
Abstract

When deleterious waste materials from the oil, gas, and chemical plants are discharged into streams or other bodies of water, they become pollutants. This chapter is intended to cover the safety and environmental control aspects as the minimum requirements for water pollution control in oil, gas, and chemical processing industries and production plants. The scope is accomplished under following titles: (1) Refinery Water Pollution Standard and Control; (2) Petrochemical Industry Water Pollution Sources, Standard and Control; (3) Organic Chemical Manufacturing; (4) Monitoring.

Keywords

Grease • Groundwater • Organic constituents • Oxygen demand • Pollution • Prevention • Turbidity • Sampling • Soil water • Spill • Wastewater • Water pollution

Wastewater from petroleum industry contains organic compounds, phenols, toxic metals, and other pollutants such as iron, dissolved and suspended solids, oil, cyanides, sulfides, and chlorine. In order to reduce these emissions, an accurate analysis of processes is necessary.

Pollutants or contaminants which enter a body of water can be divided into:

- *Degradable (non-conservative) pollutants*: Impurities which eventually decompose into harmless substances or which may be removed by treatment methods, that is, certain organic materials and chemicals, domestic sewage, heat, plant nutrients, most bacteria and viruses, certain sediments.
- *Non-degradable (conservative) pollutants*: Impurities which persist in the water environment and do not reduce in concentration unless diluted or removed through treatment, that is, certain organic and inorganic chemicals, salts, colloidal suspensions.

- *Hazardous waterborne pollutants*: Complex forms of deleterious wastes including toxic trace metals, certain inorganic and organic compounds.
- *Radionuclide pollutants*: Materials which have been subjected to a radioactive source.

2.1 Wastewater Characteristics and Classifications

Natural waters and wastewaters are characterized in terms of their physical, chemical, and biological composition. The principal physical properties and the chemical and biological constituents of wastewater and their sources are a lengthy list. Each designated water body should be controlled according to regulations which may be comprised of both basic and more detailed numerical criteria as briefly discussed below.

To the extent practical and possible, all bodies of water should attain the basic criteria of the “Five Freedoms from Pollution”:

1. Free from suspended solids or other substances that enter the waters as a result of human activity and that will settle to form putrid or otherwise objectionable sludge deposits or that will adversely affect aquatic life.
2. Free from floating debris, oil, scum, and other floating materials entering the waters as a result of human activity in amounts sufficient to be unsightly or cause degradation.
3. Free from materials entering the waters as a result of human activity, producing color, odor, or other conditions in such degree as to create a nuisance.
4. Free from substances entering the waters as a result of human activity, in concentrations that are toxic or harmful to human, animal, or aquatic life and/or are rapidly lethal in the mixing zone.
5. Free from nutrients entering the waters as a result of human activity, in concentrations that create nuisance growths of aquatic weeds and algae.

The water contaminant parameters determined in refinery wastewaters include biochemical oxygen demand (BOD₅), chemical oxygen demand (COD), oil, total suspended solids (TSS), ammonia (NH₃), phenolics, hydrogen sulfide (H₂S), trace organics, and some heavy metals.

Table 2.1 shows the major sources of each of the contaminants. Process wastewaters contribute a portion of virtually all, while other sources have more specific contaminant discharges.

2.1.1 Water Free of Oil and Organic Material

This category includes boiler blowdown, effluent from cooling water and boiler feed water makeup units, rain water from oil-free areas, and cooling water which cannot have direct contact with oil.

Table 2.1 Wastewater pollutants and sources

PollutionS	Sources
Heavy metals	Process wastewater
	Tankage wastewater discharges, cooling tower blowdown (if chromate-type cooling water treatment chemicals are used)
NH ₃ , H ₂ S, trace organics	Process wastewater (particularly from fluid catalytic cracking unit and coker)
Total suspended solids	Process wastewater
	Cooling tower blowdown
	Ballast water tank flow drainage and runoff
BOD5, COD, Oil	Process wastewater, cooling tower blowdown (if hydrocarbons leak into cooling water system)
	Ballast water, tank flow drainage, and runoff
Phenolics	Process wastewater (particularly from fluid catalytic cracking unit)

2.1.2 Water Accidentally Contaminated with Oil

This category includes water streams that are normally free of oil, but may contain oil after an accident. These streams comprise rain water from tank farms, pipe alleys, and oil-free processing areas, once-through cooling water, etc.

2.1.3 Water Continuously Contaminated with Oil but with Soluble Organic Material

This category comprises rain water from oil processing areas, tank drain water, deballasting water, cooling water blowdown, flushing, and cleaning water.

2.1.4 Process Water

This water is in contact with process streams, originating from steam stripping, crude oil washing, and some chemical oil treatment processes. It contains variable amounts of oil and soluble material such as ammonium sulfide, phenols, thiophenols, organic acids, and inorganic salts such as sodium chloride.

2.1.5 Sanitary and Domestic Water

The end result of sanitation and domestic water used in the chemical and petroleum is termed as wastewater. Relevant to the above-mentioned facts, these five categories of water may need different treatments, and for this reason, water streams are

often kept segregated in a modern refinery to reduce the cost of water treatment facilities. But in chemical and petroleum industries, different process could cause pollution which should be treated.

2.2 Water Pollution Terminals

Terminals are those storage facilities where refined petroleum products are received from either refineries or import facilities. Fuel is distributed from terminals by truck or rail to retailers or bulk users.

Terminals are the points where wholesalers, distributors, retailers, and other end users access petroleum products. All terminals have loading gantries and storage and can be supplied by pipeline, ship, and in some cases by road transport.

Import terminals, however, are only supplied by pipeline from refineries or ports. Community health and safety issues associated with the operation of terminal facilities may include potential public exposure to spills, fires, and explosions although the probability of large magnitude events directly associated with storage operations in well-designed and managed facilities is usually low. The likelihood of community exposure to chemical hazards may be greater during road, rail, or water transport activities associated with fuel delivery and distribution.

2.2.1 Wastewater Pollutant Sources Crude Oil Terminal

The onshore facilities for most crude terminals will consist of storage tanks and associated equipment for crude oil, ballast water, and sanitary water. Thus, the major environmental concern is contamination of wastewaters with oil and the treatment of the ballast and sanitary waters prior to discharge. The treating methods for oil-contaminated wastewaters include various types of gravity separators. It is most beneficial to segregate the dirty and clean waters and thereby to minimize the volume of water requiring treatment.

2.2.2 Product Terminal

Product terminals typically are separated from a refinery but in some cases may be associated with a refinery. The product typically handled at a terminal includes gasoline, diesel, fuel oil, liquefied petroleum gas (LPG), kerosene, aviation gasoline, and jet fuels.

The few environmental concerns encountered in a product terminal are similar to those in a refinery, and the pollution control methods for product terminals are similar to a refinery.

2.3 Design Procedure for Effluent Water Pollution Control

Examples of design and procedures which are generally beneficial are as follows:

- Recovery of oil spills and hydrocarbons with vacuum trucks to reduce emissions and water effluents.
- Separation of oily wastes, concentrated wastes, and other process wastes from general effluents for more effective treatment.
- Reduction of shock pollutant loads in treatment facilities through the periodic flushing of process sewers to prevent contaminant buildup and by the use of flow and load equalization prior to treatment.
- A specialized program for handling oily wastes, sludges, wash waters, and other effluents.
- Maximization of air fan cooling and employ cooling water only for those services in which low process temperatures make air fan cooling impractical or uneconomic.
- Limiting the amount of water used for process unit washdowns.
- Converting foul water strippers to reboiler strippers to reduce foul water and recover condensate.
- Using caustic injection into desalted crude to reduce NH_3 needed to control corrosion in the crude unit overhead system.

2.4 Spill Prevention and Control

Prevention of spills of oil and related petroleum products should be one of the prime objectives, both in the design and in the operation of the proposed facility, and should include, but not be limited to the siting and design criteria for all facilities, operating procedures and their periodic review, inspection and monitoring of facilities, personnel training, revision of operating procedures (where required), and redesign of facilities (if necessary).

Among specific design parameters are impervious dikes around tankage (feedstock and product), containment of storm water from the process area(s), ability to treat contaminated storm water in the wastewater treatment facility, leak detection systems capable of detecting small volume or slow rates of leakage from the pipeline system and appropriate use of valves to minimize potential spill volumes.

2.4.1 Spill Prevention Techniques

Prevention of spills is the first line of defense in protecting life, property, and the environment. Experience has shown that operational or human error and equipment failures are the principal causes of spills. Both can be reduced through the involvement and commitment of all staff to spill prevention.

Proper design, inspection, and maintenance of general facilities are of principle importance. Operator capacity is also extremely important and must be periodically tested and upgraded.

Given good equipment, good operators, and good procedures, spills will be reduced. They will not, however, be eliminated.

The difference between a minor event and a catastrophic event depends almost entirely on planning. Such planning includes plant design with spill containment features, and alarms, a workable and efficient contingency plan, trained spill control personnel, and adequate spill control equipment.

2.4.2 Bulk Storage

Oil storage tank construction and material should be compatible with the oil stored and the storage conditions such as pressure, temperature, etc.

Impervious secondary containment should be provided for the capacity of the largest single tank plus a sufficient allowance for precipitation and free board.

New metallic tanks buried underground should be protected from corrosion by coatings, cathodic protection, or other effective methods compatible with local soil conditions. The use of non-metallic tanks, if available and practical, should be given consideration.

Above-ground tanks should be subjected to appropriate integrity testing. Appropriate procedures might include hydrostatic testing, visual inspections, or inspection by a system of non-destructive shell thickness gaging.

Plant effluents which are discharged into a watercourse should have disposal facilities observed frequently enough to detect any possible system upset that could cause an oil discharge.

2.4.3 Facility Drainage

Appropriate containment or diversionary structures should be provided to prevent oil from leaving the property uncontrolled.

2.5 Groundwater Pollution Control

Two basic sources of spilled liquid petroleum products are equipment failure and operator error.

- Equipment failure includes corrosion and leaking of both above-ground and below-ground piping and tanks, valves' failure, refinery unit upsets, and sewer and drain leaks. Many of these failures may be avoided through proper inspection and maintenance procedures.

