CHAPTER - 1
1. Introduction

1.1. Sensor

Broadly defined, the sensor is a device which is capable of being actuated by energizing input from one or more transmission media and in turn generating a related signal to one or more transmission systems. It provides a usable output in response to specified input measured, which may be physical or mechanical quantity, property, or conditions. The energy transmitted by these systems may be electrical, mechanical or acoustical. The nature of electrical output from the transducers depends on the basic principle involved in the design. The output may be analog, digital or frequency modulated.

1.2. Specification of sensor

The sensor has to be physically compatible with its intended applications. They have eight specifications that should be considered while selecting a sensor.

1) Operating range: Chosen to maintain range requirements and good resolution.

2) Sensitivity: Chosen to allow sufficient output

3) Selectivity

4) Environment compatibility: Temperature range, corrosive fluids, pressure, shocks, interaction, size and mounting restrictions.

5) Limit of detection

6) Accuracy: Repeatability and calibration errors as well as errors expected due to sensitivity to other stimuli.

7) Low Cost

8) Repeatability and Reproducibility: The reading that varies is repeatedly measured under the
same environment.

1.3. Sensor classification

Sensors can be classified in many ways. Based on the analyte, sensor can be classified as

![Sensor classification diagram]

**Fig. 1.1. Sensor classification based on analyte**

1.3.1. Chemical sensor

A chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. The chemical information, mentioned above, may originate from a chemical reaction of the analyte or from a physical property of the system investigated.

Chemical sensors contain two basic functional units: a receptor part and a transducer part. Some sensors may include a separator which is, for example, a membrane. In the receptor part of a sensor the chemical information is transformed into a form of energy which may be measured by the transducer. The transducer part is a device capable of transforming the energy carrying the chemical information about the sample into a useful analytical signal. The transducer as such does not show selectivity.

From the **Fig. 1.2** describes the schematic diagram of the chemical sensors. A chemical sensor is composed of an active layer and a transducer. The active layer represents the main
part of the sensor. Many materials such as organic, inorganic or hybrid organic-inorganic
copolymers can be used as active layers, providing that pollutants can diffuse into the matrix and
be trapped, thus modifying the physical or/and chemical properties of the material. The active
layer can also be doped with specific probe-molecules able to react selectively with the targeted
pollutants, thus providing the selectivity of the sensor. The transducer role is to convert the
variation of a physical property (i.e. refraction index.), or a chemical interaction (i.e. H-bond
formation, electrostatic interaction…) or a chemical reaction (covalent bond formation) into a
measurable signal (optical, electrical, electrochemical, piezoelectrical, etc…) proportional to the
pollutant concentration. The requested properties of a chemical sensor are a good sensitivity (ppb
level), a good selectivity, fast sampling time (<15 min), a reduced maintenance and a low cost.

![Chemical Sensors](image)

Fig. 1.2. Schematic diagram of chemical sensors
A chemical sensor (Fig. 1.3) is defined as a small device where a chemical interaction occurs between the analyte gas and/or liquid and the sensor device, transforming chemical or biochemical information of a quantitative or qualitative type into an analytically useful signal. The signal from a sensor is typically electronic in nature, being a current, voltage, or impedance/conductance change caused by electron exchange. These devices contain a physical transducer and a chemically sensitive layer or recognition layer. Chemical sensors can be characterized by several features such as stability, selectivity, sensitivity, response and recovery time, and saturation. Chemical sensors [1], with recent significant developments for detection and quantification of chemical species, are becoming an enabling technology in a wide range of applications such as clinical, industrial, agricultural and military technologies thereby resulting in social and economic benefits.

Fig. 1.3. Schematic showing the working principles of chemical sensors.
1.3.2. Biosensor

By definition, a biological sensor or a biosensor [1] is a miniaturized analytical device comprising an analyte and a biological receptor layer coupled with a transducer for signal evaluation, either directly or through a mediator. The specific biological receptor layer is a biocatalytic sensing element (e.g., antibody, enzyme, receptor protein, and nucleic acid, whole cell / tissue section), capable of recognizing its specific analyte (compound whose concentration is to be determined), and regulating the specificity and sensitivity of a biosensor. The main aim of a biosensor is to generate either discrete or continuous digital electronic signals that are proportional to analyte, evaluated with physicochemical transducers such as optical, electrochemical, and micro gravimetric or calorimetric (Fig. 1.4). Because of their low cost fabrication, specificity, rapid response time, portability and easy access, biosensors are powerful analytical tools for clinical diagnosis.

