

# **U.S. BEST MANAGEMENT PRACTICES FOR MONITORING AND REDUCING EMISSIONS OF VOLATILE ORGANIC COMPOUNDS: A PETROLEUM REFINERY CASE STUDY**

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## I. Overview of VOC and Petroleum Refineries

Petroleum refineries and petrochemical plants significantly contribute to emissions of volatile organic compounds (VOC) in the United States (US) and across the world. The US Environmental Protection Agency (EPA) has developed numerous regulations with standards specifying requirements for managing VOC from various emission sources within this industry segment. Recently, the USEPA updated the emission standards for certain sources of VOC at petroleum refineries. This paper will provide an overview of the old VOC controls and the new VOC controls included in the rule updates. The petroleum refinery VOC emission standards include emission standards and monitoring requirements that can be applied to VOC emission sources at petrochemical plants and organic chemical manufacturers.

VOC include a wide range of organic chemicals, but it is specifically targeted at a group of compounds which react with oxygen (nitrogen oxides or carbon monoxide) to form ozone.

The USEPA definition is:

*"Volatile organic compounds (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions."*

The USEPA definition has a list of compounds which it has determined to have negligible photochemical reactivity and thus are exempt from applicable VOC regulations.<sup>1</sup> The USEPA definition is similar to the definition included in China's existing emission standard for the petrochemical industry with the exception of the list of compounds specifically exempted.

In addition to regulating VOC from the perspective of forming ozone, there are also regulations targeted at the acute and chronic health impacts of certain compounds referred to as hazardous air pollutants (HAP). HAP present at refineries generally include:

- organic HAP (which are also VOC, e.g., acetaldehyde, benzene, formaldehyde, hexane, phenol, naphthalene, 2-methylnaphthalene, dioxins, furans, ethyl benzene, toluene and xylene)
- reduced sulfur compounds (i.e., carbonyl sulfide, carbon disulfide)
- inorganic HAP (e.g., hydrogen chloride, hydrogen cyanide, chlorine, hydrogen fluoride)

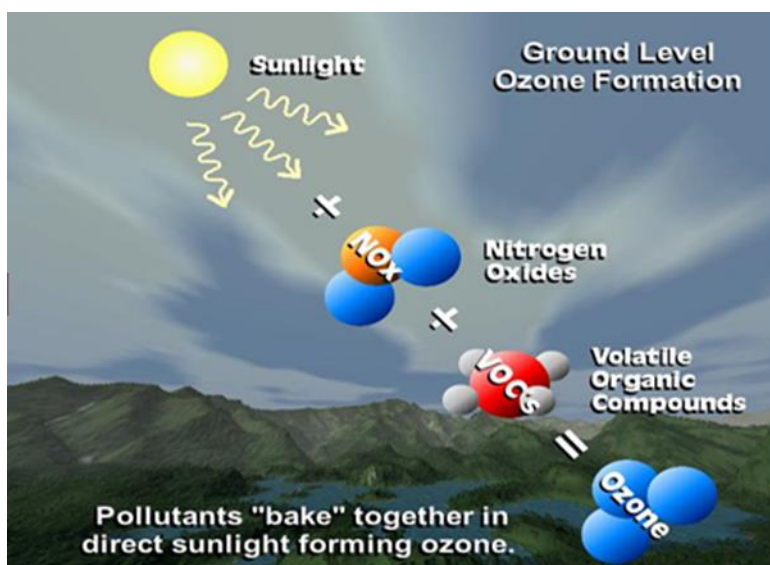


Figure 1. Ground Level Ozone Formation

<sup>1</sup> Methane; ethane; methylene chloride (dichloromethane); 1,1,1-trichloroethane (methyl chloroform); numerous fluorinated gases (CFC, HCFC, HFC, HFE).

- metals (e.g., antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, mercury, manganese and nickel)

HAP present at petrochemical plants include organic HAP, but do not generally include other types of HAP, which are largely from contaminants present in crude oil and are not typically found in the feedstocks sent to the petrochemical plants.

Petroleum refineries and petrochemical plants in the US are subject to regulations for VOC and HAP. The primary sources of VOC at a refinery or petrochemical plant include: miscellaneous process vents, flares, equipment leaks, storage tanks, wastewater treatment and heat exchange systems. For petroleum refineries, benzene is sometimes used as a surrogate for regulating total HAP because it is present in nearly all refinery process streams. Benzene is present in crude oil and gasoline, so most storage tank emission include benzene. Additionally, benzene is also present in wastewater and air emissions from the treatment of wastewater.

## II. Miscellaneous Process Vents

### A. Emission Source Description

Miscellaneous process vents emit gas, either directly to the atmosphere or after passing through a recovery and/or air pollution control device. Some of the vented streams contain HAP and VOC.

These vents include gas streams that are discharged continuously or periodically to either: the atmosphere, a control device prior to discharge to the atmosphere, or which are diverted through a product recovery device prior to discharge to the atmosphere. They can include vent streams from: caustic wash accumulators, distillation tower condensers/accumulators, flash/knockout drums, reactor vessels, scrubber overheads, stripper overheads, vacuum, pumps, steam ejectors, hot wells, high point bleeds, wash tower overheads, water wash accumulators, blowdown condensers/accumulators, delayed coking vents and onstream analyzers. Control requirements apply to vent streams which contain 20 parts per million by volume (ppmv) organic HAP generated and also emit total VOC greater than or equal to 33 kilograms per day (kg/day) for existing sources and 6.8 kg/day for new sources at the outlet of the final recovery device and prior to any control device and prior to discharge to the atmosphere.

These vents do not include emission sources for which there is a separate USEPA standard. The USEPA has separate standards for vents from: pressure relief device discharges, equipment leaks, catalytic cracking unit catalyst regeneration vents, catalytic reformer regeneration vents, sulfur plant vents, vents from control devices including stripping operations, delayed coking unit decoking operations, storage vessels and wastewater treatment.

### B. Old VOC Control Requirements

Under the old standards, miscellaneous process vents must either be vented to a flare or other air pollution control device. The flare or air pollution control device must reduce the organic HAP emissions by 98 weight-percent or to a concentration of 20 ppmv dry basis, corrected to 3-percent oxygen.

## C. New Monitoring and Control Techniques

As noted previously, the USEPA reviewed and updated, as necessary, the old standards for petroleum refineries to provide new VOC monitoring and control techniques. It was determined that the general requirement to route miscellaneous process vents to a flare or other air pollution control device was adequate.

However, the old standards included an exclusion for venting that occurred during periods of startup, shutdown or malfunction. The new VOC monitoring and control techniques now provide standards for vents that are the result of startup, shutdown, maintenance or inspection of equipment. These vents are referred to as maintenance vents. For maintenance vents, prior to venting to the atmosphere, plant operators must remove process liquids to the greatest extent possible, lower the pressure in the equipment and vent gases back to a control device (meeting 98 percent reduction or 20 ppmv concentration), fuel gas system or the process until the one of the following conditions is met:

- The vapor in the equipment served by the maintenance vent has a lower explosive limit of less than 10%; or
- If the lower explosive limit of the vapor cannot be measured, the pressure in the equipment is less than or equal to 5 psig; or
- The equipment serviced by the maintenance vent contains less than 72 pounds of VOC.

The addition of these new monitoring and control techniques ensure that a limit applies at all times including during startup, shutdown, maintenance and inspection.

As detailed in the following section III.C, there are new monitoring and control techniques for flares that will ensure 98 percent control efficiency when a flare is the selected air pollution control device.

## III. Flares

### A. Emission Source Description

Flares are defined as combustion devices which lack an enclosed combustion chamber and that use an uncontrolled volume of ambient air to burn gases. There are four main types of flares: air-assisted flares, steam-assisted flares, pressure-assisted flares, and non-assisted flares. The new requirements for flares specifically address air-assisted, steam-assisted flares, and non-assisted flares, and this section will summarize those requirements. Requirements for pressure-assisted flares are developed on an "as requested" basis. Facilities requesting to use pressure-assisted flares must submit flare design and combustion efficiency test data over a range of operating conditions to demonstrate the appropriate operating range for that specific pressure-assisted flare design.

Nearly every petroleum refinery, petrochemical plant, or organic chemical manufacturer will have at least one flare to control gases released as a result of startup, shutdown or malfunction. A typical petroleum refinery or petrochemical plant has 3 to 4 flares. In addition to emergency release control, flares may be used to routinely control a number of VOC emissions sources. VOC are emitted from flares due to incomplete combustion of the gas sent to the flare. If flare combustion efficiency is low due to poor flare operations, then VOC emissions from flares can be significant.



## B. Old VOC Control Requirements

Under the old standards, flares were required to:

- Be steam-assisted, air-assisted or non-assisted;
- Operate at all times when emissions may be vented to them;
- Be designed for and operated with no visible emissions except a total of 5 minutes during a consecutive 2-hour period;
- Operate with a pilot flame present at all times. The presence of a pilot flame must be monitored using a thermocouple or similar device; and
- Demonstrate initial compliance with minimum heat content and/or maximum tip velocity specifications depending on the type and diameter of the flare.

It was expected that flares meeting these design and operating requirements would be able to achieve 98 weight percent HAP destruction efficiency. However, there were no on-going requirements to demonstrate compliance with the minimum heat content or flare tip velocity limits. Therefore, the primary on-going requirement was to operate with no visible emissions (no black smoke) from the flare. Consequently, plant operators generally added too much assist air or steam to ensure compliance with the no visible emissions requirements. This led to poor combustion efficiency from "over-assisted" flares. Additionally, the old standards did not apply during startup, shutdown or malfunctions.



*Figure 2. Flare Stacks with Visible Emissions*

## C. New Monitoring and Control Techniques

In review of the old standards and resulting flare operations, it was determined that new requirements would be needed to ensure plant operators were minimizing routine flare use, where practical, meeting the HAP destruction efficiency, and minimizing emissions during startup, shutdown and malfunction.

### 1. Flare Management Plan

First, the new standards (under 40 CFR part 60 subpart Ja) require owners or operators of flares to develop and submit a written flare management plan with an assessment of how flare use can be minimized, either at the source or via installation of flare gas recovery systems, during normal operations and during planned startup and shutdowns. Owners or operators of flares were to establish a baseline flow rate for each flare (after implementing reduction measures identified during the flare minimization assessment). Owners or operators of flares are required to conduct and complete a root cause analysis within 45 days

of a flaring event exceeding 500,000 standard cubic feet (or 14,160 standard cubic meters) in any 24-hour period above the baseline established in the flare management plan. For each root cause analysis, owners or operators of flares are to identify and implement corrective action measures to minimize the likelihood of a similar event recurring. If the corrective actions cannot be implemented within 45 days, a corrective action plan must be prepared and submitted outlining the corrective action measures identified and providing a schedule for their implementation. The new standards also included requirements for flare gas flow monitoring. The flare management plan and associated work practices were designed to reduce VOC, greenhouse gas, and other pollutant emissions by reducing the amount of flare gas generated or improving the recovery of the flare gas for useful work in a process heater or boiler.