- Operator error includes overfilling tanks and improper alignment of valves and piping. These and other operator errors can best be corrected through developing proven operating procedures, regular training and testing of personnel, and systematic follow-up to assure that procedures are followed.

2.5.1 Preventive Measures

The preventive measures to be installed during the construction of a permanent structure must consider the following:

- The type of construction (refinery, storage tank, pipeline, etc.).
- The volume and the nature of the oil likely to pollute the site.
- The geology and hydrogeological environment, nature of the terrain, depth, activity, and quality of the aquifer.
- The economic environment, proximity to and capacity of water wells and intakes for domestic purposes, risk of pollution of a river, etc.
- The preventive system involves four areas: corrosion protection, surface preventive measures, subsurface preventive measures, and monitoring devices to detect and warn of unsuspected pollution not visible from the surface or of a dangerous change in groundwater levels.

Other methods of preventing spilled product from entering the ground and controlling its direction are as follows:

- Rendering the soil impermeable where required by means of a concrete paving, a clay or bitumen layer, plastic sheets (PVC sheets covered with gravel, fiberglass reinforced epoxy), and chemical to be mixed with the soil.
- A surface drain system in the plant area carrying all oil and oil-contaminated water to a dirty water sewer and then to an interceptor or separator, by means of a pipe system with manholes (cast iron, steel, epoxy), and gutters.

2.5.2 Types of Devices

Trench

This system of protection, which is used as a barrier to prevent the horizontal movement of the oil, can only be carried out on a practical scale if the water table is situated at a depth of less than about 3–8 m depending on soil conditions.

Spread of oil on the groundwater surface is intercepted by digging the trench to about one meter below the piezometric level. Oil flows onto the water surface where it can be recovered.

Hydrodynamic protection

The principle of oil spill control using hydrodynamic methods is to effect a change in the groundwater flow pattern such that the free oil or the contaminated water, as the case may be, can be drawn to a specific control point or points. This can be achieved by discharging or recharging the aquifer, or a combination of

both. The success of the method depends on maintaining an artificial gradient in the groundwater surface.

Monitoring

Groundwater monitoring devices are typically installed to detect and warn of unsuspected contamination not visible from the surface or of a dangerous change in groundwater levels. These devices are installed around petroleum storage areas, waste treatment/disposal facilities (including lagoons, land farms, and landfills), or an entire facility depending on the potential for contamination.

Care should be taken in choosing monitoring devices to maximize accuracy and reliability of the system. Also, monitoring should be conducted to differentiate between previous and new spills.

Mitigation measures

After a spill or any contamination is detected, remedial measures such as determination of the extent or contamination (boundaries) and a hydrogeological assessment of the contamination area to determine the corrective action necessary must be conducted. When an appropriate action is determined, steps including recovery of the oil and oily water and restoration of the site may be instituted.

Recovery measures

The principal factor to be considered when recovering free oil from the groundwater surface is to employ the natural water gradient or by inducing one or by increasing an existing gradient by artificial means. By good use and operation of recovery equipment, free oil can be concentrated at a relatively limited number of selected sites and removed. Wells and trenches are typically used for recovering oil and water.

2.6 Wastewater Pollution Control in Crude Oil Terminal

Wastewaters from petroleum industries are various. They can be process waters such as crude oil desalting waters or sour waters from hydrocracking or hydro-treatment processes, general effluents such as drained oily waters, washing waters, and finally spent caustics. In order to meet quality requirements about wastewater releases, the best way is to segregate these different waters. In this chapter, common techniques for wastewater treatments in refineries are shortly described, and then, best management practices for process wastewater are given.

The largest source of contaminated wastewater at a crude terminal is the ballast water from tankers. The quantity of ballast water requiring treatment depends upon the ship design, operation, and regulations governing the discharge of ballast waters. The ship design parameters include the amount of segregated ballast, the tank dimension, and the use of onboard oil/water separators. The operating parameters include the type of previous cargo, weather conditions, and tank cleaning. Optimizing the design and operation of a tanker can reduce the amount of water requiring treatment.

Ballast water treatment has consisted of settling the ballast in shoreside tankage for periods of 10–24 h, skimming off oil and discharging the water. This simple gravity separation may still be acceptable in some circumstances. For a better quality, effluent physical, chemical, and/or biological methods are necessary.

In some locations where shore space is at a premium offshore, deballasting facilities in the form of converted redundant tankers are utilized. One method to eliminate contaminated ballast water in tankers is the use of segregated ballast.

2.6.1 Simple Gravity Separation

Oil water separation is the first step of general treatment of residual refinery waters. Its purpose is to eliminate insoluble hydrocarbons and suspended matters. It is classically carried out by gravity. Several separators are available which can be longitudinal (API separators), circular, or lamellar.

These treatment systems rely on gravity difference to separate the oil and water. They are capable of removing the bulk of non-dissolved and non-emulsified oil. Examples include storage and settlement, once-through storage with skimming, API separator, corrugated plate interceptors (CPI), and holding basins.

2.6.2 Combination of Simple Gravity Separation Systems

Various combinations of the above individual treatment steps are used and such combinations may consist of storage and settlement plus API separators or CPI; storage and settlement plus holding basin; or storage and settlement plus API or CPI plus holding basin.

There are several reasons why a combination of steps is often the best choice of treatment process. First, storage and settlement ahead of a CPI or API will remove crude oil and prevent temporary overloading of the downstream separator.

Second, rather than sizing the CPI or API separator to handle the maximum hourly flow rate, costs can be reduced by having a combination of a settling tank and CPI or API separator, with the tank designed for the maximum flow rate and the separator design to deal with the average flow rate. Third, a CPI or API plus holding basin serves as a guard chamber to finally trap any inadvertent discharge of oil from the settling tank.

2.6.3 Residual Suspended Matter

If it is necessary to reduce the non-dissolved oil content of the effluent below 25 mg/l, there are several processes available which can be added after the chosen simple gravity system.

Such methods will also reduce suspended solids to below approximately 30 mg/l. BOD can also be reduced because of the oil and solids removed. These processes have little effect on soluble oil content.

The physical methods include dissolved air flotation, filtration (using gravity or pressure filters), physical separation plus use of chemicals such as inorganic flocculants, and/or demulsifiers or polyelectrolytes, flocculation/sedimentation, flocculation-dissolved air flotation, and induced air flotation.

2.6.4 Physical and Chemical Purification

This step is necessary before biological treatment. This technique associates one chemical reaction with a physical separation. Most used techniques are coagulation, flocculation, air flotation, and filtration. It allows elimination of colloidal suspended matters and insoluble hydrocarbons.

2.6.5 Biological Treatment

After physical and chemical treatment, dissolved pollutants are still to be removed. These pollutants include soluble hydrocarbons, soluble CODs and BODs, phenols, and nitrogen compounds. They are biodegradable and can be removed with biological treatment techniques such as activated sludge or trickling filters. Biological treatment may in some cases be appropriate for removing dissolved biodegradable materials, which are often in low concentrations in normal ballast water. Typical devices used for biological treatment include activated sludge, trickling filters, rotating disks, and lagoons (aerated or not).

2.6.6 Spills

A major environmental concern with terminal operations is oil being spilled and the effects on birds and marine life.

Depending upon the type of terminal (offshore or onshore) and the characteristics of the water (such as currents and proximity to open water), the effects of a spill can vary from insignificant to extremely damaging. For example, an enclosed area such as an inlet from the sea, which has been described as the most productive marine environment, may experience accumulation of oil to unacceptable levels over time.

The oil that is spilled offshore will have less impact on the marine environment than an equivalent oil spill within an inlet from the sea (estuary) for three reasons:

1. There will be fewer organisms offshore to be affected.
2. The concentration of toxic compounds within the water column is expected to be less because more dilution water is available in offshore.

3. The contact time with the marine life will generally be shorter for an offshore spill due to the restricted flushing of the inlet from the sea.

In addition to spilled oil, the treated ballast water can also affect the marine life in an “enclosed” area. Thus, it may sometimes be best to pipe the treated water to another location where good mixing may occur, thereby protecting the “enclosed” area and minimizing the effects on the marine environment.

Spill contaminant is an important feature of a terminal. The most common types of barrier systems are used for floating booms and sorbent ropes. Two less frequently used alternatives are the air-bubble barrier systems and an enclosed berth.

2.7 Siting and Design

In previous sections, the sources of pollution and control methods were discussed. In the following pages, the general outline of pollutant specific for management in the siting and design of a refinery or terminal will be discussed.

A major design requirement for a refinery or terminal is to minimize or eliminate the emission of pollutants to the environment.

The methods necessary to implement this depend on the types of crude oil processed, the types of products, the availability of water fuel and other utilities, and the agreed pollution parameters.

Safety requirements must also be considered at this stage to ensure that the surrounding population and plant personnel are protected from hazards such as fire, explosion and toxic chemicals.

The items of concern in siting and design of a facility are briefly reviewed. They are meant only to point out potential environmental effects.

2.7.1 Aquatic Ecosystems

A refinery or terminal siting should take into account potential impacts to aquatic ecosystems. The characterization of aquatic systems in a siting should include: the location of spawning areas, feeding zones, commercial fishing areas, and sport fishing areas, a description of the benthic populations, and an estimate of primary productivity and its limiting factors.

Design considerations should include the facility’s water supply requirements. While water use is usually non-consumptive, attention should be given to the intake and discharge zones.

At refineries or terminals, there is always the potential for a release of oil or petroleum products. All facilities should have a spill contingency plan and the basic pieces of equipment necessary to clean up a spill. All tankage should be properly diked.

2.7.2 Terrestrial Ecosystems

Impacts to terrestrial ecosystems from the siting of a refinery or terminal include a reduction or loss in total available habitat, destruction, or modification of food webs, and changes in populations. Another concern in the siting should be the sensitivity of plants and animals to pollutants.

2.7.3 Wetland Ecosystems

Where the water table is at, near, or above the land surface for a significant part of most years, the hydrologic regime is such that aquatic or hydrophytic vegetation is usually established, although tidal flats may be non-vegetated. Because wetlands are water systems, any alteration affecting the movement of quality of water in a small area is transmitted to other areas magnifying potential impacts.

Wetlands may be altered directly by filling, dredging, draining, or creating impoundments. Indirectly, alteration in water flow patterns at the locations and changes in adjacent land use can change the functions and values of wetland areas.

