineries by requiring more rapid detection of heat exchanger leaks.

### Background

The Bay Area has five large-scale petroleum refineries which operate a total of 34 cooling towers. These cooling towers are large, industrial heat exchangers that are used to dissipate significant heat loads to the atmosphere through the evaporation of water. When heat exchanger leaks go undetected for long periods of time, significant quantities of organic compounds can be stripped from the cooling tower water and emitted to the atmosphere.

### Process and Source Description

Cooling towers are part of a heat exchange system consisting of a device or a collection of devices used to transfer heat from process fluids to water without intentional direct contact of the process fluid with the water and to transport and/or cool the water in a closed-loop system (cooling tower system). Figure E1 (below) depicts a basic cooling tower structure.

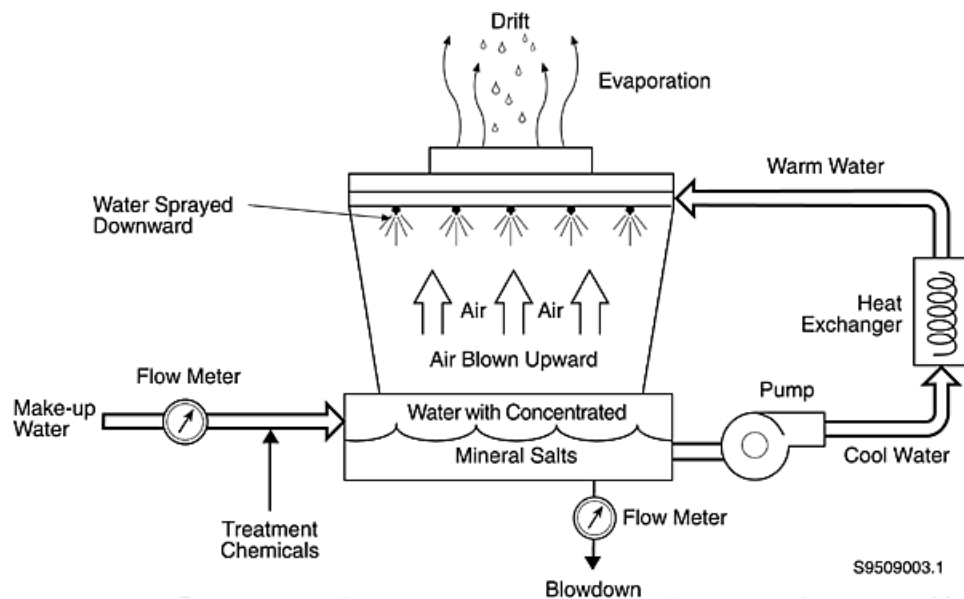


Figure E1 – Cooling Tower

Cooling towers can be designed as either natural draft or mechanical draft devices. Natural draft cooling towers are large hyperbolic structures that look similar to those found at nuclear power plants. They use natural convection of warmed air to create air to cool the water. Mechanical draft cooling towers use large fans to force air either through or across the water to cool it.

Regardless of the design, a small proportion of the cooling water is entrained in the updraft as mist, commonly called *drift*. When the water in the droplets evaporates, any dissolved solids in the cooling water form particulate matter.<sup>1</sup>

When heat exchanger leaks occur, emissions result due to the volatilization of hydrocarbons and/or HAPs in the contaminated water. Such leaks tend to occur when heat exchanger tube sheets fail or when tubes rupture as a result of corrosion or the use of inferior materials during the exchanger construction process.

Emissions resulting from leaks can become significant if heat exchanger leaks go undetected for long periods of time. In 2010 a heat exchanger leak at a Bay Area refinery resulted in emissions of at least 52 tons of VOC over a recorded period of a few weeks. The total magnitude of emissions from the leak event may have been even greater because the facility was not able to substantiate the amount VOC of emissions from the cooling tower's heat exchanger system during the first several months of the event.

### **Regulatory History and Context**

District Regulation 11, Rule 10 was developed in 1989 to reduce hexavalent chromium emissions from cooling towers.

In 2009, The U.S. Environmental Protection Agency (EPA) promulgated, and in 2013 amended, 40 CFR part 63, subpart CC, *National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries (MACT CC)*. Section 63.654 in MACT CC requires periodic monitoring (monthly or quarterly) of heat exchangers in organic hazardous air pollutant (HAP) service within the heat exchange system for leaks of organic gases, unless:

- the minimum pressure on the cooling water side is at least 35 kilopascals (5.1 psi or 10 inches of mercury) greater than the maximum pressure on the process side, or
- if an intervening fluid containing less than 5 percent by weight of organic HAP is employed between the process fluids and cooling water (provided the intervening fluid is used solely to isolate the process fluids & cooling water and is not sent through the cooling tower or discharged).