![Fig. 1.4. Schematic showing the working principles of bio sensors](image-url)
1.4. Sensor classification based on transducer

They may be classified according to the principle of operation of transducer in two main groups as “Physical” and “Chemical” sensors (Fig. 1.5). A physical sensor is a device that provides information about a physical property of the system (magnetic field, force, pressure, temperature). Chemical sensors also can be divided into sub groups such as heat sensitive, mass sensitive, electrochemical and optical sensors. They can also be classified as direct and indirect sensors or as reversible or non-reversible and respect of their applications or sizes.

![Diagram of sensor classification]

Fig. 1.5. General classifications of sensors

1.4.1. Heat sensitive sensors (or) Thermal sensors

These are often called calorimetric sensors in which the heat of a chemical reaction involving the analyte is monitored with a transducer such as a thermistor or a platinum thermometer. Heat is a general property of any chemical reaction. As such is should be an ideal physical parameter to use for sensing. Unfortunately its flow is difficult to control. The partial solution for the heat management in any integrated chemical sensor has been suggested [2].
Enzymatic reactions act as chemically selective heat generators. The thermistor appears to be the most popular temperature-sensing probe because of its cost, availability, stability and sensitivity. For this reason almost all thermal sensor rely on enzymes for their selectivity. The first integrated thermal sensor for glucose using the temperature dependence of the output of the Darlington amplifier has been constructed [3].

1.4.2. Mass sensors

The measurement of the change of mass as the means of chemical sensing is almost as universal. In principle it is applicable to any reactions in which there is a net change of mass. There are two types of mass chemical sensors. The first type are those based on piezoelectric bulk oscillators in which quartz crystal microbalance (QCM) [4] is the most common material used for the bulk oscillators, but other materials, such as poly(vinyl fluoridone) (PVF). ZnO can be used. The second type is those based on surface acoustic wave (SAW) devices.

1.4.3. Electrochemical sensors

Electrochemical devices transform the effect of the electrochemical interaction between the analyte and the electrode into a useful signal. Such effects may be stimulated electrically or may result in a spontaneous interaction at the zero-current condition. Electrochemical sensors are the largest and the oldest group of chemical sensors. In electrochemical sensors the response is derived from the interaction between chemistry and electricity. Based on the mode of measurement of electric parameters.

(a) Potentiometric sensors (measurement of voltage at zero current)

(b) Amperometric sensors (measurement of current while potential is kept constant)

(c) Conductimetric sensors (measurement of conductivity change)
(d) Voltammetric sensors (monitoring the change in current while by varying the applied potential) [5, 6].

A steady effort has been made on the development of efficient and easy-use electrochemical sensors. Electrochemical sensors with rapid and highly sensitive detection capabilities of various biological/chemical species are in great demand in many areas of science. Developing easy-to-use electrochemical sensors for detecting the concentration and activities of the various species therefore become very important.

1.4.4. Optical chemical sensors

In optical sensors there is a spectroscopic measurement associated with the chemical reaction. Optical sensors are often referred to as optodes and use of optical fibers is a common feature.

(a) Absorbance
(b) Reflectance
(c) Luminescence
(d) Fluorescence
(e) Refractive index
(f) Optothermal effect
(g) Light scattering

An optical sensor device consists of the following components:

(a) The recognition unit, where specific interaction and identification of the analyte takes place.
(b) The transducer unit that converts the recognition process into a measurable optical signal.
(c) An optical device (process unit) which consists of at least a light source.
(d) A detector (in the simplest form a photodiode), which detects and converts the change of optical properties, after amplification of the primary signal, into a unit readout. The optical properties measured can be absorbance, reflectance, luminescence, light polarization, Raman and other [7].