In addition to facility construction, the laying of pipelines associated with these facilities can have impacts on wetlands.

2.7.4 Land Use

Part of the siting for a refinery or terminal should consider the existing land use and compatibility with local and regional land use plans.

2.7.5 Water Pollution Control

The siting and design guidelines for water pollution control are as follows:

Siting

The most important aspect of water pollution control in the siting of a refinery is the effect of the wastewater effluent on the receiving water. Several factors which should be assessed in the siting investigation are as follows: heat load, total dissolved solids, heavy metal concentrations, and the effects of organics in the effluent.

Design

The design of the water pollution control depends on the degree of cleanup required to permit discharge of the wastewaters to either a body of water or public wastewater treatment plant and by the characteristics of the refinery. The following design practices are directed primarily toward segregation of process and non-process wastewaters and the recycling and reuse of raw and treated wastewaters:

- (a) Refinery wastewaters should be segregated and treated based on oil content and potential for reuse. Four common divisions are oil-free wastewaters, oily cooling water, process water, and sanity wastewaters.

- (b) Raw and treated wastewater streams should be recycled to reduce the effluent volume and thereby the makeup water required. Specific practices include the following:
 - use of catalytic cracker accumulator wastewaters rich in H_2S (sour waters) for making up to crude desalters after stripping;
- (c) Tank farm, process, and product handling areas should be sloped and graded toward sumps or sewers to permit quick removal and collection of spills.
- (d) Check valves and storage tanks should be installed at ends of pipelines specifically for spill prevention and control.
- (e) Seals should be installed on normally closed valves.
- (f) Cathodic protection systems should be installed for underground pipelines and tanks or apply a continuous coating around the pipeline to prevent direct contact between the pipe and the soil.
- (g) Where feasible, all pipelines should be located above ground to facilitate inspection and identification of leaks.
- (h) Concrete ditches, leading to either a chemical waste system or a wastewater system, should be installed under pipelines.

2.8 Source of Effluent in Petrochemical Industry

2.8.1 Water Pollution

In chemical plants, water formed by chemical reaction is generally less than the water evaporated into atmosphere, so that the water discharged tends to be less than the water intake. However, most part of the intake water is discharged.

Also, rain water is fouled while flowing through contaminated areas of a plant and is discharged as part of the wastewater.

2.8.2 Cooling Water

Most industrial water is used as cooling water. For example, there are the rapid cooling required for naphtha thermal cracking in making ethylene and EDC (ethylene dichloride) thermal cracking in the manufacture of vinyl chloride; removal of reaction heat in polymerization and oxidation; and cooling of fractionator condensers. Cooling water is not fouled since the indirect cooling method is generally adopted. However, there are instances of liquid leaking from the tubes of a cooler due to corrosion attack, resulting in contamination of cooling water.

2.8.3 Washing Water and Process Water

Considering the properties of fouled water, washing water is identical to process water, so the former is frequently called “process water.” Water is used in washing

because it dissolves various substances. For example, carbon dioxide, hydrogen sulfide, and hydrochloric acid, in gas are dissolved in dilute alkali water.

The amounts of washing water and process water being used in petrochemical plants are small compared with those of cooling water. These wastewaters contain a considerable amount of organic substances and dissolved oils. But the COD and BOD values are insufficient to indicate the amounts of organic substance contained in the wastewater from the petrochemical processes.

It is necessary that the organic matter in wastewater from petrochemical plants be indicated using total organic carbon (TOC) and total oxygen demand (TOD), but the TOC and TOD indications themselves are not always considered useful as criteria for the detection of toxic substances in the wastewater or for the selection of wastewater treating methods. As organic compounds discharged from petrochemical processes have a variety of chemical properties depending on the processes, it is necessary to pursue the emission sources. Table 2.2 shows different types of pollutions in plants' operations.

Table 2.2 Types of water pollution

Pollution	Plant operation	Examples of pollution
Water pollution (wastewater, waste liquid)	Cooling water	Direct cooling or quenching of decomposed gas-waste-water contains tar dust, hydrogen sulfate and cyanide
		Breakage of indirect cooler tubes—contamination of cooling water due to liquid inside the tubes
		Steam ejector—steam condensate from ejector contains volatile hydrocarbon
	Boiler feed water	Steam ejector—steam condensate from ejector contains volatile hydrocarbon
	Washing water	Water containing hydrogen sulfate and hydrochloric acid, etc., is discharged from the washing of gas
		Water containing hydrochloric acid, etc., is discharged from the washing of liquid
		Dust is contained in discharged water from dust collector
	Process water	Solvent for suspension and emulsion polymerization
	Feed water	Contain catalysts, emulsifier, plastic monomer, etc
	(Chemical reaction, electrolysis)	Steam condensate from steam stripping contains dissolved hydrocarbons
		Steam condensate originating from dilution steam for naphtha thermal cracking contains carbon, phenol, and light oil
	Leakage (loss)	Leakage from pump and agitator shafts, valve stems, and flanges, and due to operational error

2.8.4 Typical Pollutants of Petrochemical Industry

Aqueous effluents originating from the petrochemical industry are essentially characterized by the presence of the following substances:

- Organic substances that are not biodegradable or only slightly so;
- Nitrogen compounds;
- Heavy metals.

2.8.5 Petrochemical Waste Treatment

Petrochemicals have been defined as bulk chemicals derived principally from natural gas, petroleum, or both. A careful check should be made of processes proposed or used for the manufacture of petrochemicals to decrease the possibility of water-soluble organics entering water supplies. The following methods should be considered:

- Recycling and reuse of waste streams;
- Quenching with oil or chemicals other than water that do not produce water-borne wastes;
- Use of alternative processes that do not produce waterborne wastes;
- Use of air coolers or of cooling towers in place of once-through cooling water;
- Elimination of waste products in the manufacturing operation before they become associated with waste streams;
- Processing of waste streams to reduce the amount of chemicals in wastewaters leaving the plant.

The extensive use of automated controls, alarms, and checks by the operators to prevent loss of chemicals is also important. It is essential that adequate facilities be installed to prevent uncontrolled release of chemicals and wastes to sewers or receiving waters. A very effective means of quality control is the use of large lagoons capable of holding several days' production of wastewater; this allows the water to be checked before being released to receiving waters.

2.8.6 Fertilizer

The liquid effluents arising from a fertilizer factory originate from a variety of sources and may be summarized as follows:

- (a) Ammonia-bearing wastes from ammonia plants.
- (b) Ammonia and urea wastes from urea manufacturing plant.
- (c) Ammonium salts such as ammonium nitrate, ammonium sulfate, and ammonium phosphate.
- (d) Phosphates and fluoride wastes from phosphate and superphosphate plants.
- (e) Acidic spillages from sulfuric acid, nitric acid, and phosphoric acid plants.

- (f) Spent solutions from the regeneration of ion exchange units, acid from cation exchange units and alkali from regeneration of anion exchange units.
- (g) Phosphate, chromate, copper sulfate, and zinc wastes from cooling tower blowdown.
- (h) Salt of metals such as iron, copper, manganese, molybdenum, and cobalt.
- (i) Sludge discharged from clarifiers and backwash water from sand filters.
- (j) Carbon slurry from partial oxidation units.
- (k) Scrubber wastes from gas purification processes containing contaminants such as
 - Mono- and di-ethanol amines (MEA and DEA);
 - Arsenic as As_2O_3 ;
 - Potassium carbonate;
 - Caustic soda.

The effluents from fertilizer manufacturing are generated from a wide range of unit operations, and considerable variation between wastewaters from different factories may be noted. The age, state of repair, operational management, and degree of sophistication of each manufacturing unit will play an important role in determining the degree of in-plant materials loss, and the important factors leading to excessive losses (and subsequent pollution) may be summarized as follows:

- Outdated basic manufacturing plant with low efficiency and poor process control.
- Improper maintenance and repair, with particular emphasis on servicing of control equipment.
- Variations in feedstock and difficulties in adjusting process plant to cope with these variations effectively.
- Lack of consideration for pollution abatement and the prevention of material loss at the original plant design stage.

Overall water requirement for fertilizer manufacturing plants may be high, due to process cooling requirements. The total volume of effluent discharged is dependent to a considerable extent on the degree of in-plant recirculation, and in the case of total recycle, the raw water is used primarily for makeup purposes.

Plants designed on a once-through process cooling system generally give rise to high volumes of effluent, from $1,000 \text{ m}^3 \text{ h}^{-1}$ to volumes in excess of $10,000 \text{ m}^3 \text{ h}^{-1}$, consisting primarily of cooling water discharge.

2.8.7 Nitrogenous Fertilizers

A complex nitrogenous fertilizer plant based on the production of ammonium nitrate and urea products may give rise to pollutants such as ammonium nitrate, nitric acid, ammonia, urea, sulfuric acid, caustic soda, chromate, oil, grease, and boiler feed additives, contained within the overall effluent stream. The individual effluents from the ammonia and urea plants could be categorized as follows:

- (a) **Ammonia plant**
 - HCN stripper outlet

- Catalyst reduction
- Shift process condensate

(b) **Urea plant**

- Concentrate liquor
- Cooling water blowdown
- Additional pollutant discharges may arise from oily water and sanitary sewage effluents.

2.8.8 Phosphate Fertilizers

The examples of the sources of liquid effluents from phosphatic fertilizer manufacture are as follows:

Plant 1: Raw Water Intake

Effluent sources:

- Superphosphate plant
- Sulfuric acid plant
- Water treatment plant
- Cooling tower
- Other sources

Plant 2: Raw Water Intake

Seawater (once-through cooling)

Effluent sources:

- Ammonia plant
- Phosphoric acid plant
- Sulfuric acid plant
- Utilities plant:
- Cooling water makeup
- Boiler blowdown, washings from ion exchange units and floor washing

2.8.9 Compound NPK (Nitrogen/Phosphorus/Potassium) Fertilizers

A major component of the NPK effluent source is the direct loss of fertilizer compounds from the granulation units. Examples of the effluents from compound fertilizer manufacture are as follows:

Plant 1: Raw Water Intake

Effluent sources:

- Ammonia plant
- Urea plant
- Phosphoric acid and NPK plants
- Water treatment plant
- Cooling tower

Boiler plant

Plant 2: Raw Water Intake

Effluent sources:

Ammonia plant

Urea plant

Phosphoric acid and NPK plants

Sulfuric and nitric acid plants

Water treatment and steam generation plant

Methanol plant

2.8.10 Effect of Pollution

Wastes may be subcategorized into major and minor elements, but it should be noted that in specific instances, particular minor waste components may exercise significant polluting effects.