Once discovered, MACT CC requires leaks to be repaired as soon as practicable.<sup>2</sup> Unless applicability criteria set forth in Section 63.654 are met, not all cooling towers are subject to the monitoring, leak, and repair requirements of MACT CC.

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<sup>1</sup> Cooling tower water frequently contains additives such as biocides, anti-foaming agents and anti-scaling agents, any of which could be emitted as particulate matter

<sup>2</sup> ... but no later than 45 days after detecting the leak, unless the repair is not feasible.

## Emissions

There are five large-scale petroleum refineries within the Air District's jurisdiction that operate a total of 34 permitted cooling towers. The number of cooling towers per facility varies. One refinery has only one cooling tower while another has 13 permitted cooling towers. Based on the 2013 Air District emissions inventory, the cooling towers collectively emitted approximately 1.6 tons per day (TPD) of organic gases, estimated using AP-42 emission factors.<sup>3</sup>

### Regulatory Concepts and Proposed Regulations

Cooling Tower Emissions have been addressed by the Texas Commission on Environmental Quality (TCEQ). The TCEQ developed Chapter 115 – Control of Air Pollution from Volatile Organic Compounds, SUBCHAPTER H: HIGHLY-REACTIVE VOLATILE ORGANIC COMPOUNDS to address Highly Reactive Volatile Organic Compound (HVOCs) emissions from industrial cooling towers. As part of their strategy to better control HVOC emissions, the TCEQ modified a water sampling technique known as the Texas El Paso Method, now referred to as the Modified El Paso Method (MEPM), and required Texas petroleum refineries to use the MEPM to detect strippable hydrocarbons from leaking cooling tower heat exchange systems.<sup>4</sup>

The Texas El Paso Method, developed in the 1970's employs a "dynamic" or "flow-through" system for air stripping a sample of cooling tower water and analyzing the resultant off-gases for VOCs using a common flame ionization detector (FID) analyzer. The TCEQ developed the MEPM to concentrate on the measurement strippable hydrocarbons, compounds with lower molecular weights and boiling points that are generally lost when sampled for purge/trap analyses. When the MEPM is applied, a continuous stream of water is sampled directly into an air stripping column apparatus. Air flowing countercurrent to the water strips HVOCs from the water for analysis.

The Air District's staff is concerned about the MEPM sampling method's ability provide representative hydrocarbon emissions data on a consistent basis. Staff prefers continuous hydrocarbon analysis as a method of acquiring cooling tower water emissions data. Such a device is already in use in at two Bay Area refineries: Chevron and Shell. However, Air District staff will consider MPEM and other methods if the refineries are able to demonstrate that they provide comparable data and consistent results. Staff is seeking comment on this issue.

Regulation 8, Rule 2, Section 114 states that "Emissions from cooling towers, railroad tank cars, marine vessels and crude oil production operations are exempt from this Rule, provided best modern practices are used." Although Regulation 1, Section 207 defines *best modern practices* as "The minimization of emissions from equipment and operations by the employment of modern maintenance and operating practices used by superior operators of like equipment and which may be reasonably applied under the circumstances," it is too generic of a definition for cooling tower operations.

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<sup>3</sup> AP-42, *Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources*, Fifth Edition, January, 1995, Table 5.1-2

<sup>4</sup> The MEPM is the basis for the monitoring required by U.S. EPA in § 63.654.

Regulation 11, Rule 10 is now proposing a cooling tower-specific definition. For this concept paper version of the draft rule, Staff has compiled examples of best practices from several sources. Air District staff recognizes that some of the proposed “best modern practices” could be redundant in cases where a cooling tower has a continuous hydrocarbon analyzer installed.