## 2. Flare Performance Operating Limits

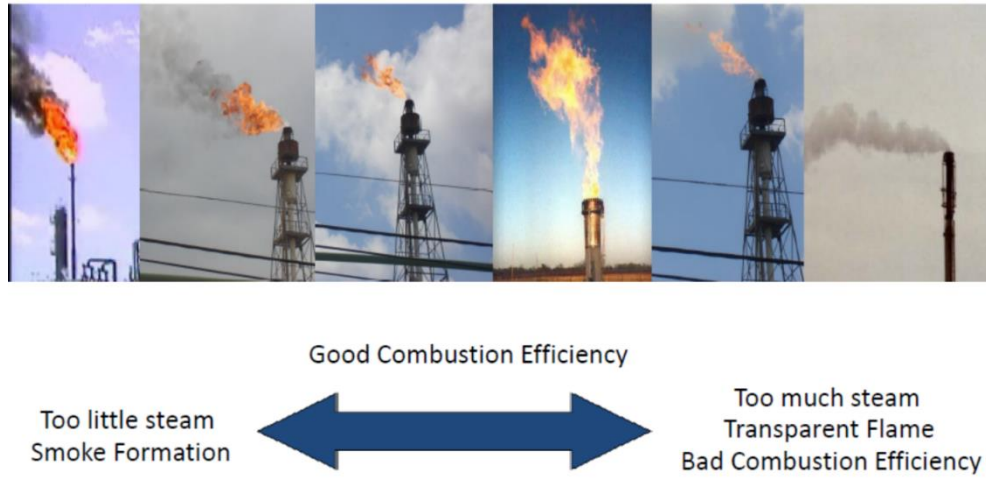
During the review of the old standards, the EPA conducted studies of flare performance. It was noted that flares which were over-assisted with air or steam did not achieve the expected VOC or HAP destruction efficiency. The results of the studies led EPA, with the input of an external peer review panel, to determine that the three primary factors which affect flare performance are: (1) the flow of the vent gas to the flare; (2) the amount of assist media (air or steam) added to the flare; and (3) the combustibility of the vent gas/assist media mixture in the combustion zone. Three potential combustibility characteristics were identified and evaluated: the net heating value, lower flammability, and total concentration of combustible components. The EPA concluded that the net heating value of the combustion zone gas calculated using an artificial net heating value of 1,212 British thermal units (Btu) per standard cubic foot (scf)<sup>2</sup> (based on a comparison of the lower flammability limit of hydrogen compared to gaseous hydrocarbon fuels) provided the best measure of flare performance. Therefore, the EPA amended the old standards to include operating limits and on-going monitoring requirements to ensure high combustion efficiencies in flares. As a short period of poor flare combustion efficiency can lead to high VOC emissions, the operating and monitoring requirements are designed to assess flare operations for each 15-minute period of flare operation. The new flare performance requirements are outlined below.

### *a. Pilot Flame Presence*

Consistent with the old standards, the new standards continue to require flares to operate with a flame present at all times when a gas stream is vented to the flare. Also, consistent with the old standard, the new standards specify that the plant operator must continuously monitor for the presence of a flame. The new standards, however, specify that for each 15-minute block for which a flame is not present for at least a minute will be considered a deviation of the standard. This new standard makes the requirement clear and enforceable.

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<sup>2</sup> The EPA set an artificial net heating value for hydrogen because hydrogen has a high value for its lower flammability limit, but a low overall heat content compared to other hydrocarbons. Because of the high value of the lower flammability limit, good combustion is expected. Therefore, the EPA set an artificial heat content to enable flare vent gas streams of mainly hydrogen to be able to comply with the requirements for the net heating value of the combustion zone gas.



*Figure 3. Flare Stacks with Varying Levels of Visible Emissions*

#### *b. Visible Emissions*

Consistent with the old standards, the new standards require that flares operate with no visible emissions except for a total of 5 minutes during any 2-hour consecutive period when a gas stream is vented to the flare. However, the new standards also require plant operators to monitor for visible emissions by either performing a daily visual observation of the flare stack lasting 5 minutes or by installing a surveillance camera. If the plant operator chooses to perform daily visual observations, they must follow a standard USEPA method to perform all such observations. Additionally, if at any time (including outside the time of the daily observation) a plant operator observes visible emissions, a visual observation must immediately be conducted. Furthermore, if during a visual observation, visible emissions are observed for more than 1 minute, the length of the visual observation must be extended to 2 hours or until 5 minutes of visible emissions are observed. If the video surveillance method is chosen, the camera must record a frame every 15 seconds and records must be date and time-stamped. Additionally, the images must be stored in a location where they can be reviewed at any time.

The new requirements specify precise monitoring requirements to ensure the visible emissions standard is met. These new monitoring requirements also ensure that the requirements are enforceable.

#### *c. Flare Tip Velocity*

The old flare tip velocity limits contained separate requirements for flares with high hydrogen content and other (hydrocarbon) flares.

The maximum allowed flare tip velocity is dependent on the net heating value of the flare vent gas. The net heating value can be determined using a continuously operated calorimeter capable of recording the value in standard conditions. Alternatively, the plant operator may use compositional data collected with a continuous monitor or by grab sample to estimate the net heating value of the flare vent gas. This calculation is performed by adding the sum product of the concentration and heating value of each component present in the flare vent gas stream, allowing the use of 1,212 Btu/scf as the net heating value of hydrogen.

The following equation is used to determine the maximum allowed flare tip velocity:

$$\text{Log}_{10}(V_{\max}) = \frac{\text{NHV}_{vg} + 1,212}{850}$$

Where:

$V_{\max}$  = Maximum allowed flare tip velocity, feet per second

$\text{NHV}_{vg}$  = Net heating value of flare vent gas, British thermal units per standard cubic feet. Actual compound-specific heating values should be used for all hydrocarbons. A value of 1,212 Btu/scf should be used for hydrogen.

1212 = Constant

850 = Constant

If the actual flare tip velocity exceeds 60 feet per second, then it must be less than 400 feet per second and also less than  $V_{\max}$ .

Unlike the old standards, the new standards require the volumetric flow rate of the flare gas to be continuously measured (at least once every 15 minutes) and used with the unobstructed cross-sectional area of the flare tip to calculate the actual flare tip velocity in feet per second. The new flow monitoring requirements include alternatives to use volumetric flow monitors, mass flow monitors and molecular weight of the vent gas measurements, and pressure/temperature monitors with appropriate engineering calculations to determine the cumulative volumetric flow (in standard conditions) for each 15-minute period gas is sent to the flare. The new requirements specify that the plant operator must calculate the actual flare tip velocity for each flare when gases are vented to the flare for more than 15 minutes.

#### *d. Combustion Zone Net Heating Value*

The new requirements specify that the net heating value of the flare combustion zone gas must be greater than or equal to 270 Btu/scf on a 15-minute block average when vent gas is being routed to the flare. The net heating value of the flare combustion zone gas is calculated using the net heating value determined for the flare vent gas (as determined to assess compliance with the flare tip velocity limits) multiplied by the ratio of the flare vent gas volumetric flow rate and the cumulative volumetric flow rates of the vent gas, assist steam and "premix" assist air (air added prior to the flare tip, which is very uncommon).

#### *e. Dilution Limits for Flares with Perimeter Assist Air*

The new requirements include special provisions for flares which have perimeter assist air. Perimeter assist air is defined as the portion of assist air introduced at the perimeter of the flare tip or above the flare tip. This air includes air intentionally entrained in lower and upper steam (not center steam). It does not include air introduced prior to the flare tip ("premix" assist air) or ambient air around the flare flame.

The new requirements specify that the net heating value dilution parameter be greater than or equal to 22 British thermal units per square foot as determined on a 15-minute block period when gas streams are routed to the flare for at least 15 minutes. This requirement only applies when perimeter assist air is actively being used. The net heating value dilution parameter is calculated using the net heating value determined for the flare vent gas (as determined to assess compliance with the flare tip velocity limits) multiplied by the effective diameter of the flare tip (in feet) multiplied by the ratio of the flare vent gas

volumetric flow rate and the cumulative volumetric flow rates of the vent gas, assist steam and assist air (including both premix and perimeter assist air).

The new requirements for flares provide more robust monitoring and in turn assure that flares will meet the 98% HAP destruction efficiency on a continual basis.

### 3. Emergency Flaring Provisions

As mentioned previously, the old standards for flares did not apply during times of startup, shutdown or malfunction. The new standards for flares require the combustion zone net heating value and the dilution limit, if applicable, to be met at all times, including periods of startup, shutdown, or malfunction. Additionally, the new standards require the design smokeless capacity of the flare to be included in the flare management plan as well as preventive measures implemented for each pressure relief device vented to the flare. Below the design smokeless capacity of the flare, any exceedance of the visible emissions or flare tip velocity requirement is a violation of the standard. Above the design smokeless capacity of the flare, an exceedance of the visible emissions or flare tip velocity requirement triggers a root cause analysis and corrective actions to minimize the recurrence of a similar flaring event. If the root cause identifies operator error or poor maintenance, the event is a violation. Additionally, the new emergency flaring provisions establish a maximum number of emergency flaring events that can occur in 3- year period to two, with the third event, not counting flaring events caused by natural disasters or other *force majeure* events, being a violation. Also, a second event in the 3-year period that has the same root cause as the first event (not considering *force majeure* events) is a violation. These provisions ensure high flare combustion efficiency during emergency events and require flare owners or operators to implement effective prevention measures to limit the occurrence of large emergency flaring events.

## **IV. Equipment Leak**

### **A. Emission Source Description**

Equipment leaks are releases of process fluid or vapor from processing equipment, including pump and compressor seals, process valves, relief devices, open-ended valves and lines, flanges and other connectors, agitators and instrumentation systems. These releases occur primarily at the interface between connected components of equipment or in the seal.

### **B. Old VOC Control Requirements**

Equipment leaks that are subject to the old standard are those associated with a piece of equipment that contains or contacts a fluid (liquid or gas) that is at least 5 percent by weight of VOC.