Major pollutants

General water pollution effects from fertilizer manufacturing wastes are dependent primarily on the elements, nitrogen and phosphorus, in their varying chemical forms.

2.8.11 Nitrogen

Compounds in following sections are related to nitrogen.

2.8.12 Ammoniacal Nitrogen and Urea

These two compounds are grouped together since urea may be hydrolyzed to ammoniacal nitrogen. The pollution problems which may be attributable to ammoniacal nitrogen include toxicity, oxygen demand, and eutrophication. Ammonia can be toxic to fish and other aquatic life forms at relatively low concentrations, and urea itself may be toxic to some aquatic life.

Ammoniacal nitrogen and urea may both be oxidized biologically. As such, their presence must be considered a potential oxygen demand in receiving water. In addition, ammoniacal nitrogen may act in its role as a fertilizer in an aquatic environment, leading to excess growth of algae and aquatic macrophytes and contributing toward accelerated eutrophication.

The presence of high ammonial levels may also cause problems if the receiving water is used for water supply purposes, due to chemical interference with chlorination (i.e., formation of chloramine intermediates) and resultant increase in chlorine demand.

2.8.13 Nitrate

The water pollution problems resulting from high nitrate levels may be categorized into eutrophication and public health effects. High levels of nitrate can give rise to increased eutrophication, leading to the promotion of growth of algae and macrophytes, adversely affecting water quality and amenity value. Health hazards related to nitrate in water used for supply purposes are considered to be infant methemoglobinemia and carcinogenic potential.

2.8.14 Phosphate

The presence of significant levels of phosphate has important effects on eutrophication. In terms of inorganic nutrient enrichment of receiving waters, phosphate may in many instances be more important than nitrogenous compounds, due to the fact that some forms of aquatic plant life may fix atmospheric nitrogen, so removing the absolute requirement for soluble forms of nitrogen to promote growth.

Under these circumstances, phosphate becomes the growth-limiting agent, and programmes to control eutrophication have generally sought to reduce available phosphate limits, to prevent excessive algal and macrophyte growth, with subsequent increase in nutrient retention.

2.8.15 Minor Constituents

In addition to pollution arising from the discharge of nitrogenous or phosphatic elements in liquid waste streams, pollution can be caused by a number of secondary waste components. The most important of these may be listed as follows:

- Oil and grease

- Hexavalent chromium

- Arsenic

- Fluoride

In specific instances, one or more of these individual pollutants may give rise to detrimental effects in receiving water, due primarily to toxicity, or can cause inhibition of nitrification. In addition, oil and grease may adversely affect the oxygen transfer characteristics of a watercourse.

2.8.16 Olefin Plants

2.8.16.1 Liquid Effluents

The main liquid effluent streams of olefin plants are oily drains, flare system pump-out, caustic oxidation effluent, dilution steam generator blowdown, and fouled condensate.

2.8.16.2 Oily Drains

The major oily drain sources are water draw-offs from vessels and hydroblast decoking wastewater.

Hydroblast wastewater producing during cleaning coke-fouled equipment contains entrained coke fines which are screened before discharge to the oily wastewater treatment system.

2.8.16.3 Flare System Effluent

Flare system is required for safe disposal of hydrocarbons which may be released at pressure during mal-operation and emergency conditions.

The hot flare knockout drum is primarily provided in order to receive liquids from the flare seal drum, excess fuel gas, hot relief, and hot blowdown.

2.8.16.4 Spent Caustic Neutralization

The cracked gas from the cracking furnaces is scrubbed in a caustic wash tower to remove in convenient remained gas including carbon dioxide, hydrogen sulfate, and mercaptans prior to further processing in the plant cold section.

The spent caustic is purged from the wash tower and is laden with sulfidic constituents plus volatile organic compounds (VOC) such as condensed oils and benzene. The spent caustic scrubbing liquor is commonly the most problematic waste stream generated by an olefin plant. This is due primarily to the sulfate concentrations which can range as high as 6 % (expressed as NaHS), depending on the cracking furnace feed stock and wash tower operation. The most effective means for on-side treatment of spent caustic is wet air oxidation which can achieve the oxidation of reactive sulfate to soluble thiosulfate, sulfate, and sulfate.

2.8.16.5 Fouled Condensate

Suspect condensate consists of all condensate streams from heat exchangers where hydrocarbon side pressure is more than the heating steam. A leakage in one of these heat exchangers will result in a hydrocarbon contamination of the condensate. Normally, the condensate flow to the surge tank is zero. The possibility constituents in suspect condensate are propane, propylene, butane, butadiene, and pentane with their concentrations related to the maximum solubility.

2.8.16.6 Dilution Steam Generator Blowdown

The main sources of wastewater in an olefin plant are as follows:

- Process water below down during normal and upset operating conditions;
- Process water from quench tower;
- Surface runoff from possibly contaminated or non-contaminated areas.

The wastewater components are variable depending on respective sources. But the major components are oil, phenols, H_2S , and hydrocarbons.

2.8.17 Polymeric Plants

Polyethylene plant (HDPE/LLDPE/LDPE)

- **Process wastewater**

The process wastewater discharged from the bottom of the dryer scrubber entrained polymer fines typically has following characteristic:

Temperature <50 °C

BOD5 <100 ppm

COD <200 ppm

Suspended solid 100 ppm max.

- **Rainwater and floor washing water**

Rainwater and floor washing water shall be collected and treated separately according to their origin.

- **Polymerization Area**

The ceiling of polymerization area has been considered potentially polluted with polymer powder and oil that may be sometimes spilled from pumps, compressors, and other mechanical equipments.

The rainwater and the washing water falling on paved areas may carry away powder and oil and therefore shall be gathered to the basins separately, where the entrained material is retained.

- **Extrusion building area**

The floors of the extrusion buildings may be occasionally polluted by polymer/scrapes and lubricating oils.

Polypropylene plants (PP)

2.8.17.1 Process Wastewater Effluent

The sources of continuous process wastewater effluent are dryer scrubber and palletizing section. The wastewater contaminated by trace polymer fines leaves bottom of the dryer scrubber. It has typically the following characteristics:

pH, 6–8

Temperature 40–60 °C

Contaminant polymer powder.

The wastewater from palletizing section combined oil and trace suspended solid. It has typically the following characteristics:

PH 7–8

Suspended solids 25 ppm

Oil content 1 ppm max

COD 5–10 ppm

Temperature 50–80 °C.

2.8.18 Polyvinyl Chloride Plants

Polyvinyl chloride plants (PVC) is polymerized just as any other plastics. During the chemical process of the polymerization, an extremely large heat is generated. For removing heat, two emulsion and suspension-PVC (E&S-PVC) processes have been established. The wastewater effluent coming out of E-PVC plant is similar to S-PVC plant.

The sources of the wastewater effluent are polymerization reactor additive coating, vacuum station, and recovered vinyl chloride monomer. The wastewater streams coming out of these sources are collected in the wastewater settling basin which consists mainly of two compartments. The wastewater contaminated with wet PVC and VCM components have typically the following characteristics reported in Table 2.3:

2.8.19 Aromatic Plants

The effluent in aromatics plant mainly is coming out from naphtha hydrotreating and catalyst regeneration units in normal operating condition.

- **Naphtha hydrotreating unit**

The main effluent is sour water coming from the reactor effluent separator drum. Depending on the naphtha quality as feed, sour water contains hydrocarbons, H_2S , and NH_3 .

The typical characteristic of sour water is specified as follows:

Temperature 45 °C

HC content 100 ppm wt

H_2S content 50 ppm wt

NH_3 20 ppm wt

In this case, the water collected and treated in batch stage by direct oxidizing with hydrogen peroxide in the sour water treatment unit.

- **Catalyst regeneration unit**

Catalyst regeneration unit as a part of aromizing section regenerates continuously deactivated catalyst coming from aromizing unit and introduces to aromizing reactor automatically.

Table 2.3 Wastewater contaminated with wet PVC and VCM characteristics

Temperature	40–70 °C
pH	6–7
COD	150–250 ppm wt
BOD5	75–150 ppm wt
Wet PVC	15–20 mg per kg water
VCM	0.5–1 mg per kg water

The major effluent streams consist of water from washing drum, liquid from oxychlorination drum and liquid from dryer package.

(a) **Water from washing drum**

The major constituents of water from washing drum are carbon dioxide dissolved in water with tracing of carbonate sodium, hydroxide sodium, chloride sodium, oxychloride sodium.

(b) **Liquid from oxychlorination effluent drum**

The liquid effluent from oxychlorination drum consists of some sodium salts. The wholly specified composition of liquid are sodium combinations such sodium hydroxide, sodium carbonate, sodium oxychloride, and sodium chloride which shall be neutralized with hydrochloric acid.

2.9 Environmental Protection for Industrial Waste

All industrial complexes which produce waste in higher quantity above the standards should have waste treatment facilities before final release to environment. The dilution of treated wastewater to the standard level is not permitted. Monitoring system in final stage of treatment should be provided. Tables 2.4, 2.5, and 2.6 illustrate typical standards for municipal waste, effluent permissible concentrations, and characteristics of potable water.

2.10 Water Monitoring

Monitoring may be necessary for a number of reasons, such as

- (a) To measure water problems (what, where, why, when).
- (b) To measure waste parameters for use in calculation of waste treatment charges for municipal or regional treatment system.
- (c) To measure waste parameters to allow detection and triggering of emergency actions in case of spills or process upsets.
- (d) To measure the effect of a wastewater discharge on the quality of a receiving body of water.
- (e) To measure the quantity and quality of all process wastes as well as influent liquid raw materials.
- (f) To gather enough information on water used and contamination to allow design of pretreatment and/or reclamation systems.

Oil, gas, and chemical industries discharging to municipal or regional treatment systems shall be required to monitor their wastewater discharges or allow monitoring by others.