Elements to be added to Regulation 11, Rule 10 are as follows:

1. The elements of the petroleum refinery cooling tower regulation will be incorporated into an existing regulation that was adopted in 1989 to limit hexavalent chromium emissions from all Bay Area cooling towers that were subject to the provisions of the rule. The regulation’s description will be modified to include NMOC emissions from petroleum refinery cooling towers.
2. Regulation 8, Organic Compounds, Rule 2: *Miscellaneous Operations* exempts cooling tower emissions provided Best Modern Practices are used. Regulation 11, Rule 10 will define Best Modern Practices and will require refinery staff to take steps to ensure heat exchanger equipment is kept corrosion free and in good working order; to make visual and odor inspections on a regular basis; to perform surrogate testing, such as residual chlorine measurements every shift, and to track the amount of biocide added to cooling tower water on a daily basis to maintain water chemistry. As mentioned above, staff welcome’s comment on how to best craft this particular provision to avoid redundancy while ensuring timely detection and repair of heat exchanger leaks.
3. The regulation will also require each cooling tower to use parametric monitors to measure cooling tower water hydrocarbon concentrations on an ongoing basis. Refineries must comply with applicable requirements for parametric monitors specified in Regulation 1, Section 523, unless an alternative sampling method has been approved by the APCO.
4. The regulation will include an NMOC concentration standard of 84 ppb (by weight) in the water of existing cooling towers and a 42 ppb concentration for new cooling towers. When either of these NMOC standards is exceeded, a leak action response will be required.
5. The refinery shall be required to minimize the leak within 3 calendar days and shall repair the leak within 14 days.
6. If the refinery cannot comply with either requirement, it must submit a report to the APCO to substantiate their reasons and also provide a repair plan with an estimated completion date for the leak repair. Detailed diagrams and technical data must be included with the report.
7. Regulation 11, Rule 10 would also include detailed recordkeeping requirements.

Staff proposes that the new requirements in Regulation 11, Rule 10 go into effect on July 1, 2016

### **Control Mechanisms**

No additional controls are proposed, only additional monitoring and more frequent repair.

### **Costs and Emissions Reductions**

Estimated emission reductions are based on implementing a total hydrocarbon concentration standard (for hydrocarbons in cooling tower water) equivalent to the EPA controlled emission factor of 0.7 lbs of

hydrocarbons emitted for every million gallons of recirculated water. The table below lists the estimated total amortized cost (over ten years), total annual cost (capital plus operating), and emission reductions for each petroleum refinery to purchase and install continuous hydrocarbon analyzers for their cooling towers.

Capital costs in the table above do not include a probable discount for the cost to purchase multiple analyzers nor does do the costs include the savings refineries will incur from saving product that would have otherwise escaped during drift loss from the cooling tower. The figure for saved product is yet to be calculated. Therefore, the costs stated in the table are likely somewhat conservative.

<b>Facility</b>	<b>VOC Emissions Reduction (tpy)</b>	<b>Capital Cost (\$/yr)</b>	<b>Total Annualized Cost (\$ M)</b>
Chevron	239.4	\$35,000	\$59,000
Shell	227.6	\$14,000	\$26,000
Tesoro	36.3	\$60,000	\$99,000
Phillips 66	4.3	\$35,000	\$56,000
Valero	9.3	\$35,000	\$38,000

**REGULATION 11  
HAZARDOUS POLLUTANTS  
RULE 10  
HEXAVALENT CHROMIUM EMISSIONS FROM COOLING TOWERS AND  
TOTAL HYDROCARBON EMISSIONS FROM PETROLEUM REFINERY  
COOLING TOWERS**

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**REGULATION 11  
HAZARDOUS POLLUTANTS  
RULE 10**

**HEXAVALENT CHROMIUM EMISSIONS FROM COOLING TOWERS AND NON-METHANE  
ORGANIC CARBON EMISSIONS FROM PETROLEUM REFINERY COOLING TOWERS**

(Adopted November 15, 1989)

**11-10-100 GENERAL**

**11-10-101 Description:** The purpose of this Rule is to reduce emissions of hexavalent chromium from cooling towers by eliminating chromium based circulating water treatment programs. In addition to the above, this Rule will also reduce total hydrocarbon (THC) emissions from cooling towers operating at, and establishes best modern practices for the control of THC emissions from, petroleum refinery cooling towers.

**11-10-102 Exemption, Discontinued Chromate Treatment:** Sections 11-10-502 and 503 do not apply to cooling tower operators who have not used hexavalent chromium for water treatment since March 1, 1989.

**11-10-103 Exemption:** Fin-fan coolers and cooling towers used exclusively in heating, ventilating, and air conditioning systems are exempt from the THC requirements of this Rule.

**11-10-200 DEFINITIONS**

**11-10-201 Best Modern Practices:** The minimization of emissions from equipment and operations by the employment of modern maintenance and operating practices used by superior operators of like equipment and which may be reasonably applied under the circumstances.