Equipment leak surveys of components must occur at least quarterly, unless specific criteria are met that allow "skip period" (semiannual) monitoring. The leak detection must be performed using a portable instrument that can detect VOC at the leak definition. Example detectors include catalytic oxidation, flame ionization, infrared absorption and photoionization. The portable instrument must have an electrically driven pump to provide samples to the detector at a constant flow rate. A leak is detected at an existing source if an instrument reading of 10,000 ppm for pumps and valves. For new sources, a leak is detected for pumps at 2,000 ppm and for valves at 1,000 ppm.

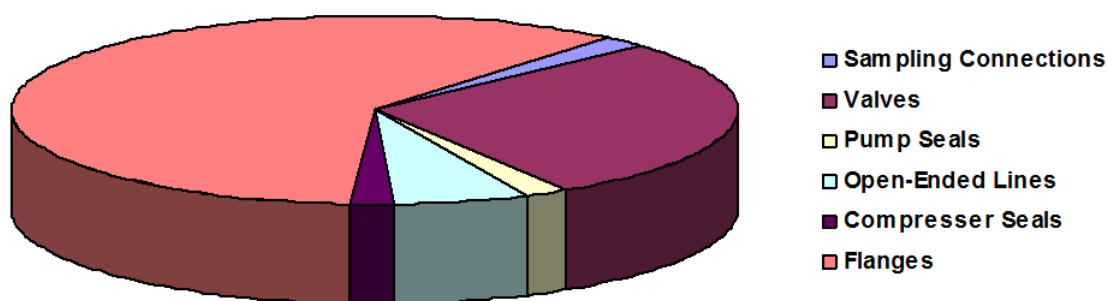
New and existing sources are required to install a cap, plug or blind flange, as appropriate, on open-ended valves or lines. It should be noted that there are no requirements to perform instrument monitoring of connectors/flanges for either new or existing petroleum refinery sources. However, connectors/flanges are required to be monitored annually for organic chemical manufacturers and petrochemical plants.

A repair of detected leaks must be made within 15 calendar days. A first attempt at repair must be made within 5 calendar days.

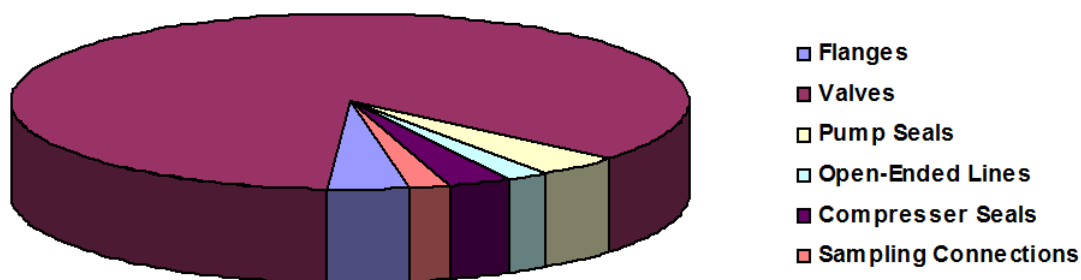
## C. New Monitoring and Control Techniques

### 1. Monitoring

#### a. Leak Definition



*Relative Number of Pieces of Equipment  
in a Typical Petroleum Refinery*



*Percentage of Total Equipment Leak Emissions  
in a Typical Petroleum Refinery*

Figure 4. Number of Equipment Leak Components and Associated Contribution to Fugitive Emissions

During review of the old standards, the EPA considered lowering the leak definition for pumps and valves. They considered a leak definition of either 500 ppm or 2,000 ppm for pumps and 500 ppm for valves at both new and existing sources. Additionally, the EPA considered adding leak monitoring requirements for connectors/flanges. In a detailed analysis, the EPA determined that these changes are not cost effective. Due to the large number of connectors/flanges at a petroleum refinery and their limited contribution to emissions, the costs to perform monitoring for connectors/flanges at petroleum refineries were not justified considering the limited reduction in emissions expected to be achieved.

#### *b. Leak Detection Methods*

The EPA also considered updating the old standards to provide optical gas imaging as an alternative method to using a portable analyzer. In this method of detecting leaks, a plant operator scans equipment using a device or system specially designed to use one of several types of remote sensing techniques. Examples of remote sensing techniques are: optical gas imaging of infrared wavelengths, differential absorption light detection and ranging (DIAL), and solar occultation flux.

The most common remote sensing instrument is a passive system that creates an image based on the absorption of infrared wavelengths (also referred to as a “camera”). A gas cloud containing VOC (i.e., leaks) will show up as colored plumes on the optical gas imaging instrument screen. These cameras can be used to identify specific pieces of equipment that are leaking. We expect that fugitive streams from refineries or petrochemical plants will include at least one of the compounds visible with a camera, such as benzene, methane, propane or butane. Therefore, a camera can be used to detect leaks. The camera can monitor many more pieces of



*Figure 5. FLIR Camera*

equipment than can be monitored using instrument monitoring over the same period. Therefore, the EPA determined using a camera to detect leaks is a suitable alternative to the EPA’s portable analyzer method.

Other optical methods, such as DIAL and solar occultation flux, are used primarily to assess emissions downwind of a source. The DIAL and solar occultation flux methods cannot be used to identify specific leaking equipment. Therefore, the DIAL and solar occultation flux were determined by EPA not to be suitable alternatives to the EPA’s portable analyzer method for equipment leaks.

In the new standards, the EPA provides that plant operators can use a camera under the special provisions for the use of alternate test methods, but operators are still required to validate the alternate method once per year using conventional EPA Method 21 monitoring. Additionally, the EPA is preparing a standard test method for the use of these optical gas imaging cameras for leak detection. When this EPA method is finalized, this alternative leak detection method will be added to the new standards and will allow operators to use optical gas imaging without annual validation using EPA Method 21.

### *c. Recordkeeping Requirements*

The EPA updated the old standards for VOC equipment leaks at organic chemical manufacturers and petroleum refineries. Enforcement activities at petroleum refineries found that many Method 21 monitoring events were conducted far too quickly to properly monitor the equipment components. Monitoring of individual components must be performed slowly enough to allow the instrument to respond to a small area of high concentration (leak) near the equipment component. USEPA enforcement personnel found approximately 3 to 4 times as many leaking components as the facility did in their monitoring events. These new standards require the monitoring reading with date and time stamps for every component monitored during a monitoring event. This information helps ensure that the individual equipment monitoring is not conducted too quickly, thereby improving the effectiveness of each monitoring event.

## 2. Controls

In addition to reviewing lower leak definitions and monitoring methods, the EPA has reviewed new controls for equipment leaks. These controls are for low-emission equipment which is designed to have smaller leaks. The most common types of low-emissions technology are for valves and valve/packing. Advances have also been made for connectors, flanges and pumps. The EPA has not required the use of these technologies in the new standards. However, they have added them to certain facility-specific requirements as a result of compliance enforcement.

### *a. Valves and Valve Packing*

Leaks from valves and valve stems are a significant source of fugitive emissions from refineries and petrochemical facilities. In performing research for equipment leaks, the EPA found that valve manufacturers are making devices with guarantees that the valve or packing will not leak above 100 ppm for 5 years. These guarantees are confirmed by testing protocols from standards organizations such as the International Organization for Standardization, Association of German Engineers, American Petroleum Institute, and the American National Standards Institute.

Valve packing reduces emissions by sealing the area between the stem and the bonnet. The type of packing required depends how often it is actuated. All packing will wear with each stroke. Extending the life of the packing depends on the:

- Use of the appropriate lubricants,
- Physical condition of the valve (including proper smoothness of the plug stem surface),
- Ensuring that operations remain in the material temperature range for the packing chosen,
- Proper tensioning of packing, and
- Elimination of stick-slip effects.

Most valve stem packing systems today are one of the three packing material groups:

- Polytetrafluoroethylene (PTFE) or elastomer-based,
- Pure graphite, or
- Graphite with incorporated materials.

PTFE or elastomer-based packings produce less friction. They have a longer lifetime and with lower leakage rates, but cannot be used at high temperatures. Pure graphite packings are used higher



temperatures but have a shorter lifetime and higher leak rate. Packings made of graphite with incorporated materials perform in between the two in terms of lifetime, leakage rates, and temperature of the material being handled.

Low-emissions valve packings include braided flexible graphite and engineered sets. One braid of a braided flexible graphite seal can be used to pack multiple sizes of valves. The flexibility means that installation requires multiple steps and adjustment of the packing may be needed upon valve startup. These packings can be used at high temperatures and pressures. Engineered sets combine more traditional die-formed flexible graphite rings with the braided flexible graphite seal. These sets are designed to fit a specific valve and stem box size. These packings provide the emissions performance of a braided flexible graphite seal but the ease of installation of the die-formed flexible graphite seal. These packings can also be used at high temperatures and pressures.

Some US refineries have reported success at preventing leaks using bellows seal valves. The valves are designed to reduce the stress on the valve. Methods for reducing the stress include:

- Reducing the movement of the valve and external forces,
- Increasing the number of convolutions per unit of measure (to spread the stress over more convolutions),
- Increasing the length of the components, and
- Increasing the wall thickness (but keeping the wall a uniform width).

These valves can achieve the long lifetimes and low leakage rates of the PTFE or elastomer-based packings while still being appropriate for operation in high-temperature environments. However, the cost of these valves is several times the cost of a standard packed valve.

#### *b. Flanges*

The EPA also found that several vendors have low-emissions gaskets for flanges. The gaskets are called spiral-wound. One such vendor's gasket is made of a metallic strip and a soft filler material, which are wound together under regulated pressure. The gasket has an outer guide ring and an internal solid ring to fill the space between the flanges. The external guide ring centers the gasket in the flange. It also gives the sealing elements resistance to external radial movement and limits compression. The inner ring provides anti-buckling resistance and limits compression. These gaskets are flexible and able to maintain a seal even when faced with pressure and temperature changes.

#### *c. Pumps*

Most pumps have a seal at the point where the pump shaft penetrates the housing. Leaks through this seal are the cause of fugitive emissions from pumps.

Dual mechanical seal pumps have two seals with a barrier fluid. These seals reduce emissions from pumps. The barrier fluid is maintained at a higher pressure than the fluid being pumped. Therefore, the only way emissions could result is if both seals fail at the same time.

Sealless pumps is another type of pump with lower emissions. A magnetic drive pump is an example of a sealless pump. This type of pump uses two radial-aligned magnets to couple a motor with a pump. One magnet is attached to the motor, and when it rotates, the magnet attached to the pump shaft rotates the

pump shaft. The pumped fluid is prevented from reaching the atmosphere by a hermetic seal (typically a static O-ring).