Table 2.4 Typical maximum effluent standard for municipal waste (daily average)

Effluent characteristic	Unit	Maximum concentration	Note
BOD5	mg/l	30	BOD5 should not increase to more than 50 mg/l
COD	mg/l	60	COD should not increase to more than 120 mg/l
Cl	mg/l	1	
Chloroform	MPN	100/100 ml	
Color	Color unit	16	
Detergents	mg/l	1.5	Equivalent to A.B.S
Dissolved oxygen	mg/l	2	
F	mg/l	2.5	
Ammonia (as N)	mg/l	2.5	
Nitrite (as N)	mg/l	50	
Nitrate (as N)	mg/l	10	
Oil and grease	mg/l	10	
pH	–	6.5–8.5	
Phosphate	mg/l	1	
Settleable solid	mg/l	0.1	
Suspended solid	mg/l	40	S.S should not increase to more than 60 mg/l
Sulfate	mg/l	400	Should not increase the sulfate content of supply water more than 10 %
Sulfite	mg/l	1	
Turbidity	N.T.U (nephelometric turbidity unit), (previously J.T.U.)	50	

2.10.1 Design Considerations for a Water Monitoring System

The following for questions when preparing to establish a water monitoring program should be answered:

- What must be or should be monitored?
- When should samples be collected and monitoring equipment located?
- When should samples be collected and monitoring equipment located?
- How should monitoring be done? (collection of samples, storage, analysis).

Table 2.5 A typical effluent permissible concentrations

CONTAMINANTS	Discharge to surface runoff, (mg/L)	Discharge to groundwater, (mg/L)	Irrigation and agriculture usage, (mg/L)
Al	5	5	5
Ba	2	1	1
Be	0.1	1	0.1
B	2	1	1
Cd	1	0.01	0.01
Ca	75	—	—
Cr ⁶⁺	1	1	1
Cr ³⁺	1	1	1
Co	1	1	0.05
Cu	1	1	0.2
Fe	3	0.5	5
Li	2.5	2.5	2.5
Mg	100	100	100
Mn	1	0.5	0.2
Hg	0	0	0
Mo	0.01	0.01	0.01
Ni	1	0.2	0.2
Pb	1	1	1
Se	1	0.01	0.02
Ag	1	0.05	0.01
Zn	2	2	2
Sn	2	2	—
V	0.1	0.1	0.1
AS	0.1	0.1	0.1
Cl ⁻¹	Amount of chloride in industrial effluents should not exceed 250 mg/L (ppm) for freshwater	Amount of chloride in industrial effluents should not exceed 250 mg/L (ppm) for freshwater	Amount of chloride in industrial effluents should not exceed 250 mg/L (ppm) for freshwater
F	2.5	2	2
P	1	1	—
CN	0.2	0.02	0.02

(continued)

Table 2.5 (continued)

CONTAMINANTS	Discharge to surface runoff, (mg/L)	Discharge to groundwater, (mg/L)	Irrigation and agriculture usage, (mg/L)
C ₅ H ₅ OH	1	0	1
CH ₂ O	1	1	1
NH ₄ ⁺	2.5	0.5	—
NO ₂ [−]	50	10	—
NO ₃ [−]	50	1	—
SO ₄₂ [−]	300	300	500
SO ₃ ^{2−}	1	1	1
TSS	30	30	100
SS	0	0	0
TDS	Total dissolved solids in industrial effluents should not increase the amount of these materials more than 10 % in the underground water/ river and any other sources in a distance of 200 m, in which effluent is dumped	Total dissolved solids in industrial effluents should not increase the amount of these materials more than 10 % in the underground water/river and any other sources in a distance of 200 m, in which effluent is dumped	Total dissolved solids in industrial effluents should not increase the amount of these materials more than 10 % in the underground water/ river and any other sources in a distance of 200 m, in which effluent is dumped
Oil and grease	10	10	10
BOD	20	20	100
COD	50	50	200
DO	>2	>2	>2
ABS (detergent)	1.5	0.5	0.5
Turbidity	50	50	50
Color	Color of source water should not exceed more than 16 standard units due to industrial effluent, dumped	75 unit of color	75 unit of color
Temperature	Temperature of industrial effluent should not change the temperature of source water more than ±3 °C in a distance of 200 m	—	Temperature of industrial effluent should not change the temperature of source water more than ±3 °C in a distance of 200 m

(continued)

Table 2.5 (continued)

CONTAMINANTS	Discharge to surface runoff, (mg/L)	Discharge to groundwater, (mg/L)	Irrigation and agriculture usage, (mg/L)
pH	6.5–8.5	5–9	5–9
Radio actives	0	0	0
Digestible coliform	400/100 mL	400/100 mL	400/100 mL
MPN	1,000/100 mL	1,000/100 mL	1,000/100 mL

These four questions cannot always be completely answered in the sequence shown; usually, information is gathered and tabulated and several questions are answered simultaneously. Conflicts may arise with selection of a monitoring station at a hazardous location because the proper type of explosion proof equipment necessary for the area is not available or is prohibitively expensive. In this case, the “where” and “how” are not compatible and a compromise must be made. In general, the parameters and the equipment which should be monitored are covered in next sections of this chapter.

2.11 On-site Portable Instruments for Water Pollution Control

The sources of pollution and T.L.V (threshold limit value) of these pollutants in wastewater are described in previous sections. An effort has been made to present the most appropriate methods and equipment that apply as generally as possible for monitoring surface water, ground waters, cooling or circulating water, boiler water, boiler feed water, wastewater effluents after varying degrees of treatment, and untreated municipal or industrial wastewaters.

Here again, the effort has been made to present methods and equipment of the widest possible application, but when monitoring of sample of highly unusual composition is encountered, the equipment of this manual may require modification or may be wholly inappropriate.

All parameters which have been mentioned in previous sections of this chapter (Maximum Effluent Standard for Industrial Waste) could be monitored by this portable instrument excluding organic and radioactive substances.

This equipment has been developed to meet the need for a simplified, convenient, and accurate means of testing water in the field. The colorimetric tests are made with colorimeter using pre-calibrated meter scales for direct readout.

The volumetric tests are conducted by titration using a unique buret and titration stand with a precision screw plunger.

This device is shown at the right of the kit. It dispenses titration solution so that accurate, reliable results are obtained from test to test.

Table 2.6 A typical physical characteristic of potable water

Characteristic	Desired threshold limit value (T.L.V)	Maximum value
Color	5 units	5 units
Odor	2	3
Turbidity	5	25
pH	7–8.5	6.5–9.2

Chemical characteristic of potable water mg/L

Characteristic	Desired threshold limit value (T.L.V)	Maximum value
As	0	0.05
Cd	0	0.01
Cn	0	0.05
Pb	0	0.1
Hg	0	0.001
Se	0	0.01
Cr	0	0.05
Ba	0	1
Ag	0	0.05
B	0	1
Hardness	150	500
Ca	75	200
Mg	50	150
Mn	0.05	05
Fe	0.3	1
Zn	5	15
Cr	0.5	1.5
SO ₄	200	400
Cl	200	600
N	0.002	0.05
Detergent	0.1	0.2
P	0.1	0.2
Total dissolved solid	500	1,500

2.11.1 Alternative Current Colorimeter

As mentioned above, the basic of measurement is colorimetric which some reagent could be added to water sample to produce colored solution. This should be tested later. Type of portable instrument could be determined by relevant authorities.

See also the following Technical Data in Table 2.7 for more information:

2.11.2 Calibration and Inspection

- In general, this type of instrument is factory calibrated, but can be calibrated by competent person in accordance with the manufacturer's recommended standard.
- All reagent and chemical must be refreshed or in case of changing color and precipitation replaced by new one.

2.12 Online Fixed Measurement or Continuous Monitoring

The use of continuous monitoring equipment will permit the frequent measurement of several water quality parameters and the recording of this data at the measurement site or the transmitting of it to another location.

2.12.1 Continuous Water Sampling and Clarification System

The monitoring instruments should contain a sampling module, the sensors, a signal conditioning module, and a data logging or transmission module. A continuous flow of sample must be provided to the sensors by a submersible pump.

Each sensor in the instrument should be supplied with its own signal conditioner which converts the input to a standard electrical output. See Table 2.8 for more detail on sensors and ion-selective electrode.

A typical electrode placement for continuous monitoring is shown in Fig. 2.1. Further information has been given hereunder (see also ASTM Volume 11.01, 1989).

2.12.2 Calibration and Inspection

Calibration of the sensor signals should be carried out by adjustment of the controls on the signal conditioner.

The sample intake should be shielded with a screen and must be inspected according to manufacturer's instructions to prevent debris from clogging the system or damaging the pump.

Table 2.7 Technical data

<i>Alkalinity</i>	<i>Iron</i>
Titration for phenolphthalein and total alkalinity; enough of each indicator for 100 tests; enough titrant for 100 average (125 ppm) tests	Simplified phenanthroline method Colorimetric range: 0–3 ppm Enough reagent for approximately 100 tests
<i>Carbon dioxide</i>	<i>Manganese</i>
Standard titration procedure; enough reagent for approximately 100 tests	Cold periodate oxidation method Colorimetric range: 1–10 ppm Enough reagent for approximately 100 tests
<i>Chloride</i>	<i>Nitrate, nitrogen</i>
Mercuric nitrate titration—enough reagent for approximately colorimetric range: 0–1.5 ppm N, 100 tests; 0–15 ppm N, approximately 100 tests	Cadmium reduction–diazotization method; colorimetric range: 0–1.5 and 0–150 ppm N; enough reagent for 100 tests
<i>Chlorine</i>	<i>Nitrite, nitrogen</i>
Improved orthotolidine method; Colorimetric range: 0–1 ppm; enough reagent for 60 tests	Diazotization method; colorimetric range: 0–0.2 ppm N; enough reagent for approximately 100 tests
<i>Chromate</i>	<i>Oxygen dissolved</i>
Diphenylcarbohydrazide method; improved Winkler method; alkaline–colorimetric range: 0–1.5 ppm; enough reagent for approximately 100 tests; Titration. 1 drop = 1 ppm	Improved Winkler method; alkaline–colorimetric range: 0–1.5 ppm iodide–azide modification; enough reagent for approximately 100 tests; Titration... 1 drop = 1 ppm, tests. 1 drop = 0.2 ppm Enough reagent for approximately 100 tests.
<i>Color</i>	<i>pH, Wind range</i>
Colorimetric range: 0–500 APHA; platinum–cobalt units. No reagents required	Colorimetric range: 4.0–10; enough reagent for approximately 100 tests; no reagents required
<i>Copper</i>	<i>phosphate, ortho and meta</i>
Cuprethol method; colorimetric range: 0–3 ppm; enough reagent for approximately 100 tests	Stannous reduction method Colorimetric range: 0–3, 0–2, and 0–8 ppm; enough reagent for approximately 100 tests
<i>Fluoride</i>	<i>Silica</i>
SPADNS method; colorimetric range: 0–2 ppm Enough reagent for approximately 10 tests	Heteropoly blue method; colorimetric range: 0–3 ppm; enough reagent for approximately 100 tests