**11-10-202 Continuous Total Hydrocarbon Analyzer:** An Air District-approved parametric monitoring device that measures total hydrocarbon vapor concentration in cooling tower water to detect process fluids leaks from the heat exchange system.

**11-10-203 Cooling Tower:** ~~Any open water recirculation device that uses fans or natural draft to draw or force air to contact and cool water by evaporation.~~ A device used to remove the heat absorbed in circulating cooling water systems by transferring the heat to the atmosphere using natural or mechanical draft.

**11-10-204 Existing Cooling Tower:** A cooling tower built prior to July 1, 2016.

**11-10-205 Hexavalent Chromium/Chromate:** Hexavalent chromium is a cancer-causing (toxic) substance existing as part of various inorganic chromate compounds, for example, sodium dichromate or lead chromate.

**11-10-206 Leak Action:** A THC concentration greater than 84 parts per billion by weight (ppbw) as measured by a continuous total hydrocarbon analyzer for cooling towers operating prior to July 1, 2016. Cooling towers constructed after July 1, 2016, shall be subject to a THC leak action level of 42 ppbw.

**11-10-207 Leak Repair:** A leak repair shall reduce the concentration of THC in cooling tower water to comply with the applicable standard in Section 11-10-305, and may include but is not limited to the following actions:

207.1 Physical modifications to the leaking heat exchanger, such as welding the leak or replacing a tube; blocking the leaking tube within the heat exchanger;

207.2 Changing the pressure so that water flows into the process fluid;

207.3 Replacing the heat exchanger or heat exchanger bundle; or isolating, bypassing, or otherwise removing the leaking heat exchanger from service until it is otherwise repaired.

**11-10-208 New Cooling Tower:** A cooling tower constructed on or after July 1, 2016.

**11-10-209 Petroleum Refinery:** An establishment that is located on one or more contiguous or adjacent properties, and under common control, and that processes crude oil to produce more usable products such as gasoline, diesel fuel, aviation fuel, lubricating oils, asphalt or petrochemical feedstocks. Petroleum refinery processes include

separation processes (e.g., atmospheric or vacuum distillation, and light ends recovery), petroleum conversion processes (e.g., cracking, reforming, alkylation, polymerization, isomerization, coking, and visbreaking) petroleum treating processes (e.g., hydrodesulfurization, hydrotreating, chemical sweetening, acid gas removal, and deasphalting), feedstock and product handling (e.g., storage, blending, loading, and unloading), and auxiliary facilities (e.g., boilers, waste water treatment, hydrogen production, sulfur recovery plant, cooling towers, blowdown systems, compressor engines, and power plants).

**11-10-210 Petroleum Refinery Cooling Tower Heat Exchange System:** A device or collection of devices used to transfer heat from process fluids to water without intentional direct contact of the process fluid with the water (i.e., noncontact heat exchanger) and to transport and/or cool the water in a closed-loop recirculation system (cooling tower system). For closed-loop recirculation systems, the heat exchange system consists of a cooling tower, all petroleum refinery process unit heat exchangers serviced by the cooling tower, and all water lines to and from these petroleum refinery process unit heat exchangers. Sample coolers or pump seal coolers are not considered heat exchangers for the purpose of this definition and are not part of the heat exchange system.

**11-10-211 Petroleum Refinery Heat Exchanger:** A device consisting of fins and/or tubes that is used to transfer heat from process equipment or process fluid streams to cooling water.

**11-10-212 Petroleum Refinery Owner/Operator:** Any person who owns, operates, or exercises operational control over the majority of operations at a petroleum refinery. The refinery owner/operator is responsible for compliance this rule for the entirety of the petroleum refinery, including any refinery processes or auxiliary facilities that may be separately owned or operated. Any person who owns, operates, or exercises operational control over a portion of a petroleum refinery that is less than a majority of the total refinery operations must provide the Owner/Operator with information sufficient to allow the owner/operator to comply with this rule, and must make that information available to the APCO upon request.

**11-10-214 Responsible Manager:** An employee of the facility or corporation who possesses sufficient authority to take the actions required for compliance with this rule.

**11-10-213 Total Hydrocarbon (THC):** Any compound of carbon excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate.

**11-10-203<sup>5</sup> Water Treatment Chemicals:** Any combination of chemicals added to cooling tower water including tracers, corrosion inhibitors, antiscalants, dispersants, biocide.