## V. Storage Tanks

### A. Emission Source Description

Storage tanks are used to store liquid and gaseous feedstocks for use in a process, as well as liquid and gaseous products coming from a process. Most storage tanks are designed for operation at atmospheric or near atmospheric pressures; high-pressure tanks are used to store compressed gases and liquefied gases. Atmospheric storage tanks are typically cylindrical with a vertical orientation, and they are constructed with either a fixed roof or a floating roof. Some, generally small atmospheric storage tanks are oriented horizontally. High pressure tanks are either spherical or horizontal cylinders.

Emissions from storage tanks result from filling and emptying the tank contents. Emissions also result from evaporative losses due to changes in temperature and pressure. Emissions can also result from leaks from improperly closed openings, fittings or other controls. Finally, emissions also result from shutdown and maintenance activities which require that the tank be emptied and degassed.

### B. Old VOC Control Requirements

The old VOC requirements specify controls for tanks based on their capacity, the true vapor pressure of the liquid stored, the annual average of the true vapor pressure of the liquid stored and the HAP content. The old VOC requirements specified that storage vessels must be equipped with an internal floating roof with proper seals, an external floating roof with proper seals, an external floating roof converted to an internal floating roof with proper seals or a closed vent system routed to an air pollution control device (APCD) that reduces HAP emissions by 95 percent.

#### 1. Internal Floating Roof Tanks

The old VOC standard specifies that the internal floating roof must remain on the liquid surface at all times. The only exceptions are when leg supports must be used including initial fill, after the vessel has been emptied or degassed for the purposes of inspection or maintenance. The tank must be equipped with a closure device at the wall of the vessel and the roof edge. Closure devices include liquid-mounted seal, metallic shoe seal, or two seals mounted above one another.

#### 2. External Floating Roof Tanks

The old VOC standard specifies that external floating roof must remain on the liquid surface at all times. The only exceptions are when leg supports must be used including initial fill, after the vessel has been emptied or degassed for the purposes of inspection or maintenance. The tank must be equipped with a closure device between the wall and the roof edge of the vessel. The closure device should include two seals mounted above one another. The lower seal is referred to as the primary seal and the upper seal is referred to as the secondary seal. The primary seal must be a metallic shoe seal or a liquid-mounted seal.

### 3. External Floating Roof Tanks Converted to Internal Floating Roof Tanks

External floating roof tanks converted to internal floating roof tanks are required to comply with requirements listed for internal floating roofs.

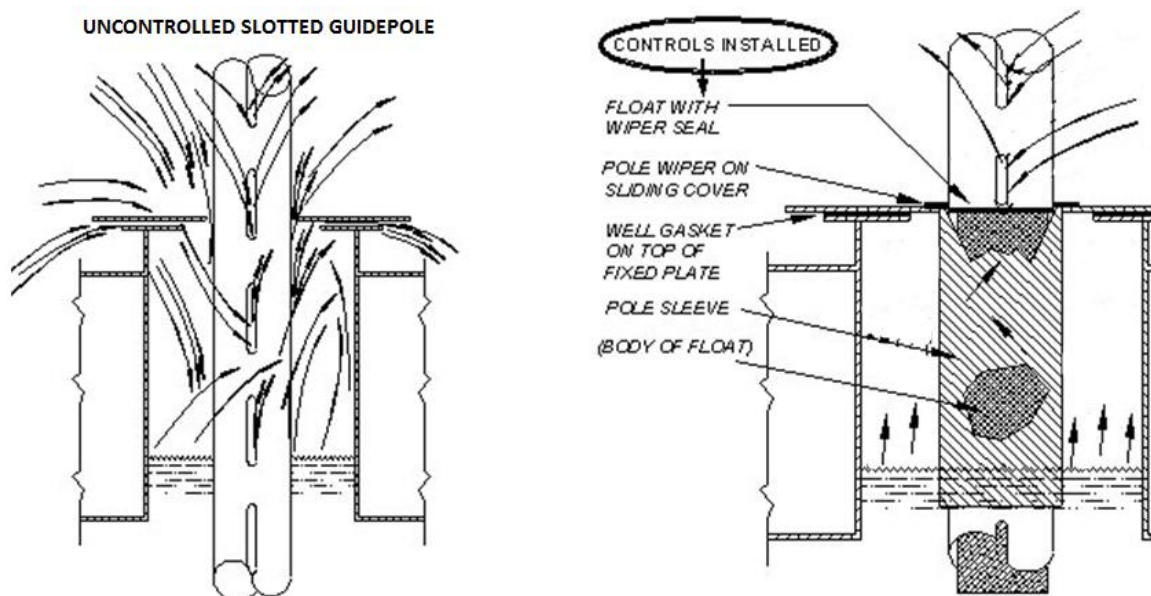
### 4. General Tank Requirements

Periodic visual inspections are required of tank closures, seals and gaskets to assure there are no leaks. Additionally, a periodic internal inspection is required to ensure tank integrity.

### C. New Monitoring and Control Techniques

In review of the old VOC standards, EPA conducted an analysis of developments in control technologies for storage tanks at chemical manufacturing facilities and petroleum refineries. As a result of this analysis, the EPA identified fitting controls as developments in control technologies for storage tanks. The new requirements for floating roof fittings follow:

All openings except those for automatic bleeder vents (vacuum breaker vents) and rim space vents must have its lower edge below the surface of the stored liquid. All openings except those for automatic bleeder vents (vacuum breaker vents), rim space vents, leg sleeves, and deck drains shall be equipped with a gasketed cover and shall be closed at all times, except when the cover must be open for access. Each automatic bleeder vent (vacuum breaker vent) and rim space vent shall be equipped with a gasketed lid, pallet, flapper, or other closure device. Each opening for a fixed roof support column may be equipped with a flexible fabric sleeve seal instead of a deck cover. Each sample well or deck drain may be equipped with a slit fabric seal or similar device that covers at least 90 percent of the opening, instead of a deck cover. Each opening for an unslotted guide pole or unslotted ladder shall be equipped with a pole wiper and equipped with a gasketed cap on the top of the guide pole. Each opening for a slotted guide pole or slotted ladder leg shall be equipped with either: 1) a pole wiper and a pole float whose seal shall be at or above the height of the pole wiper; 2) a pole wiper and a pole sleeve; or 3) a flexible enclosure device and



*Figure 6. Comparison of Uncontrolled and Controlled Slotted Guide Poles*

gasketed cover. These controls, which are also required for petrochemical plants, minimize fugitive emissions from the storage tank.

In addition to requiring fitting controls on floating roof tanks, the EPA revised the size and pressure limit standards that define which tanks require control. The size and vapor pressure requirements for refineries in the old rule were higher than comparable standards for petrochemical plants and organic chemical manufacturers. The EPA lowered these criteria so the size and vapor pressure requirements are more aligned across these sectors. Controls are required for existing storage tanks if the tank's design capacity is 151 m<sup>3</sup> or larger and it is used to store liquid with a maximum true vapor pressure greater than or equal to 5.2 kilopascals (kPa). Controls are also required for existing storage tanks and for tanks with a design capacity of 76 m<sup>3</sup> or larger but less than 151 m<sup>3</sup> used to store liquids with a maximum true vapor pressure greater than or equal to 13.1 kPa. Floating roofs are only allowed for storage tanks storing liquids with a maximum true vapor pressure less than 76.6 kPa. Venting the tank through a closed vent system to a control device is allowed for any tank, but must be used for tanks with a maximum true vapor pressure of 76.6 kPa or higher.

## **VI. Wastewater Systems**

### **A. Emission Source Description**

Industrial wastewater systems include both collection systems and treatment systems. There are varying levels of treatment depending on the end use.

Air emissions from wastewater systems occur from wastewater collection, treatment and storage systems that are uncovered or open to the atmosphere through volatilization of VOC at the liquid surface. The organics volatilize into the air to reach equilibrium between aqueous and vapor phases. Factors that can affect the rate of volatilization include:

- Speed of air flow over the water surface;
- Wastewater surface area in the unit;
- Temperature of the wastewater;
- Turbulence in the unit;
- Duration of time in the unit;
- Depth of the wastewater in the unit;
- Concentration of organic compounds in the wastewater and their physical properties, such as volatility and diffusivity in water; and
- Presence of oil film or biodegradation that inhibits or competes with volatilization.

#### **1. Wastewater Collection System**

EPA considers a wastewater collection system to include components such as drains, manholes, trenches, junction boxes, sumps, lift stations and sewer lines. Drains are the first component of the collection system and typically channel wastewater to the process sewer line, although drains can route wastewater to sumps, trenches or ditches. Manholes are access points to the sewer line that allow for inspection,

maintenance, and cleaning of sewer lines. Junction boxes combine wastewater from multiple sewer lines together for transport to the treatment system.

Many of the emission sources in the wastewater collection system can be open to the atmosphere including drains, junction boxes, trenches, sumps and lift stations, thus resulting in fugitive VOC emissions.

## 2. Wastewater Treatment System

Wastewater treatment systems are divided into three categories: primary treatment operations, secondary treatment systems, and tertiary treatment systems. In primary treatment systems, physical operations remove solids and oil. Typical primary treatment operations include settling basins and oil-water separators. In secondary treatment systems, biological separation and chemical processes remove most of the organic matter in the wastewater. Secondary treatment systems typically include biological treatment units or steam strippers. In tertiary treatment systems, further treatment or filtering of wastewater is done to allow for discharge to a receiving body of water or reuse in a process.

Wastewater can be stored at any point in the wastewater collection and treatment system. However, wastewater storage tanks usually collect and store wastewater at the entrance to or exit from a wastewater treatment unit. Treatment of wastewater does not occur in wastewater storage tanks. Examples of wastewater storage tanks include steam stripper feed, bottoms and overheads tanks and tanks used to store wastewater removed from sludge.

Primary treatment system emissions occur from wastewater treatment tanks. Similar fugitive emissions also result from wastewater storage tanks. Emissions from these types of tanks occur if the storage tanks are uncovered. Alternatively, if the tank has a fixed roof cover that is vented to the atmosphere, emissions can result from purging the vapor space between the liquid level and the tank roof.

The most common secondary treatment systems at petroleum refineries is biological treatment. The rate of emissions of organic compounds from biotreatment depends on how well the unit is designed and operated. The quantity of emissions also depends on specific compound properties such as the efficiency of biodegradation or volatilization.