(continued)

Table 2.7 (continued)

<i>Hardness, calcium</i>	<i>Sulfate</i>
EDTA titration method; enough reagent for approximately 100 tests	Turbidimetric method; range: 0–300 ppm; enough reagent for approximately 100 tests.
<i>Hardness, total</i>	<i>Turbidity</i>
EDTA titration method 100 tests	Absorption method; range: 0–500 JTU; no reagents required
<i>Hydrogen sulfide</i>	
Screen test color chart comparison...0.1–5 ppm	
Enough test paper for 100 tests	

Table 2.8 Electrodes and ion-selective electrodes

Ion determined	Recommend Ref. electrode
Ammonia	Not applicable
Ammonium	Calomel
Barium	Calomel
Bromide	Double junction
Cadmium	Calomel
Calcium	Calomel
Chloride	Double junction
Copper	Calomel
Cyanide	Double junction
Fluoride	Double junction
Fluoroborate	Not applicable
Iodide	Double junction
Lithium	Double junction
Nitrate	Double junction
Oxygen	Not applicable
Potassium	Double junction
Silver/sulfide	Double junction
Sodium	Double junction
Sulfur	Not applicable

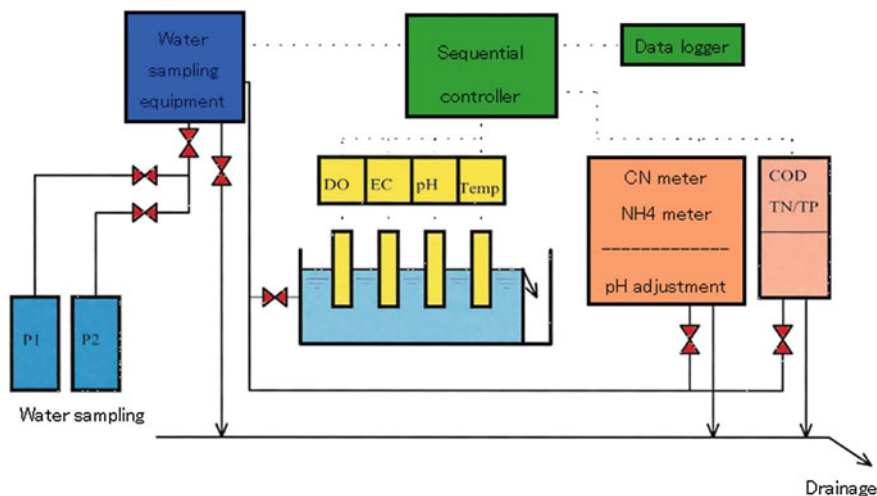


Fig. 2.1 Continuous water sampling and monitoring system

2.13 Laboratory Instruments

All parameters which are summarized in the following sections could be monitored in laboratory using instrumental or wet chemical methods.

2.13.1 Collection and Preservation of Samples

Sampling of different sources

The summary of different kinds of sampling is mentioned here, and for more details, see BS 6068-6.2, Water Quality Sampling.

Sampling of atmospheric precipitation

Atmospheric precipitation usually occurs in discrete events of limited duration.

Sampling precipitation equipment

Equipment for sampling precipitation includes a polyethylene polypropylene bucket and a stand.

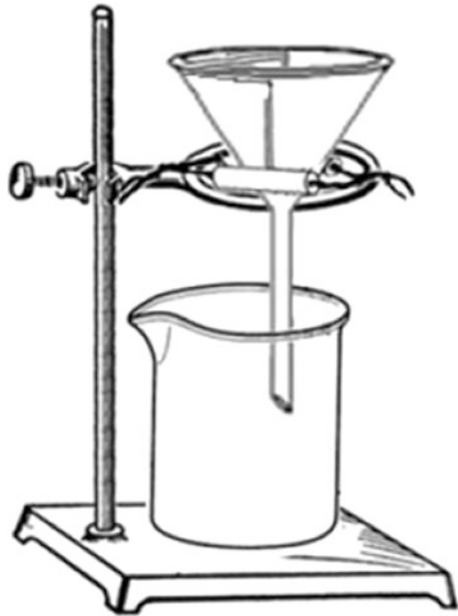
Construction

The basic of this equipment is shown in Fig. 2.2. The equipment could be operated manually or automatically.

The equipment must be designed to minimize pollution during its operation. It should be manufactured from chemically inert materials to avoid contamination.

Surface water samples are usually taken directly into the sample container. It is not possible to take the sample by submerging the container by hand, laboratory forceps, or a holder with a sliding sleeve should be used.

Fig. 2.2 Sampling of atmospheric precipitation



For such sampling, the container, which should have a volume of at least two liters, is usually made of stainless steel.

2.13.2 Soil Water Sampling

Soil water is defined as being all of the water contained in the soil.

Soil water sampling system

A common soil sampling system comprises a ceramic vessel with two pressure (vacuum) hoses inserted into it. The system operates by developing a vacuum through one hose, which causes the soil water to be drawn in through the porous walls of the vessel.

Construction

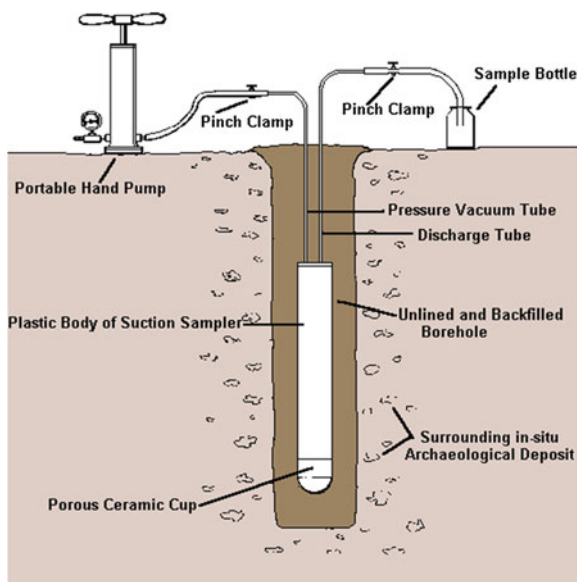
A schematic of soil water sampler is shown in Fig. 2.3.

2.13.3 Groundwater Sampling

The sampling of groundwater is usually carried out with devices and equipment very similar to that used for surface waters.

Similar containers are used for groundwater, mainly glass or polythene bottles.

Fig. 2.3 The installation of a suction sampler



2.14 Physical Examination

2.14.1 Color

Color in water may result from the presence of metallic ion humus and peat materials, plankton, weed, and industrial waste.

The unit of color is produced by 1 mg/L platinum in the form of the chloro-platinate ion.

For color monitoring, see ASTM D 1882-00 and BS 2690: Part 9, 1970.

2.14.2 Conductivity

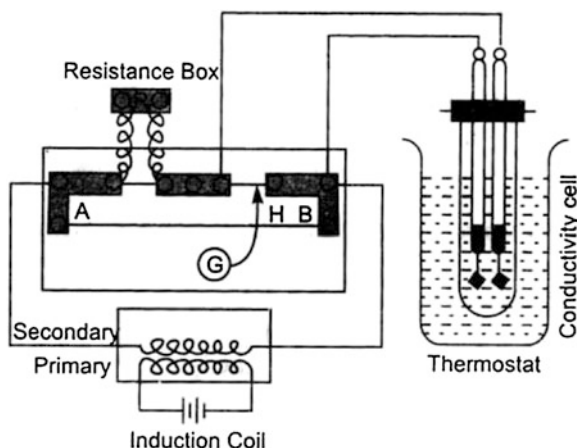
Conductivity is a numerical expression of the ability of a water sample to carry an electric current and is defined as $\mu \text{ moh/cm}^2$. This number depends on the total concentration of the ionized substances dissolved in the water. See also BS 2690: Part 9 1970.

Conductivity instruments

Measurement of electrical conductance is usually based on the use of conductivity bridges (Wheatstone bridge). The bridge circuit should always be arranged so that at the balance point, the detector indicates either zero or minimum potential. Basic of instrument is shown in Fig. 2.4.

In Fig. 2.4, we have

Fig. 2.4 “Inductive-type” conductivity cell



Determination of conductivity of the solution

We know that conductivity is the reciprocal of resistance and the resistance is more frequently determined by means of some form of Wheatstone bridge circuit. But, when direct current is passed through the solution, the following difficulties arise:

1. The concentration of the charges,
 2. The polarization set in due to the substance liberated at electrodes. With the result, a back EMF is set up and the resistance of the electrolyte is altered.
- Kohlrausch (1868) avoided these difficulties as follows:
- (a) Using an alternating current: The polarizing effects of the deposition of substances due to the current in one direction are neutralized by the effect of current in the other direction.
 - (b) Increasing the surface of electrodes: Polarization is decreased further if the surface of the electrodes is increased. This is done by coating electrodes in the cell with finely divided platinum.
 - (c) Using headphone: Since, with the passage of an alternating current, the ordinary galvanometer in Wheatstone bridge cannot be employed to determine the null point, it is replaced by a headphone.
 - (d) Using an oscillator: To obtain still better results, the induction coil is replaced by an oscillator having a frequency of 2,000–4,000 cycles per second.

Method

The solution of an electrolyte whose conductivity to be determined is taken as a special type of cell known as conductivity cell. This is made of Pyrex glass and is fitted with platinum electrodes. The electrodes usually consist of stout platinum plates sealed into glass tubes which pass through mercury placed in the tubes. The relative positions of the electrodes are fixed by cementing the tubes to the ebonite cover. The electrodes are coated with finely divided platinum. To maintain definite

temperature, it is placed in a thermostat. Copper wires are dipped in mercury placed in glass tube to make connections.