## **11-10-300 STANDARDS**

**11-10-301 Hexavalent Chromium Removal:** Effective March 1, 1990, a person shall not operate any cooling tower in the Air District using hexavalent chromium chemicals.

**11-10-302 Circulating Water Concentration-Wooden Cooling Towers:** Effective March 1, 1990, a person shall not operate a wooden cooling tower in the Air District unless the following requirements are met:

302.1 March 1, 1990 to September 1, 1990: Hexavalent chromium levels in the circulating water are not to exceed 8 milligrams/liter of circulating water

302.2 After September 1, 1990: Hexavalent chromium levels in the circulating water are not to exceed 0.15 milligrams/liter of circulating water.

**11-10-303 Circulating Water Concentration-Non-Wooden Cooling Towers:** Effective March 1, 1990, a person shall not operate a non-wooden cooling tower unless the hexavalent chromium levels do not exceed 0.15 milligrams/liter of circulating water.

**11-10-304 Continuous THC Analyzer Installation Requirement:** Effective July 1, 2016, the owner/operator of a petroleum refinery cooling tower shall install and continuously measure and monitor the THC concentration in cooling tower water with at least one (1) continuous hydrocarbon analyzer(s) per tower. The location of the analyzer installation shall be subject to APCO approval. The analyzer shall be maintained and operated in accordance with Regulation 1, Section 523: Parametric Monitoring and Recordkeeping Procedures, Sections 1-523.1, 523.2, 523.4 and 523.5. The



owner/operator may request APCO approval, in writing, of an alternative THC measurement method if the owner/operator can demonstrate equivalency.

**11-10-305 Leak Action Level:** Effective July 1, 2016, if cooling tower water measured by the owner/operator in accordance with the requirements in Section 11-10-304 has a THC concentration greater than 84 ppbw for existing cooling towers, or greater than 42 ppbw for new cooling towers, the owner/operator shall comply with all of the following requirements:

- 305.1 Minimize the leak as soon as practicable or within three-calendar days, whichever is sooner, and repair the leak within 14-calendar days.
- 305.2 If the leak cannot be minimized with three calendar days, or if the leak cannot be repaired within 14 calendar days because the necessary equipment or parts, are not available, or if repairs to the heat exchange system are not technically feasible without shutting down the process operation, the owner/operator must substantiate their findings to the APCO's satisfaction within 5 calendar days from the day the leak was initially detected and provide the APCO with an estimated date for completion of the leak repair.
- 305.3 The information provided to the APCO as required by Section 11-10-305.2 shall be certified and signed by a Responsible Manager and shall include, but shall not be limited to, the following technical data:
  - 3.1 A detailed process flow diagram and associated piping and instrumentation diagrams (P&IDs) that accurately depict all process units and heat exchange systems serviced by the cooling tower and the cooling tower's circulation pumps. The information provided shall include full and accurate as-built dimensions and design capacities.
  - 3.2 A root cause analysis explaining the source and magnitude of the leak, reasons explaining why the leak cannot be minimized and/or repaired, furnish correspondence from vendors/contractors that explain why the required materials cannot be procured and supplied in time, and provide explicit dates and milestones indicating when the leak will be repaired.
- 305.4 The Air District shall reply to the owner/operator's request to extend the leak minimization deadline or the leak repair deadline, in writing, within five calendar days upon receipt of the owner/operator's extension request.
- 305.5 If the Air District denies the owner/operator's request to extend the leak minimization deadline or the leak repair deadline, the owner/operator shall repair the leak within 14 days from the date the leak was first detected.

**11-10-306 Best Modern Practices:** Effective July 1, 2016, the owner/operator shall minimize THC emissions from cooling tower equipment and operations by employing best modern practices that shall include:

- 306.1 Use of an Air District approved continuous total hydrocarbon analyzer in the cooling tower return line or any representative riser within the cooling tower to measure THC vapor concentration in cooling tower water prior to exposure to air;
- 306.2 Close examination of all heat exchangers upstream of the cooling tower during turnaround for corrosion/damage and back flushing if required;
- 306.3 Repassivation of the steel contained in the heat exchangers during turnaround;
- 306.4 Seal tubes within the heat exchangers if there is evidence of corrosion or pitting during turnaround;
- 306.5 Perform daily visual observations, at least once every eight (8) hours, of the cooling water to detect any changes in the appearance of the water that could indicate hydrocarbon contamination and confirm presence of microbial growth;
- 306.6 Monitor cooling tower decks daily, at least once every eight (8) hours, if access to the decks is possible, to detect any unexpected odors from the water;

