Industry Guide

Petroleum Refineries

Modern petroleum refineries utilize a vast array of chemical processes to convert raw material and crude oil into a variety of products. These products include fuels, petrochemical feedstocks, solvents, process oils, lubricants, and specialty products such as wax, asphalt, and coke.[1] Throughout the refining process, workers can be potentially exposed to various health and safety hazards including:

Chemical agents
- such as hydrogen sulfide, acids, hydrocarbons, carbon monoxide, polynuclear aromatic hydrocarbons, nickel carbonyl, and elemental mercury

Physical agents
- such as heat and noise

This publication is designed to assist health and safety professionals in choosing the appropriate equipment and methodology to assess the major chemical agents found in petroleum refineries. Sources of additional information are described below.

***The American Petroleum Institute (API)** at 202-682-8000 or www.api.org offers publications on a variety of safety and health issues in petroleum refineries.*

***SKC Inc.** at 724-941-9701 or www.skcinc.com offers equipment to sample chemical agents and to evaluate noise and heat stress.*

Hydrogen Sulfide

Petroleum workers can be exposed to hydrogen sulfide from various operations such as crude oil desalting, catalytic desulfurization, maintenance and manual sampling of gas streams, regeneration of cobalt-molybdenum catalyst, and atmospheric distillation.[2]

Hydrogen sulfide is an irritant to the eyes, mucous membranes, and upper respiratory tract. Higher concentrations can effect the nervous system and lead to asphyxiation by paralyzing the respiratory system.[3] The U.S. Occupational Safety and Health Administration (OSHA) recommends a Ceiling of 20 ppm for hydrogen sulfide.

To sample for hydrogen sulfide using direct-reading instruments, contact SKC for information on single- or multi-gas detectors.

Acids

Sulfuric acid and hydrofluoric acid are used to extract sulfur-based compounds from crude oil. Phosphoric, hydrofluoric, or sulfuric acids are also used as catalysts to form naphtha and other specific products. Exposures to these compounds can result in skin, eye, and respiratory irritation.

OSHA has established an eight-hour Time-Weighted Average (TWA) of 3 ppm for hydrofluoric acid and an eight-hour TWA of 1 mg/m^3 for sulfuric and phosphoric acids.

For information on sampling acid gases according to government methods, reference the following SKC publications:

Chemical Fact Files®

Inorganic Acids
By NIOSH Method 7903
SKC Publication #1016

Sulfuric Acid
By OSHA Method ID 113
SKC Publication #1465

Phosphoric Acid
By OSHA Method ID 111
SKC Publication #1466

Fluorides (F and HF)
By OSHA Method ID 110
SKC Publication #1227

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Hydrocarbons

Workers in petroleum refineries may be exposed to aliphatic and aromatic hydrocarbons present in many different processes. Aromatic hydrocarbons such as benzene, toluene, and xylene are characterized by the presence of the benzene ring; aliphatic hydrocarbons such as ethylene, propylene, and butylene are open-chain carbon compounds. During normal operations, the largest potential for exposures occurs when personnel walk into the operating unit to collect samples of process streams. High exposures can also occur during maintenance operations and turnarounds and during refinery unit disassembling, overhauling, and reassembling.[2]

The toxic effects of hydrocarbons vary. Some act as irritants or cause narcosis while others have more serious, long-term effects. Benzene is a human carcinogen that can cause myeloid leukemia.

OSHA currently regulates benzene as an eight-hour TWA of 1 ppm with a 5 ppm Short-Term Exposure Limit (STEL). Other hydrocarbons have individual exposure limits.

For information on sampling hydrocarbons using passive sampling methods, contact SKC and request technical information on the compounds of interest.

For details on sampling hydrocarbons according to government methods, reference the following SKC publications:

Chemical Fact Files

Benzene
By OSHA Method 12
SKC Publication #1009

Ethyl Benzene (And Other Hydrocarbons)
By OSHA Method 7
SKC Publication #1108

Ethyl Benzene (And Other Aromatic Hydrocarbons)
By NIOSH Method 1501
SKC Publication #1053

Carbon Monoxide

Carbon monoxide exposures can present a problem in areas such as the coking unit and in catalyst regeneration operations. Carbon monoxide can cause asphyxiation by interfering with the oxygen-carrying capacity of blood. OSHA established an eight-hour Permissible Exposure Limit (PEL) of 50 ppm for carbon monoxide.

For details on sampling carbon monoxide by OSHA Method ID 209 using a direct-reading instrument, ask for information on SKC equipment: Pac III Datalogging Instrument 805-30011 with software kit 805-300PAC and carbon monoxide sensor.

Polynuclear Aromatic Hydrocarbons (PAHs)

Petroleum workers can be exposed to PAHs in areas such as the catalytic cracking, asphalt processing, and coking units. PAHs are human carcinogens. OSHA has set PELs of 0.2 mg/m^3 for PAHs such as benzo(a)pyrene, phenanthrene, and chrysene. For details on sampling these compounds according to government methods, reference the following SKC Publications:

Chemical Fact Files

Coal Tar Pitch Volatiles and Selected Polynuclear Aromatic Hydrocarbons
By OSHA Method 58
SKC Publication #1076

Polynuclear Aromatic Hydrocarbons
By NIOSH Methods 5506 and 5515
SKC Publication #1464

Nickel Carbonyl

Nickel carbonyl can be formed in cracking processes that use nickel as a catalyst. Nickel carbonyl is highly irritating to the lungs and can produce asphyxia by decomposing to liberate carbon monoxide. It is also a probable human carcinogen.[3]

OSHA regulates nickel carbonyl as an eight-hour TWA of 0.001 ppm. At this time, OSHA has no fully validated sampling method for this compound. Contact SKC for further information.

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Elemental Mercury

Elemental mercury is found naturally in crude oil and can be concentrated to potentially hazardous levels as part of the refining process. Petroleum workers risk exposure when performing maintenance procedures such as turnarounds on process units. Reports indicate that some of the greatest mercury deposits are in the lighter streams of fuel such as light naphthas or in alkylation units.

Elemental mercury that has been adsorbed into the body circulates in the blood and is stored in various organs. It targets the central nervous system to produce tremors and psychic disturbances. Some first symptoms of mercury poisoning may be pain on chewing and gingivitis and loosening of teeth. The U.S. OSHA PEL is 0.01 mg/m^3 as an eight-hour TWA.

To sample for elemental mercury, OSHA ID-140 recommends either an active sampling method using sorbent tubes or a passive sampling method using an SKC passive sampler. Contact SKC for information on sorbent tubes and 520 Series Passive Samplers. For spot checks of mercury levels, a direct-reading instrument may also be used.

For information on sampling inorganic (elemental) mercury according to government methods, request the following SKC publication:

Chemical Fact Files

Elemental Mercury
By OSHA ID-140
SKC Publication #1677

References

(1) Jeanne Mager Stellman, *Encyclopedia of Occupational Health and Safety,* 4th Ed., Vol III, International Labor Organization, Geneva, 1998, pp 78.2-78.30.

(2) William A. Burgess, *Recognition of Health Hazards in Industry: A Review of Materials and Processes*, 2nd Ed., John Wiley & Sons, New York, 1995, pp 303-317.

(3) N. Irving Sax and Richard J. Lewis, Sr., *Hazardous Chemicals Desk Reference*, Van Nostrand Reinhold, New York, 1987, p 660.

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