Determination of specific conductivity

The cell is connected to resistance box, R on one side and thin uniform wire AB of Meter Bridge on the other; secondary of induction coil is connected to the ends of the V bridge, while the primary is connected to a battery. The headphone, G , is connected to a sliding key, P , and the binding screw in between the cell and resistance box.

The sliding key, P is placed near the middle. When the circuit is complete, a buzzing sound is heard in the headphone. Plugs are taken out from the resistance box. The sliding key is moved along the wire until the sound in the headphone is reduced to a minimum. Thus, point H is recorded. The observed conductivity of solution is then calculated by applying the following formula:

$$\text{Resistance of solution} = (BH/AH) \times (\text{Resistance, } R)$$

Or

$$1/(\text{Obs. Conductivity}) = (BH/AH) \times (\text{Resistance})$$

Thus, AH and BH are measured on graduated scale and R in ohms from resistance box.

2.15 Turbidity

Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through sample.

Turbidity in water is caused by the presence of suspended matter, such as clay, silt, finely divided organic and inorganic matter, plankton, and other microscopic organisms. See also BS 2690: Part 9, 1970.

2.16 Determination of Metals

The presence of metals in potable water, domestic wastewater, and industrial effluents is a matter of serious concern. Metals could be monitored by atomic absorption spectroscopy, polarography, ICP, and colorimetric methods.

2.16.1 Atomic Absorption Spectroscopy

In atomic absorption, the sample is atomized into a flame, producing atomic vapor of the elements in question. The atoms absorb the radiation from the light source. The amount of light absorbed is proportional to the amount of the element.

Atomic absorption instrument

Figure 2.5 shows schematic diagram of an instrument.

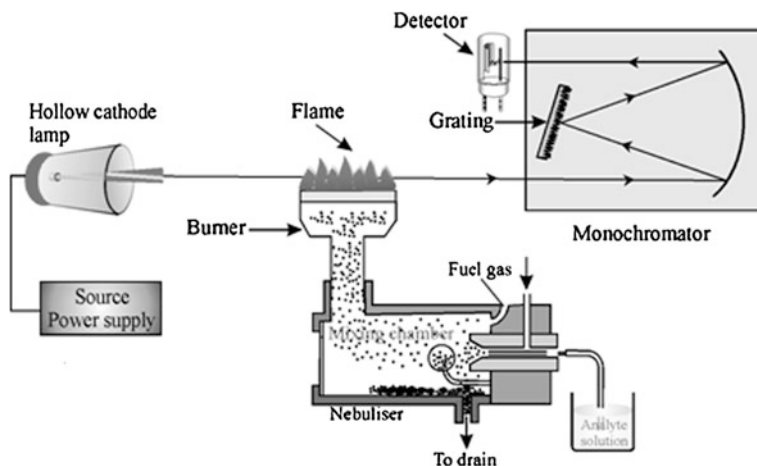


Fig. 2.5 Atomic absorption spectrometer

A mechanical modulated chopper alternately passes and reflects the light beam. One beam bypasses the sample and its intensity is measured as I_0 and the sample's beam is measured as I_1 . The absorbed light is as $I_0 - I_1$.

Calibration

The instrument should be calibrated according to manufacturer's manual book. The toxic pollutants such as Pb, As, Hg with low concentration (PPb) part per billion should be monitored by special device (vapor generation and hydride generation) which could be installed on atomic absorption instrument.

2.17 Polarography

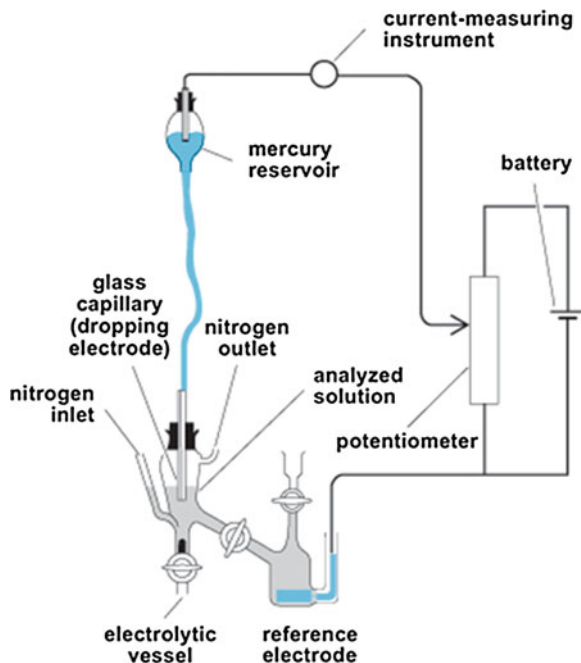
Electrochemical methods are used for analysis of raw water and wastewaters.

2.17.1 Polarography Instrument

A schematic diagram of a classical polarography is shown in Fig. 2.6.

Polarography measurement is based on determining the time-averaged current of the dropping mercury electrode (DME) under diffusion condition.

Fig. 2.6 Schematic diagram of classical polarograph



2.18 Chloride

Chloride, in the form of Cl^- ion, is one of the major inorganic anions in water and wastewater. Chloride could be monitored by titrimetric, potentiometric, and ion-selective electrode. More detail could be obtained from ASTM D 512-2004.

2.19 Chlorine (Residual)

The chlorination of water supplies and polluted water serves to destroy or deactivate disease, producing microorganisms. It could improve water quality by reaction with ammonia, iron, manganese, sulfide, and some organic substances. It should be monitored by titrimetric and colorimetric techniques. More detail should be obtained from ASTM D 1253-2003.

2.20 Cyanide, Fluoride, and Iodide

These three pollutants should be measured by titrimetric and/or colorimetric methods (UV-VIS spectroscopy) and ion-selective electrodes.

2.21 Nitrogen (Ammonia, Nitrate, Organic)

Nitrogen group should be monitored by titrimetric and/or colorimetric methods.

2.22 Ozone

Ozone should be measured by titrimetric method as given in ASTM Volume 11.02.

2.23 pH Value

The pH value of a solution is defined as the logarithm of the reciprocal of the hydrogen-ion concentration. Detail on effect of pH could be provided in API, manual on disposal of refinery wastes volume on liquid wastes, [Chap. 2](#). pH should be monitored by electronic pH meter.

2.23.1 Calibration

It should be calibrated with standard buffer solution with known pH.

2.24 Phosphate

Phosphate content should be monitored by colorimetric method. For detail, see ASTM 11.02 and BS 6068 [Sect. 2.28](#) 1986.

2.25 Silica

Silica concentration could be measured by calorimetric and gravimetric method. For detail, see ASTM 11.02.

2.26 Sulfate

Sulfate could be measured by gravimetric method.

2.27 Sulfide

For sulfide monitoring, in general, it should be measured by colorimetric and titrimetric methods.

2.28 Determination of Organic Constituents

2.28.1 Grease and Oil

Solvent extraction infrared absorption

In this sort of monitoring, the oil is extracted from sample and the infrared absorption of the oil in solution is then measured.

Infrared spectrophotometer instrument

Radiation from the source is split into two beams: half passing into the sample cell and the other half into the reference cell. The reference beam then passes through the attenuator and onto the chopper. After dispersion by the prism or grating, the alternating beams fall on the detector and are converted to an electrical signal.

Schematic diagram is shown in Fig. 2.7.

Calibration of instrument should be according to manufacturer's manual book.

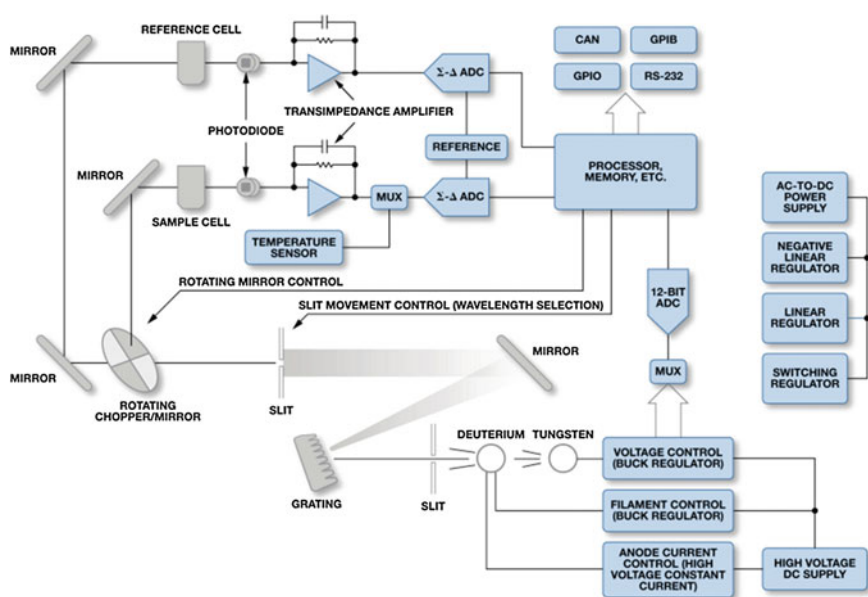


Fig. 2.7 Schematic diagram of a double-beam spectrophotometer

2.29 Combustible Gas Indicator

Equilibrium is established between methane in solution and the partial pressure of methane in the gas phase above the solution. The partial pressure of methane could be determined with a combustible gas indicator.

2.29.1 Combustible Gas Indicator Instrument

The heat generated by the oxidation of the gas increases the electrical resistance of the filament. The resulting imbalance of the electrical circuit causes deflection of a milliammeter.

2.30 Organic Carbon (Total)

Organic carbon TOC could be monitored by carbon analyzer in the range of 1–150 mg/L in water and wastewater.

2.30.1 Total Carbon Analyzer Instrument

Microportion of sample is injected into a heated packed tube in a stream of oxygen or purified air.

The water is vaporized and the organic matter is oxidized to carbon dioxide, which is measured by means of a non-dispersive type of infrared analyzer.

2.31 Oxygen Demand (Biochemical)

The biochemical oxygen demand (BOD) is a test in which standardized laboratory procedures should be used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters.