Optical sensors have found many applications in various fields, including biomedical, clinical, and environmental monitoring and process controlling. They are an attractive analytical tool, whenever continues monitoring and real-time information is desired. They can track sources of contamination in an industrial process, follows the formation and movement of environmental pollutants and can raise the alarm when a toxic species exceed an expected level of exposure. In recent years, chemical sensors for hazardous materials have seen an increasing interest. A ‘metal sensor’ is described as a device which is capable of responding to the presence of a heavy metal ion in a reversible and continuous manner.

1.4.4.1. Optical sensors based on chromophores

The majority of heavy metal ion sensors or toxic compound sensors are based on the use of an indicator dye which undergoes a binding reaction with the analyte. This reaction is accompanied by a change in the absorbance or fluorescence of such chelates or compounds. In other words, an indicator acts as a transducer for the chemical species that cannot be determined directly by optical means. Many indicators cannot be used in optical sensors because of unfavorable analytical wavelengths, poor photo stability, low molar absorptivity or the need for additional reagents. Most of them bind with the metal ion irreversibly or only at low or high pH so they cannot be used for continuous sensing at near neutral pH. Upon binding with the metal ion, most indicators undergo a change in color, with one band appearing as another disappears, rather than an intensity change of one single band.
In contrast to chromogenic reagents, fluorescent indicators are of on/off type in that only one of the species (the complexed or the noncomplexed) is fluorescent. Fluorescent indicators frequently provide improved sensitivity (which is important in miniature sensors) and also selectivity because it is unlikely that an interfering species would have the same absorbance and emission as the analyte complex [8]. Fluorimetry (and luminescence spectrometry in a wider sense) also offers a broad variety of spectroscopic techniques including the measurement of lifetime, polarization and energy transfer. An important group of indicators is based on quenching of luminescence by heavy metals and transition metals. In the case of static quenching, the quencher interacts with the fluorophores in its ground state. In dynamic (collisional) quenching, the interaction between the metal ion (quencher) and the fluorophore occurs in the excited state only and leads to a reduction in both the emission intensity and the decay time.

1.4.4.2.1. Luminescence

Generation of luminescence through excitation of a molecule by ultraviolet or visible light photons is a phenomenon termed photoluminescence, which is formally divided into two categories, fluorescence and phosphorescence, depending upon the electronic configuration of the excited state and the emission pathway (Fig. 1.6).

Luminescence is the emission of light that occurs at low temperatures from a photochemically generated excited electronic state of any substance. The singlet ground, first and second electronic states are depicted by $S_0$, $S_1$ and $S_2$ respectively. At each of these electronic energy levels the fluorophores can exist in a number of vibrational energy levels, denoted by 0, 1, 2, etc. Absorption of a photon of appropriate energy results in the promotion of an electron to
an orbital of higher energy $S_n$ ($n=1, 2, \ldots$). This process is known as excitation and has an instantaneous nature ($10^{-15}$ s, depicted as vertical lines on the diagram) [9]. The lowest energy and the most important electronic transitions from an organic perspective are between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the ground state configuration; $n-\pi^*$ and $\pi-\pi^*$ transition are of particular importance. Following light absorption, several processes usually occur: a fluorophore is excited to a higher vibrational level of $S_1$ ($S_2$ followed by internal conversion (IC) to $S_1$) then relaxes to the lowest vibrational level of $S_1$. This process occurs in $10^{-12}$ s or less. Intersystem crossing (ISC) takes place if the singlet excited state undergoes a change in spin multiplicity. Emission from the singlet state is defined as fluorescence. It typically occurs in $10^{-9}$ s. The emitted light is
always of longer wavelength than the incident light, a characteristic of fluorescence emission known as Stokes shift. Emission from triple state is called phosphorescence. The spin-forbidden process of ISC and formation of the triplet excited state is facilitated by the presence of \( n-\pi^* \) states or heavy atoms.

**1.4.4.3. Fluorescent chemosensors**

There are several reasons for which fluorescence may be identified as the optimal signaling in potential sensing application. Fluorescence is an enormously sensitive technique. Fluorescence signaling permits the monitoring of both excitation and emission wavelengths. The emission signal may be observed by intensity, intensity ratio or life time measurement. Fluorescence is usually non-destructive [10]. The most common type of fluorescent chemosensor is ion (cation or anion) selective chemosensor that is molecules that are capable of reporting the ion coordination process. In the concept for ion recognition binding sites can be coupled to certain groups that are capable of “reporting” the ion coordination process. In this case the binding process is transduced into a signaling event. One basic principle in this multicomponent system is that the sensing event has to be related with an easy-to measure signal [11].