Units that remove organics from wastewater through destruction are enclosed units and emissions are from a stack (e.g., steam strippers). Emissions from destructive units are also dependent on how well the unit is designed and operated.



*Figure 7. Example of Fugitive Wastewater Emissions Source*

## B. Old VOC Control Requirements

There is both a benzene-specific standard that applies to new and existing refineries and a VOC standard that applies to new wastewater treatment systems at refineries. Controls are required for wastewater collection and treatment systems at a petroleum refinery with a total annual benzene loading (determined at the point of generation) of 10 megagrams per year or greater. Individual waste streams with a flow-weighted annual average benzene concentration less than 10 parts per million by weight (ppmw) or a flow rate less than 0.02 liters per minute at the point of generation are exempt from the control requirements ("unregulated").

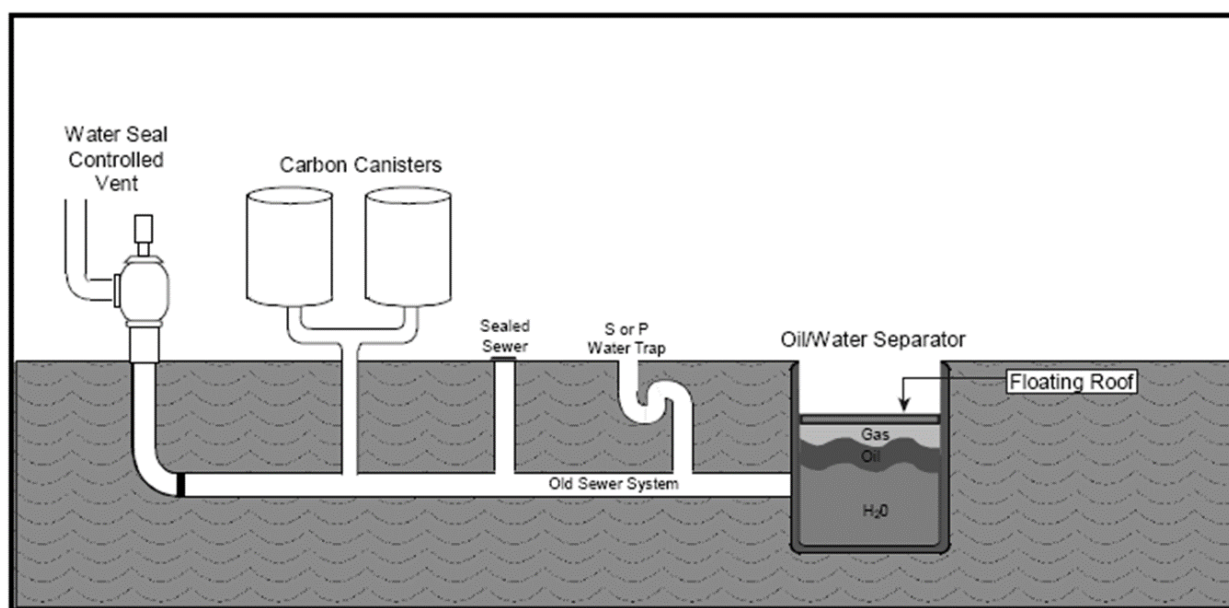
### 1. Wastewater Collection System

Old standards require a cover, water seal, plug or cap on all drains. If the drain is vented, the gas must be sent to a process or a control device. These requirements also specify that covers, water seals, plugs or caps be visually inspected semi-annually for conditions which may reduce the seal's effectiveness, such as low water levels. The visual inspection should also look for gaps or cracks and other sources of fugitive emissions.

Junction boxes shall be equipped with a cover that has a tight seal around the edge. The cover may have an open vent pipe. If the junction box is vented, the gas must be sent to a process or a control device. The vent pipe must be at least 90 cm in length with a diameter less than or equal to 10.2 cm. The cover shall be in place at all times except during maintenance or inspection. Inspection of the cover must be performed at least semi-annually.

Sewer lines must also be covered or enclosed so there are no visible gaps, cracks in joints or seals. The sewer must be inspected semi-annually for cracks or gaps.

For all required inspections, if a problem is found, a first attempt at a repair is required within 5 days. A completed repair must be made within 45 days. Extensions for repair may be allowed if the plant operator



Source: U.S. EPA

Figure 8. Wastewater Collection System

can show they are infeasible without a shutdown. For repairs granted an extension, the repair must be made by the end of the shutdown.

## 2. Wastewater Treatment System

The old VOC standards provide that oil water separators and wastewater tanks may have a fixed roof. Gases in the vapor space under a fixed roof tank must be directed to a control device. The roof seals, access doors and other openings must be inspected semi-annually.

Alternatively, oil water separators and wastewater tanks may be controlled using an internal or external floating roof meeting the same requirements as floating roofs used for organic liquid storage (see Section V. Storage Tank Emission Sources in this document). The old requirements specify semi-annual visual inspection of the tank for control failures. Failures for floating roofs include:

- Floating roof is not resting on the surface or the leg supports
- Liquid is on the floating roof
- Rim seal is detached from the floating roof
- Holes, tears, crack or gaps in the rim seal or seal fabric of the floating roof
- Visible gaps between the seal of the internal floating roof and the wall of the tank
- Visible gaps between the primary or secondary seal of an external floating roof and the wall of the tank

Additionally, the old requirements specify taking seal gap measurements periodically.

For all required inspections, if a problem is found, a first attempt at a repair is required within 5 days. A completed repair must be made within 45 days. Extensions for repair may be allowed if the plant operator can show they are infeasible without a shutdown. If extended the repair must be made by the end of the shutdown.

The old VOC control requirements provide facilities with two options for compliance. One option is to reduce benzene by 99 mass percent or to a concentration of less than 10 ppmw (dilution of regulated water streams with exempt waste streams is not allowed for compliance with the concentration limit). Similar total VOC reduction requirement is to either achieve a 95 percent mass reduction or reduce total VOC concentration to less than 1,000 ppmw. Typically, this treatment standard is accomplished using a steam stripper. Steam strippers meeting appropriate design requirements are not required to conduct performance evaluations to demonstrate compliance with the required reductions. Acceptable steam stripper design criteria are as follows:

- Minimum column height of 5 meters,
- Countercurrent flow configuration with a minimum of 10 trays,
- Minimum steam flow rate of 0.04 kilograms steam per liter of wastewater feed,
- Minimum wastewater feed temperature to the steam stripper of 95°C or a minimum column operating temperature of 95°C;
- Maximum liquid loading of 67,100 liters per hour per square meter, and
- Operate at nominal atmospheric pressure.

The second option is to treat the wastewater using a biological treatment unit. Under this option, diluting the regulated waste streams with exempt waste streams is specifically allowed. The biological treatment



unit is exempt from the fixed or floating roof cover requirements provided that the annual average benzene concentration entering the unit is less than 10 ppmw (after dilution with exempt streams) and the biological treatment unit meets general design requirements (i.e., an “enhanced” biological treatment unit is a suspended-growth process that generates biomass, uses recycled biomass, and periodically removes biomass from the process). An enhanced biodegradation unit typically operates at a food-to-microorganism ratio in the range of 0.05 to 1.0 kg of biological oxygen demand per kg of biomass per day, a mixed liquor suspended solids ratio concentration in the range of 1 to 8 grams per liter (0.008 to 0.7 pounds per liter), and a residence time in the range of 3 to 36 hours). Similar VOC standards for petrochemical plants require an assessment of the fraction of VOC biodegraded using the Method in Appendix C to Part 63 “Determination of the Fraction Biodegraded (F<sub>bio</sub>) in a Biological Treatment Unit”. The EPA also provided technical support guidance to ensure units are thoroughly mixed.

In summary, the old VOC standards for wastewater require that facilities suppress VOC emissions until it reaches an appropriate treatment unit.

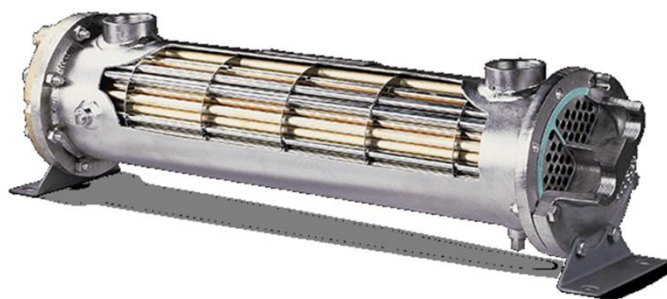
### C. New Monitoring and Control Techniques

In reviewing the old VOC standards, the USEPA determined that the current requirements are sufficient. This determination was made in consideration of the available technologies for controlling wastewater and the cost of such measures. The USEPA evaluates cost effectiveness using a metric of cost of requirements per ton of emissions reduced. The USEPA specifically found that it was not cost-effective to require controls for wastewater treatment systems with small organic loads (less than 10 Mg/yr benzene or about 100 Mg/yr total VOC at the point of generations) or to apply more stringent requirements on the refineries already required to comply with the old standards.

## VII. Heat Exchange Systems

### A. Emission Source Description

Heat exchangers are devices or collections of devices used to transfer heat from process fluids to another fluid (typically air or water) without intentional direct contact of the process fluid with the cooling fluid (i.e., non-contact heat exchanger). At times, the heat exchanger’s internal tubing material can corrode or crack, allowing some process fluids to mix with the cooling water. VOC in the process fluids may then be released from the cooling water into the atmosphere when the water is exposed to air.



*Figure 9. Heat Exchanger*

The term “heat exchange system” is used in this report to refer to water-cooled heat exchangers and the associated cooling water handling system. There are two types of heat exchange systems: closed-loop recirculation systems and once-through systems.



## 1. Closed-loop Recirculation Heat Exchange System

Closed-loop recirculation systems use a cooling tower to cool the heated water leaving the heat exchanger and then return the newly cooled water to the heat exchanger for reuse. For closed-loop recirculation systems, the heat exchange system consists of a cooling tower, all heat exchangers that are serviced by that cooling tower, and all water lines to and from the heat exchanger(s).

Closed-loop heat exchange systems typically use closed piping to transport the water to and from the cooling tower. Emissions from closed-loop heat exchange systems occurs at the cooling tower because this is the point at which the water is exposed to the atmosphere. Emissions primarily occur due to the volatilization of organics in the cooling water. Emissions can also occur when some of the recirculating water becomes entrained in the exhaust air and leave the cooling tower as water mist, known as drift.

## 2. Once-through Heat Exchange System

Once-through systems typically use river or pond water as the influent cooling fluid to the heat exchangers. The heated water leaving the heat exchangers is then discharged from the facility. For once-through systems, the heat exchange system consists of one or more heat exchangers servicing an individual process unit and all water lines to and from the heat exchanger(s).