- 306.7 Measure the residual chlorine in the cooling tower water once every eight (8) hours;
- 306.8 Use hand-held monitors, such as PIDs or FIDs, once every eight (8) hours, to detect the presence of hydrocarbons in the air above the cooling tower water;
- 306.9 Measure the oxidation reduction potential in the cooling tower water with hand-held monitors;
- 306.10 Routinely track and record the amount of chlorine (or biocide) added to the cooling tower water on a daily basis;
- 306.11 Measure the pH and iron concentration in the cooling tower water with hand-held monitors on a daily basis; and
- 306.12 Data collected pursuant to Sections 11-10-306.1, 306.7, 306.9, 306.10 and 306.11 shall be retained for at least five (5) years from the date of entry and shall be analyzed by the owner/operator once per week for trends that could serve as an early warning/detection system for potential hydrocarbon leaks.

## **11-10-500 MONITORING, AND RECORDS AND REPORTING**

- 11-10-501 Reporting-General:** By December 1, 1989, any owner/operator of a cooling tower shall notify the [Air](#) District in writing regarding the following information about the cooling tower. After December 1, 1989, any operator/owner of any newly constructed cooling water tower shall provide the APCO with the following information at least 90 days before the tower is operated.
- 501.1 Where the cooling tower is located.
- 501.2 Who is the owner/operator of the tower.
- 501.3 Cooling tower type and materials of construction.
- 501.4 Whether hexavalent chromium based treatment chemicals were used in the cooling tower.
- 501.5 If hexavalent chromium based chemicals were previously used, when they were discontinued.
- 501.6 A description of the alternate treatment program chosen, as well as the circulating water monitoring plan.
- 11-10-502 Monitoring-General:** Effective March 1, 1990, any person subject to Sections 11-10-302 and 303 shall test the circulating water at least once every six calendar months to determine the concentration of hexavalent chromium. The first test shall be performed during March, 1990. Testing may be discontinued when two consecutive required tests show hexavalent chromium concentrations less than 0.15 milligrams per liter of circulating water. The APCO reserves the right to require testing of the circulating water at any time, if the [Air](#) District has reason to believe the water may contain hexavalent chromium.
- 11-10-503 Monitoring-Wooden Cooling Towers:**
- 503.1 March 1, 1990 until September 1, 1990: Any person subject to Section 11-10-302.1 shall test the circulating water at least once every calendar month to determine the concentration of hexavalent chromium.
- 503.2 After September 1, 1990: Any person subject to Section 11-10-302.2 shall test the circulating water at least once every six calendar months to determine the concentration of hexavalent chromium. Testing may be discontinued when two consecutive required tests show hexavalent chromium concentrations less than 0.15 milligrams per liter of circulating water. The APCO reserves the right to require testing of the circulating water at any time, if the [Air](#) District has reason to believe the water may contain hexavalent chromium.
- 11-10-504 Operating Records:** Any person subject to Sections 11-10-302 and 303 shall maintain records of the results of all required tests of circulating water for two years and give them to the [Air](#) District when requested. Refinery owner/operators subject to the provisions of Sections 11-10-304, 305, 507, and 602 shall retain records of all recordings on site for at least five years from the date of entry.

- 11-10-505 Petroleum Refinery Cooling Tower Reporting Requirements:** When the sampling of cooling tower water results in a leak action level the owner/operator shall:
- 505.1 Notify the APCO via fax or email within one (1) day of detecting the leak;
  - 505.2 Record the date, time, and THC concentration of the leak when it was first detected;
  - 505.3 Document the reasons for any delay in repair;
  - 505.4 Provide the APCO with a schedule for completing the repair as soon as practicable
  - 505.5 Record the dates, times, and THC concentrations from the time the leak was first detected until the time the leak is repaired; and
  - 505.6 Provide the APCO with documentation confirming the leak has been repaired and the cooling tower is back in compliance.

**11-10-600 MANUAL OF PROCEDURES**

**11-10-601 Determination of Hexavalent Chromium in Circulating Water:** Samples of circulating water shall be analyzed for hexavalent chromium as prescribed by American Public Health Method 312B or an equivalent method, as approved by the APCO.

**11-10-602 Cooling Tower Water THC Measurement Methodology:** The owner/operator shall analyze, on a continuous basis, cooling tower water at the inlet line and the return line of each cooling tower to determine the THC vapor concentration in each line using an APCO approved continuous hydrocarbon analyzer installed in accordance with Section 11-10-304.