For this procedure, see ASTM Volume 11.02. See also BS 6068 [Sect. 2.3](#) 1984.

2.32 Oxygen Demand (Chemical)

COD is an important measured parameter for stream and industrial waste control.

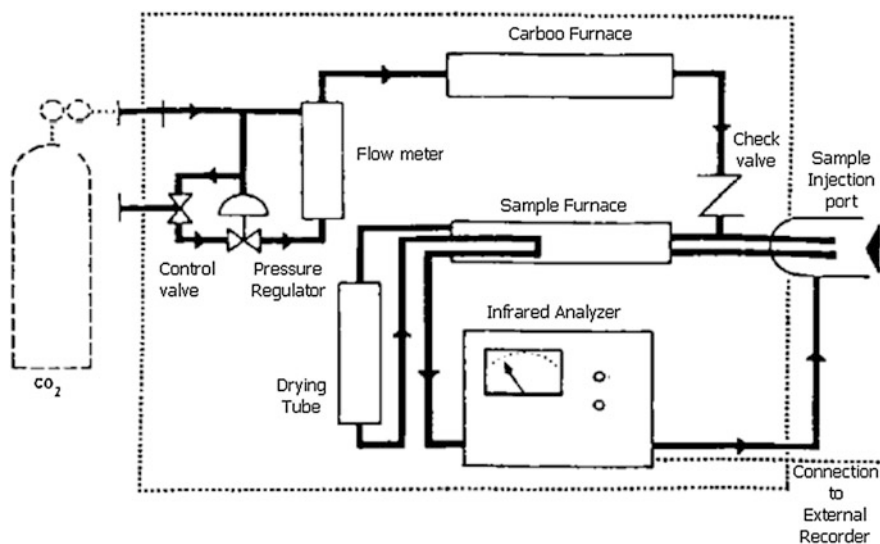


Fig. 2.8 Chemical oxygen demand (COD) analyzer flow diagram

2.32.1 COD Analyzer Instrument

Use dry CO_2 to carry the organic matter through a platinum catalytic combustion furnace which oxidizes it to CO and H_2O . Following the water removal and passage through a second catalytic treatment, the CO concentration is measured using an infrared analyzer. A schematic of instrument is shown in Fig. 2.8.

2.33 Examination of Water and Wastewater Radioactivity

The radioactivity in water and wastewater originates from natural and artificial or man-made sources. Artificial sources of radioactivity include fission, fusion, or particle acceleration, giving rise largely to alpha, beta, and gamma radioactivity.

2.33.1 Counting Room

The room should be free of dust and fumes that may affect the electrical stability of instrument. The background could be stabilized and lowered considerably by making the walls, floor, and ceiling out of several centimeters of concrete. Generally, temperature could be constant within $3\text{ }^\circ\text{C}$ and should not exceed $30\text{ }^\circ\text{C}$.

Samples containing appreciable activity should be stored at a distance so as not to affect instrument background counting rate.

2.33.2 Alpha Particle Counter Instrument

Alpha particle counter consists of either a proportional detector or a scintillation detector, and a scaler conforming to the following requirements. For method, see ASTM 11.02 1989 and Technical Data.

Proportional detector

This may be one of the several types commercially available. The material used in the construction of the detector should be free from detectable radioactivity.

The manufacturer should supply voltage plateau and background counting rate data. Voltage plateau data should show the threshold voltage, slope, and length of plateau for a particular input sensitivity.

Scintillation detector

It should consist of an “activated” zinc sulfide phosphor having a minimum effective diameter of 36.5 mm. The phosphor should be mounted so that it could be attached and optically coupled to a multiplier phototube.

Scaler

Mechanical register, power supply, and amplifier are contained in a single chassis, generally termed the scaler.

Sample mounting disks or dishes

Having a flat bottom of a diameter slightly less than the inside diameter of the detector. Flat disks are preferred, but dishes could be used that have 3.2 mm high side walls. Platinum and stainless steel have been used for this purpose.

Calibration and standardization for general monitoring

Place a known amount of alpha standard into a volume of water sufficient to dissolve salts equivalent to those of the test samples and prepare for counting.

2.33.3 Beta-Particle Radioactivity Instrument

Beta-particle radioactivity of water and wastewater in general monitored by beta-particle counter which consists of the following components:

Detector

The end-window Geiger–Muller tube and the internal or external proportional gas-flow chambers are the two most commercially available types of detector.

Detector shield

The detector assembly shall be surrounded by an external radiation shield of massive metal equivalent to approximately 51 mm of lead and lined with 3.2 mm-thick aluminum.

2.33.4 Gamma-ray Monitoring

This section covers the monitoring equipment for gamma-ray-emitting radionuclides in water or wastewater by means of gamma-ray spectrometry.

Gamma-ray instrument

Gamma-ray spectra are measured with modular equipment consisting of a detector, and analyzer, memory, and a permanent data storage device. Lithium-drifted detectors, *p*-type or *n*-type, are used. A multichannel pulse-height analyzer should be used to determine the amplitude of each pulse originating in the detector.

2.34 Automated Laboratory Equipment for Monitoring Water and Wastewater

Automated instrument are available and in use to monitor individual samples at rate of 10–60 samples/hr. The same instruments could be modified to make analysis for multiple constituents simultaneously from one sample. The readout system includes sensing elements with indicators, alarms, and recorders.

Appropriate methodology could be supplied by the manufacturer for many of the common constituents of water and wastewater.

Table 2.9 Saturation (*S*) factors for calculating petroleum liquid loading losses

Cargo carrier	Mode of operation	<i>S</i> factor
Tank trucks and rail	Submerged loading of a clean cargo tank	0.5
Tank cars	Submerged loading: dedicated normal service	0.6
	Submerged loading: dedicated vapor balance service	1
	Splash loading of a clean cargo tank	1.45
	Splash loading: dedicated normal service	1.45
	Splash loading: dedicated vapor balance service	1
Marine vessels	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

2.35 Loading Losses

2.35.1 Total VOC Estimation

Emissions from the loading petroleum liquid can be estimated (with a probable error of $\pm 30\%$) using the following equation:

$$LL = 0.12 \times SPM/T \quad (2.1)$$

where

- LL VOC loading loss (kg/m^3 of liquid loaded);
S A saturation factor—see Table 2.9 below);
P True vapor pressure of liquid loaded (kilopascals (kPa));
M Molecular weight of vapors ($\text{kg}/\text{kg-mole}$);
T Temperature of bulk liquid loaded (K (i.e., $^{\circ}\text{C} + 273$))

The saturation factor “S” accounts for the variations observed in emission rates from the different loading and unloading methods. Table 2.9 lists suggested saturation factors.

Emissions from controlled loading operations can be calculated by multiplying the uncontrolled emission rate (as determined using the equation above), by a reduction efficiency term:

$$\text{Controlled Emission} = \text{Uncontrolled Emission} \times (1 - \text{Efficiency}/100) \quad (2.2)$$

The overall reduction efficiency should account for the capture efficiency of the collection system, as well as both the efficiency and any downtime of the control device. These data should be obtained from the supplier or manufacturer of the collection system.

2.36 Emissions to Water

This section will be divided into two principal parts as follows:

- Point source wastewater discharges as released by refinery treatment plants; and
- Diffuse wastewater that arises through storm water and other miscellaneous runoff from the refinery site that is not captured and treated prior to discharge.

2.36.1 Point Source Discharge

The following tables should be used to provide “default” emission data for refinery effluent discharges that are not classified as transfers (transfers include discharging to sewer).

Table 2.10 Default speciation factors for organics in refinery effluent

Substance	Weight percent of DOC
Toluene	9.2×10^{-4}
Benzene	9.1×10^{-4}
Xylenes	1.4×10^{-3}
Phenol	6.9×10^{-4}
1,2-Dichloroethane	2.7×10^{-4}
Hexachlorobenzene	4.4×10^{-6}
PAHs	1.6×10^{-3}
Styrene	1×10^{-4}
Ethylbenzene	1.2×10^{-4}
1,1,2-trichloroethane	3.6×10^{-5}
Chloroform	2.5×10^{-3}

Table 2.11 Default emission factors for trace elements and inorganic in refinery effluent

Substance	Emission factors (kg/m ³ of flow)
Zinc	4.4×10^{-4}
Phosphorous	4.1×10^{-7}
Arsenic	6.7×10^{-6}
Chromium (VI)	7.7×10^{-6}
Selenium	3.1×10^{-6}
Nickel	3.6×10^{-6}
Copper	2.9×10^{-6}
Antimony	5.8×10^{-7}
Cobalt	1.6×10^{-6}
Mercury	1.1×10^{-8}
Cadmium	3.3×10^{-7}
Lead	1.9×10^{-6}
Cyanide	7.6×10^{-9}
Ammonia	1.3×10^{-6}

Based on discussions with the petroleum refining industry, the “dissolved organic carbon” (DOC) content of refinery effluents is a known parameter. Hence, the speciation factors for organic compounds in Table 2.10 are based on this parameter.

The document from which these data in Table 2.10 were derived indicates a ratio of DOC/COD of 0.267. In the absence of site-specific information regarding DOC, this ratio can be used to determine DOC from measurements of COD.

A similar parameter to DOC was not identified for trace elements and other inorganics in wastewater effluent. Therefore, trace elements and inorganic compound emissions are expressed as default emission factors in Table 2.11.

These speciation factors are applied to this effluent parameter in the following manner:

$$WWE_i = DOC \times (WPI/100) \times \text{Flow} \tag{2.3}$$

where

- WWE_i The wastewater emission of component “i” from the treatment plant (kg/hr);
- DOC The dissolved organic carbon (DOC) content of the treated effluent discharged by the plant (kg/m³);
- WPI The weight percent of component “i” as provided in Table 19 above;
- Flow The wastewater flowrate discharged to the receiving body of water (m³/hr)

The emission factors in Table 2.11 are applied in the same way as factors are applied to air emissions, with the exception that they are based on the flow of effluent from the treatment plants (i.e., the emission factors are kg/m³ of wastewater flow).

Pollution Control in Oil, Gas and Chemical Plants

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2014, XVII, 318 p. 64 illus., 39 illus. in color., Hardcover

ISBN: 978-3-319-01233-9