Once-through heat exchange systems generally transport the cooling water leaving the heat exchangers in open sewer lines or trenches. From the sewer lines or trenches, the cooling water is held in a pond to cool prior to discharge. Emissions from once-through heat exchange systems are similar to those observed from wastewater. The emissions are fugitive releases from volatilization of VOC at the air-liquid surface.

Note: Not all pollutants will be emitted from the cooling water. The highly volatile pollutants are expected to be nearly completely released. Only a small fraction of less volatile, water soluble pollutants (such as phenol) are expected to be released to the air. The concentration of these pollutants can build up over time in the cooling water for closed-loop recirculation systems.

## B. Old VOC Control Requirements

The old standard for petroleum refineries did not include requirements for heat exchange systems. Heat exchange systems were expected to have non-contact cooling water, so the VOC emissions from cooling towers or once-through cooling water was not expected to be significant.

USEPA developed heat exchange control requirements for the organic chemical manufacturing and petrochemical industries. These old VOC requirements specified that plant operators perform sampling of the



*Figure 10. Heat Exchange System*

cooling water. These samples were required for total hydrocarbon, total organic carbon or specific pollutants. Sampling of total hydrocarbon or total organic carbon is not best for detecting small leaks. This is because industrial water generally has total hydrocarbon or total organic carbon in the background. Alternatively, knowledge of the process fluid can be used to perform pollutant specific sampling for detecting smaller leaks. For example, for an ethylene unit, monitoring for ethylene in the cooling water leaving the heat exchanger can be used to identify the leak.

Sampling can either be performed at the cooling water exit of the heat exchanger or at the inlet and the exit of the heat exchanger. When inlet/exit sampling is used, the concentration difference is expected to be the volatilization loss. When only exit sampling is used, the direct water concentration and the flowrate is used to estimate emissions (assumed to be 100% of the pollutant will be emitted). A leak can be defined based on the VOC concentration (or concentration difference) as required for organic chemical manufacturers or based on the projected emissions (accounting for cooling water flow rates) as required for petrochemical plants.

Generally, once there is an indication of a leak, isolation of the leak and a repair is required. Additional sampling may be required to determine where the leak originates. The old VOC requirements specify that a repair be made with 45 days. For specially designed heat exchange systems which require special order parts the repair can be delayed to 120 days. Longer delays are also allowed if a process unit shutdown is required to repair the heat exchanger and the emissions from the process unit shutdown are projected to be larger than the emissions associated with the heat exchange system.

### C. New Monitoring and Control Techniques

The primary issue with the old VOC requirements for heat exchange systems developed for other industries is that the analytical methods for hydrocarbons in water often require analysis of individual compound concentrations and have relatively high method detection limits. The direct water analysis method is only effective if the organics in the heat exchangers are limited to one or two major constituents, like those in ethylene plants. However, most refinery process streams have dozens or even hundreds of compounds. In this case, due to detection limit problems, direct water analysis methods can significantly underestimate the total amount of VOC in the cooling water.

In its review of the potential heat exchange system requirements for petroleum refineries, the USEPA identified an analytical method that could be used to determine the total concentration of strippable hydrocarbons in cooling water. This method, referred to as the "Air Stripping Method" (also known as the "Modified El Paso Method"), uses a small air stripping column that mimics the cooling tower. Cooling water from the water line exiting the heat exchanger prior to any atmospheric release is fed to the top of the stripping column and air is fed at the bottom of the column. VOC that volatilizes from the cooling water into the stripping air is detected using conventional flame ionization detection to determine the total strippable hydrocarbon content in the cooling water. Because of the relative flow rates used in the stripping column and the low detection limits associated with air stream analyses, the Air Stripping method can detect VOC leaks in the cooling water at water concentrations of about 10 to 20 parts per billion (ppb). Furthermore, as the method uses an air stripping column, non-volatile hydrocarbons will not be present in the stripping air, so the stripping column's air concentration provides an accurate measure of the VOC losses from the heat exchange system.

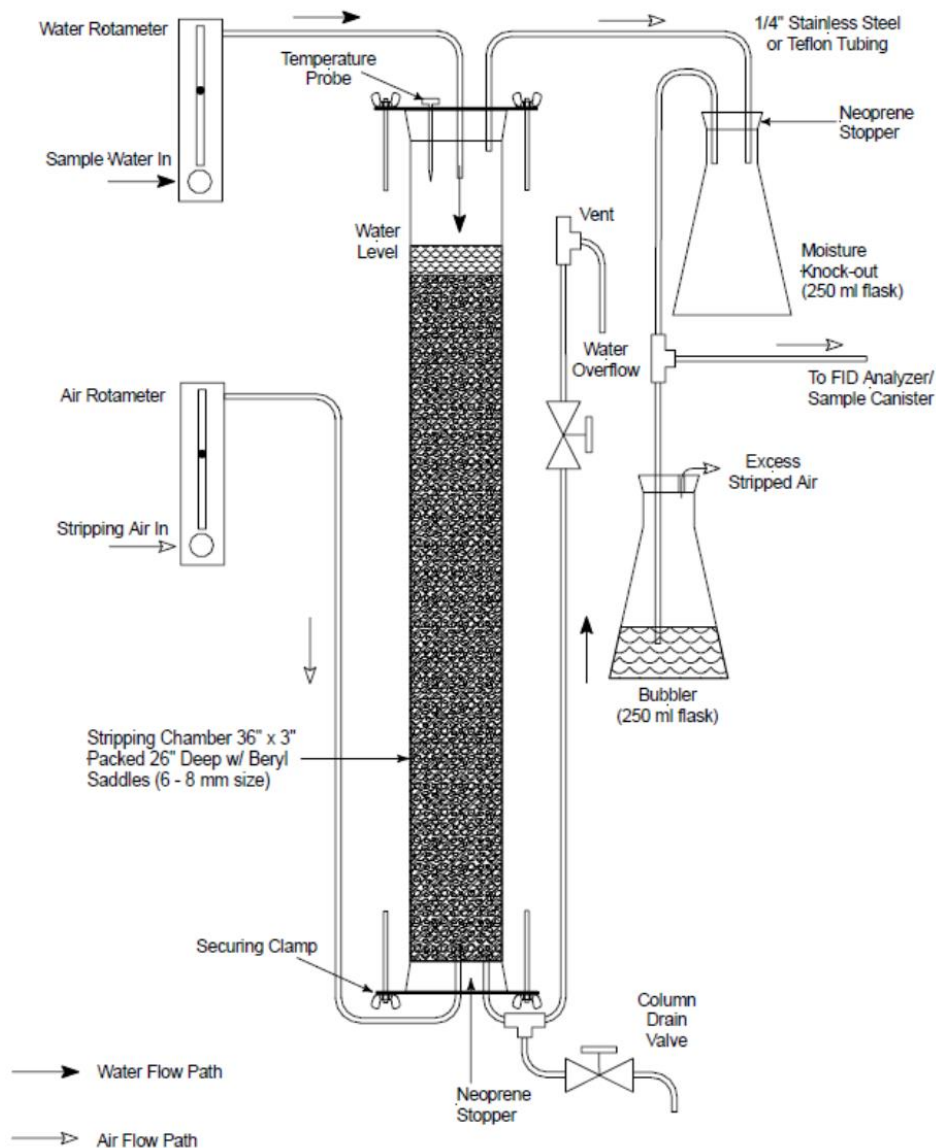


Figure 11. Equipment for Air Stripping Method

The new VOC standards require the use of the Air Stripping Method. Plant operators must either obtain samples for the Air Stripping Method analysis monthly and use a leak definition of 6.2 ppmv (as methane) or obtain the samples quarterly and use a leak definition of 3.1 ppmv (as methane). If a leak is detected, then actions must be taken to repair the leak. These actions include:

- Physical modification to the heat exchanger such as welding or replacing a tube,
- Blocking the leaking tube within the heat exchanger,
- Changing the pressure so that water flows into the process fluid,
- Replacing the heat exchanger
- Isolating, bypassing or removing the leaking heat exchanger from service.

Repairs must be made in 45 days after identifying the leak unless delay in repair is allowed. The new VOC requirements have similar delay of repair provisions as the other USEPA heat exchanger standards: 120

days if parts are unavailable or until the next scheduled shutdown if a process unit shutdown is needed to complete the repair. However, the delay of repair provisions includes a maximum delay of repair leak threshold of 62 ppmv (as methane). Delay of repairs are not allowed if the Air Stripping Method yields a concentration of 62 ppmv or more. Monthly monitoring is required during any delay of repair. If subsequent analysis of a heat exchange system for which a repair is delayed yields an Air Stripping Method result of 62 ppmv or more, repairs must be made within 30 days of the monitoring event exceeding the delay of repair leak threshold.

Heat exchange systems where the minimum water pressure at any point in the heat exchange system is greater than the maximum process pressure at any point in the heat exchange system by 35 kilopascals or more are not required to be monitored. These heat exchangers will leak water into the process fluid rather than have VOC entering the cooling water. Also, heat exchange systems that use an intervening cooling fluid and the intervening fluid contains less than 5 percent VOC are not required to be monitored.

The Air Stripping Method provides an effective and affordable means to identify leaks in heat exchanger systems and reduce VOC emissions from cooling water. Because heat exchange system leaks result in lost product, the costs associated with monitoring and repairing heat exchange system leaks is often offset by the cost of the product that would otherwise be lost as air emissions.

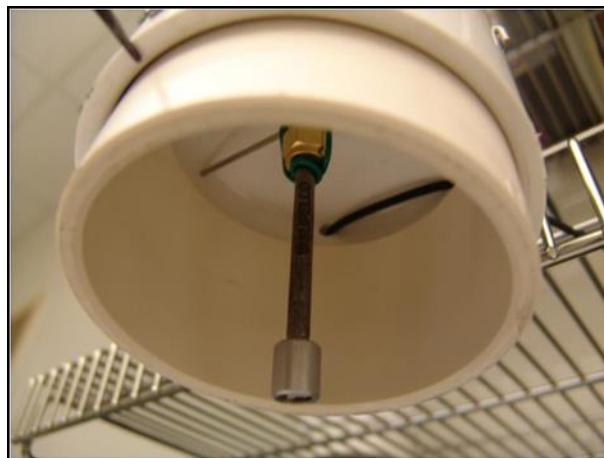
## VIII. Overarching Enhancements

### A. Fenceline Monitoring Requirements

In their review of VOC requirements for petroleum refineries, the USEPA added fenceline monitoring requirements. The program is the first of its kind. The goal of the program is to ensure that facilities monitor and manage fugitive emissions. As described in more detailed below, the program requires refineries to monitor air concentrations of benzene at the facility perimeter. The plant operators must report the monitored benzene concentration to the EPA. The collected and reported data is compared to the action level of 9 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) for benzene. If a facility exceeds the action level, they must conduct a root cause analysis and implement corrective actions to resolve the high fenceline concentration.

#### 1. Description of Passive Monitors

The fenceline monitoring program uses passive diffusive tube monitors. The monitoring networks are made of groups of samplers along the fenceline to measure a time integrated ambient air concentration at each sampling location. A diffusive tube sampler consists of a small tube filled with an adsorbent, selected based on the pollutant(s) of interest, and capped with a specially designed cover with small holes that allow ambient air to diffuse into the tube at a small, fixed rate.



*Figure 12. Passive Sampler for Fenceline Monitoring*



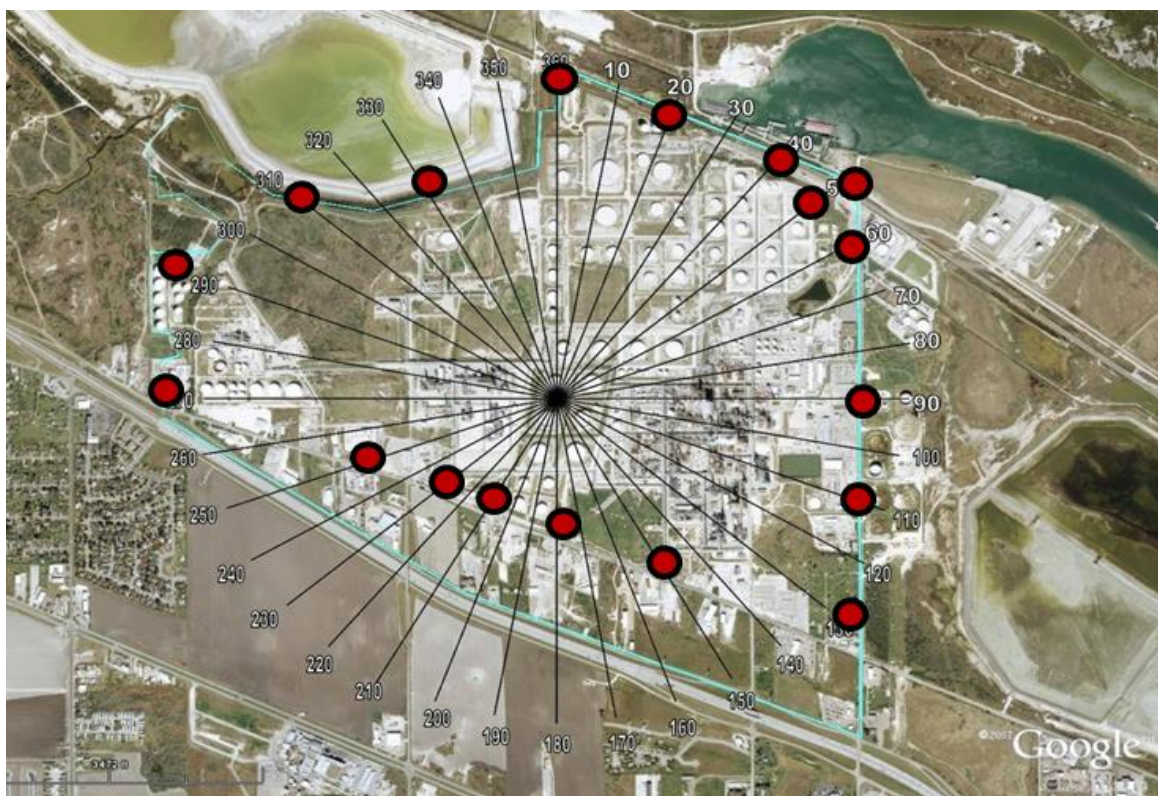
Diffusive tube samplers have been demonstrated to be a cost-effective, accurate technique for measuring ambient concentrations of pollutants resulting from fugitive emissions in a number of studies.

It can be performed by modestly trained personnel. It provides information on overall concentration levels and source identification using simple upwind and downwind comparisons. The results are combined with on-site meteorological measurements. The on-site meteorological data and the results provide facility emission diagnostics.

There are some disadvantages to using this kind of sampler. They lack immediate feedback of the acquired data. Additionally, time integrated monitoring usually requires the collected sample to be transported to another location for analysis. This could lead to possible sample integrity problems (e.g., loss or contamination). However, time integrated monitoring systems are generally lower cost and require less labor than time resolved monitoring systems. Furthermore, the specified sampling frequency in the fence-line monitoring program represents a much shorter time interval than many of the current source-specific VOC monitoring and inspection requirements (annually or less frequently).

## 2. Monitoring Siting

The fence-line monitoring siting requirements are detailed in USEPA Method 325A. The fence-line monitoring requirements specify that monitors be placed at 15 to 30 degrees along the perimeter of the refinery, depending on the size of the refinery. Smaller refineries use the wider spacing, while larger refineries use the tighter spacing. Thus, smaller refineries are required to have fewer monitors than large refineries. For the purposes of siting, the size of the refinery is the land size in acres. An alternative siting procedure is provided. This procedure specifies that monitors can be placed every 2,000 feet along the



*Figure 13. Fence-line Monitor Siting at a US Petroleum Refinery*

fenceline of the refinery, with a minimum of 12 evenly spaced monitors for facilities with a monitoring perimeter length of less than 24,000 feet (7,315 m). If there is a known VOC source within 50 meters of the monitoring boundary and located between two of the standard monitoring locations, an additional monitor is required between the two standard monitors (e.g., at angles of 7.5 degrees using the 15-degree placement method or distance of 1,000 feet when using the 2,000 feet placement method).

### 3. Monitoring Frequency and Analysis

The monitors assess the concentration of fugitive emissions which disperse to the facility perimeter from all fugitive emissions sources at the refinery. Plant operators are required to collect samples at each monitoring location every two weeks, with new monitoring period starting immediately after the preceding monitoring period, so the fenceline concentration is continuously monitored. The collected samples must be analyzed following USEPA Method 325B to determine the benzene concentration at each monitor. The refinery standards use benzene as a surrogate for VOC, but the method can be used to determine the concentration of a wide range of individual VOC.

### 4. Corrections for Background

The EPA acknowledges that sources outside the refinery boundaries may influence benzene levels monitored at the fenceline. Furthermore, background levels driven by local upwind sources are spatially variable. Both of these factors could result in inaccurate estimates of the actual contribution of fugitive emissions from the facility itself to the concentration measured at the fenceline. Many refineries and petrochemical industries are found side-by-side along waterways or transport corridors. With this spatial positioning, there is a possibility that the local upwind neighbors of a facility could cause different background levels on different sides of the facility. To remove the influence of benzene emissions from sources outside the refinery on monitored fenceline values the standard allows plant operators to adjust monitored fenceline values to account for background concentrations.

The simplest method to correct for background is to assume the lowest measured concentration is the background concentration. Thus, the standards provide that the lowest measured concentration can be subtracted from the highest and the resulting difference (or " $\Delta c$ ") is the refinery's contribution to the fenceline pollutant concentration for that monitoring period.

Acknowledging that background contributions are specific to the facility, site-specific monitoring plans may be developed to afford better corrections for background. The facility must develop a written plan to collect sufficient data to demonstrate the measured emissions are in fact from offsite sources. The plan must be approved by the EPA in order for a facility to correct their measurements for background using the site-specific method. Some of the plans could include placing additional passive monitors. Alternatively, the facility could add active monitors near off-site sources. The plan could also include the use of meteorological data to support expected dispersion of fugitive emissions for off-site sources.

For each 2-week monitoring period, the maximum fenceline concentration, corrected for background, is referred to as the 2-week  $\Delta c$  value. The 2-week  $\Delta c$  values for 26 consecutive monitoring periods are averaged together to determine the annual average  $\Delta c$  value. It is this annual average  $\Delta c$  value that is compared with the  $9 \mu\text{g}/\text{m}^3$  benzene action level. As described in section I of this document, benzene has been determined to be an appropriate surrogate for VOC at refineries.

## 5. Work Practice Requirements

If the rolling annual average  $\Delta c$  value exceeds the action level, the facility must initiate a root cause analysis within five days of receiving the analytical results. Corrective actions must be implemented to resolve the exceedance with 45 days of initiating the root cause analysis.

If the next monitoring period's 2-week  $\Delta c$  values exceeds  $9 \mu\text{g}/\text{m}^3$  benzene or if the corrective actions take more than 45 days to implement, then the facility must develop a corrective action plan. The corrective action plan must:

- Describe the corrective action(s) completed to date,
- Describe additional measures that the owner or operator proposes to employ to reduce fenceline concentrations below the action level, and
- Outline a schedule for completion of these measures.

The fenceline monitoring program was implemented as a development in fugitive VOC monitoring methods to improve overall fugitive emissions management at the regulated facility.

## B. Other New Leak Detection Methods

This section describes other fugitive emissions monitoring systems evaluated by the USEPA. While the EPA elected to implement the fenceline monitoring program using passive diffusive tubes based on the currently available technologies and methods, there have been advances in VOC emissions monitoring systems and the fenceline monitoring program allows the use of alternative methods once the methods can achieve the following basic requirements.

- The alternative method must be validated according to EPA Method 301 in Appendix A to Part 63.
- The method must be capable of achieving a lower detection limit of  $0.9 \mu\text{g}/\text{m}^3$  benzene.
- The method must provide the same or better spatial coverage as the passive diffusive tube monitoring sited according to EPA Method 325A.
- Non-integrated sampling alternatives must have a sampling and analysis frequency of 15 minutes or less.

### 1. Remote Sensors

Emerging technology to monitor for fugitive leaks includes remote sensing. One such system is optical gas imaging based. It is an optical gas imaging camera that has two infrared sensors in each camera housing, slightly offset from one another. One sensor tracks the background signature in a given field of view, and the other captures and processes both hydrocarbons and the background signature. Associated software analyzes the images captured by the lenses and subtracts the background image, including interferences such as people and vehicles, making it easier to see the potential leaks. Once the system has determined that a leak has been detected, the plume is colored red in the image and an alert is sent to operators. Leaks can be detected from up to 500 feet away, and alarms can be adjusted based on the user's needs.

A second system includes both a highly sensitive infrared camera and a high definition color camera in a sealed casing. The images are processed with proprietary analytics and image processing algorithms. The cameras are installed throughout the facility and then networked to provide real-time data to the control room. The system analyzes both the color images and infrared video and can provide on-screen gas

plume coloring for improved visibility of leaks. When a leak is detected, the system provides an alert to the control room. The images can be saved locally in the camera or remotely in the control room.

## 2. Active Samplers

Active monitoring station networks are similar to passive diffusive tube monitoring networks in that a series of discrete sampling sites are established. However, each sampling location uses a pump to actively draw ambient air at a known rate through an adsorption tube.

Because of the higher sampling rate, adsorption tubes can be analyzed on a daily basis, providing additional time resolution compared to diffusive tube sampling systems. Alternatively, the active sampling system can directly feed an analyzer for even more time resolution. However, this direct analysis of ambient air generally has higher detection limits than when the organic vapors are collected and concentrated on an adsorption matrix prior to analysis. Active monitoring stations have been used for a variety of pollutants in a variety of settings and the methods are well-established. However, compared to the passive diffusive tube monitoring stations, the sampling system is more expensive, more labor-intensive, and generally requires highly-trained staff to operate.

## 3. Open-path Monitors

### *a. UV-DOAS*

UV-DOAS fenceline monitoring is an “open-path” technology. An electromagnetic energy source is used to emit a beam of electromagnetic energy (ultraviolet radiation) into the air towards a detection system some distance from the energy source (typically 100 to 500 meters). The electromagnetic energy beam interacts with components in the air in the open path between the energy source and the detector. The detector measures the disruptions in the energy beam to determine an average pollutant concentration across the open path length. Because the UV-DOAS system can monitor integrated concentrations over a fairly long path-length, fewer monitoring “stations” (energy source/detector systems) would be needed to measure the ambient concentration around an entire refinery. However, each UV-DOAS monitoring system is more expensive than an active or passive monitoring station and generally requires significant instrumentation shelter to protect the energy source and analyzer when used for long-term (on-going) measurements. Advantages of UV-DOAS systems include providing real-time measurement data with detection limits in the low ppb range for certain compounds. Fog or other visibility issues (e.g., dust storm, high pollen, wildfire smoke) will interfere with the measurements. UV-DOAS systems have been used for fenceline monitoring at several U.S. petroleum refineries and petrochemical plants.

### *b. Fourier Transform Infrared (FTIR)*

Open-path FTIR is similar to UV-DOAS monitoring except that an infrared light source and detector system are used. Like the UV-DOAS monitoring approach, the open-path FTIR monitoring system will measure the average pollutant concentration across the open path length between the infrared source and detector. Path lengths and equipment costs for an open-path FTIR system are similar to those for a UV-DOAS system, and the open-path FTIR system provides real time measurement data. The open-path FTIR system has spectral interferences with water vapor, carbon monoxide and carbon dioxide, which can impact the lower detection limit for organic vapors. Open-path FTIR fenceline monitoring has also been used to measure ambient air concentrations around several petroleum refineries and petrochemical



plants. Although open-path FTIR can be used to measure a larger number of compounds than UV-DOAS, the detection limit of open-path FTIR for benzene is higher than for UV-DOAS. In other words, open path FTIR is not as sensitive to benzene levels as is UV-DOAS. As benzene is an important pollutant from fugitive sources at petroleum refineries and can often be used as a surrogate for other organic HAP emissions, this high detection limit for benzene is a significant disadvantage.

#### *c. DIAL*

DIAL monitoring systems employ a pulsed laser beam across the measurement path. Small portions of the light are backscattered due to particles and aerosols in the measurement path. This backscattered light is collected through a telescope system adjacent to the laser and measured via a sensitive light detector. The timing of the received light provides a measure of the distance of the emission plume. Two different wavelengths of light are pulsed in quick succession: one wavelength that is absorbed strongly by the pollutant of interest and one that is not absorbed. The difference in the returned signal strength between these two light pulses provides a measure of the concentration of the pollutant. Thus, a unique advantage of the DIAL monitoring system is that it can provide spatially resolved pollutant concentrations in two dimensions. Measurements can be made in a relatively short period of time, so the method also provides good time resolution.

The DIAL monitoring system has been used in a variety of studies to measure emissions from petroleum refinery and petrochemical sources. It is typically used for specific, shorter-term studies (one to several weeks in duration). The equipment is expensive, has limited availability in the U.S., and requires highly trained professionals to operate.

#### *d. Solar Occultation Flux*

Solar occultation flux uses the sun as the light source and uses an FTIR or UV detector to measure the average pollutant concentration across the measurement path. In this case, the measurement path is vertical. In order to measure the concentrations around an industrial source, the measurement device is installed in a specially equipped van, which is slowly driven along the perimeter of the facility. Measurement signal strength and a global positioning system (GPS) enables determination of pollutant concentrations along the perimeter of the site. This method provides more spatial resolution of the emissions than the UV-DOAS or open-path FTIR methods and is less expensive than a DIAL system. It has the advantage that only one monitoring system is needed per facility, assuming a mobile device is used. Disadvantages of this method include the need of full-time personnel to drive the equipment around the perimeter of the facility (or the need to buy a detector for each measurement location around the perimeter of the facility, if set locations are used), potential accessibility issues for some fenceline locations (e.g., no road near the fenceline), and the measurement method cannot be used at night or during cloudy periods. It would be possible to purchase numerous detection devices and establish fixed monitoring stations similar to the passive or active monitoring approaches described earlier, but this would be very expensive. Furthermore, any application of solar occultation flux is dependent on the sun, so this approach would mean significant periods each calendar day when the monitoring system would not be able to provide data.

## C. Emergency Release Management Provisions

As part of the review of the old standards, the USEPA specifically assessed emissions that occur during times of startup, shutdown or malfunction that had been previously excluded from the standards (and often excluded from emissions inventories). In addition to the maintenance vent and flaring provisions described earlier in this document, the EPA identified pressure relief devices (PRD) that discharge to the atmosphere as a potentially significant emissions source that were not adequately addressed in the old standards.

The EPA considered requiring all atmospheric PRD to be vented to a flare or similar control device. The cost of such a requirement was extremely high. Additionally, this control strategy would likely require the installation of new flares to handle these emergency releases. The new flares would require purge and pilot gas to keep the flare on ready-standby for an event that may only occur a few times per year or less often. Thus, requiring all PRD to be controlled was likely to have significant secondary (negative) environmental impacts through increased flare emissions. Therefore, the EPA elected to implement a work practice standard aimed to minimize atmospheric pressure releases, and focus further control requirements on those PRD that have multiple emergency releases within a 3-year period.



*Figure 14. Pressure Relief Device Release*

The new emergency release management provisions require PRD that release to the atmosphere to be equipped with a monitoring system capable of detecting a pressure release, recording the time and duration of the release, and notifying the operators of the release. The provisions also require that operators implement at least 3 redundant prevention measures for each PRD that releases to the atmosphere. Examples of prevention measures include:

- Flow, temperature, liquid level and pressure indicators with deadman switches, monitors, or automatic actuators. Independent, non-duplicative systems within this category count as separate redundant prevention measures.
- Documented routine inspection and maintenance programs and/or operator training (maintenance programs and operator training may count as only one redundant prevention measure).
- Inherently safer designs or safety instrumentation systems.
- Deluge systems.
- Staged relief system where initial pressure relief device (with lower set release pressure) discharges to a flare or other closed vent system and control device.

For each atmospheric pressure release from a PRD, the operators must conduct a root cause analysis and implement corrective actions to minimize the recurrence of a similar release event. If the root cause identifies operator error or poor maintenance, the event is a violation. Additionally, the new emergency release management provisions establish a maximum number of emergency release events that can occur in 3- year period to two, with the third event, not counting PRD release events caused by natural disasters or other *force majeure* events, being a violation. Also, a second event in the 3-year period that has the same root cause as the first event (not considering *force majeure* events) is a violation.

The following types of PRD are exempt from these emergency release management provisions:

- PRD vented to a control or flare meeting the required control efficiency (98 percent reduction or to a concentration of 20 ppmv or less).
- Pressure relief devices in heavy liquid service.
- PRD that only release material that is liquid at standard conditions (1 atmosphere and 68 degrees Fahrenheit) and that are hard-piped to a controlled drain system.
- Thermal expansion relief valves.
- PRD designed with a set relief pressure of less than 2.5 psig.
- PRD that do not have the potential to emit 72 lbs/day or more of VOC based on the valve diameter, the set release pressure, and the equipment contents.
- Pressure relief devices on mobile equipment.

These provisions ensure that operators of PRD that have a potential to emit significant quantities of VOC to the atmosphere implement effective prevention measures that limit the frequency and duration of emergency release events.

## IX. References

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- The following contains a list of referenced EPA regulations as the Electronic Code of Federal Register (eCFR):  
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Available at: <https://www.ecfr.gov/cgi-bin/ECFR?page=browse>:
- 40 CFR part 60 subpart Ja: Standards of Performance for Petroleum Refineries for Which Construction, Reconstruction, or Modification Commenced After May 14, 2007
  - 40 CFR part 60 subpart VVa: Standards of Performance for Equipment Leaks of VOC in the Synthetic Organic Chemicals Manufacturing Industry for Which Construction, Reconstruction, or Modification Commenced After November 7, 2006
  - 40 CFR Appendix A-7 to part 60, EPA Test Method 21 – Volatile Organic Compound Leaks

40 CFR part 63 subpart G: National Emission Standards for Organic Hazardous Air Pollutants from the Synthetic Organic Chemical Manufacturing Industry for Process Vents, Storage Vessels, Transfer Operations, and Wastewater

40 CFR part 63 subpart H: National Emission Standards for Organic Hazardous Air Pollutants for Equipment Leaks

40 CFR part 63 subpart CC: National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries

40 CFR part 63 subpart XX: National Emission Standards for Ethylene Manufacturing Process Units: Heat Exchange Systems and Waste Operations

40 CFR Appendix A to part 63, EPA Method 304A or 304B – Method for the Determination of Biodegradation Rates of Organic Compounds

40 CFR Appendix A to part 63, EPA Method 325A – Volatile Organic Compounds from Fugitive and Area Sources: Sampler Deployment and VOC Sample Collection

40 CFR Appendix A to part 63, EPA Method 325B – Volatile Organic Compounds from Fugitive and Area Sources: Sampler Preparation and Analysis

40 CFR Appendix C to part 63, Determination of the Fraction Biodegraded (Fbio) in a Biological Treatment Unit