![Scheme 1.1. Principle of fluorescent chemosensor.](image)
1.4.4.3.1. Factors affecting fluorescence spectra

A variety of environmental factors affect fluorescence emission, including interactions between the fluorophore and surrounding solvent molecules (dictated by solvent polarity), other dissolved inorganic and organic compounds, temperature, pH, and the localized concentration of the fluorescent species. The effects of these parameters vary widely from one fluorophore to another, but the absorption and emission spectra, as well as quantum yields, can be heavily influenced by environmental variables. In fact, the high degree of sensitivity in fluorescence is primarily due to interactions that occur in the local environment during the excited state lifetime.

1.4.4.3.2. Quenching

Decrease of fluorescence intensity by interaction of the excited state of the fluorophore with its surroundings is known as quenching. Quenching is any process in which a sample constituent decreases the fluorescence quantum yield for the analyte. Among the most common fluorescence quenchers is O$_2$; removal of oxygen from a sample before fluorometric analysis is often advisable. One-way that fluorescence quenching can occur is intermolecular electronic energy transfer:

$$A^* + B \rightarrow A + B^*$$

Here an excited analyte molecule ($A^*$) transfers excitation energy to a quencher molecule $B$, causing de-excitation of $A$ and forming an excited quencher molecule, $B^*$. If $B^*$ is a fluorescent species, its fluorescence (called sensitized fluorescence) may then be observed. This phenomenon can allow one to observe fluorescence from a molecule ($B$) that may be difficult to excite directly. More often, however, these processes are a nuisance. Not only do they cause a decrease in the fluorescence signal observed for a given concentration of analyte ($A$) in the
sample, but also they may produce unwanted background fluorescence signals; that is, $B$ may act both as a multiplicative and an additive interference.

### 1.4.4.3.3. Strategies of the “Chemical Sensors”

The strategies (Fig. 1.7) developed by the “Chemical Sensors” to improve the trapping of the pollutants and enhance the selectivity of the sensor are based on:

(a) The use of nanoporous transparent matrices as active layers. The size of the pores of the porous matrices can be tailored for a selective trapping of the pollutants. The matrices act as filters and provide a first selectivity based on the size of the pollutants. Moreover, their storage capacity, they act as sponges and concentrate the pollutants within the pores, thus enhancing the probability of their interaction or reactive collisions with the probe molecules. These porous matrices are elaborated via the Sol-Gel process, an easy-to-use and cheap method of synthesis.

(b) These sponges are doped with probe molecules able to react selectively with the targeted pollutants. Moreover, as optical transduction is involved in the sensing process, the choice of the probe molecules is based on their optical properties. They must have high values of absorption coefficient or display luminescent properties.

(c) Optical methods of transduction based on absorption or fluorescence measurements provide the fast response of the sensor.

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**Fig. 1.7. Strategies of the Chemical Sensors**
1.5. Hazardous materials

One of the critical global environmental problems is human and ecological exposure to hazardous compounds from agricultural, industrial, military and mining activities. These compounds often include heavy metals, hydrocarbons and other organic chemicals. Traditional field and laboratory detection and monitoring of these compounds are generally expensive and time consuming. The intentional or accidental release of hazardous substances into the environment is an inevitable consequence of anthropogenic activity. Industrial, commercial, mining, military and even domestic activities can result in the release of substances into the air, land and water that are harmful to environmental quality and human health. The combined industrialization and population growth of the twentieth century has resulted in unprecedented events of fugitive, transitory, and ephemeral releases of contamination that today threaten many plant and animal species and may ultimately threaten the survival of the human race [12]. The detection and remediation of many hazardous substance problems consist of a variety of monitoring and analysis strategies that are time-consuming and expensive, such as laboratory chemical analysis. The United States Environmental Protection Agency (USEPA) estimates that complying with hazardous waste regulations cost U.S. businesses nearly $32 billion in 2000 [13].

1.5.1. Definition of hazardous materials

Substances are considered hazardous materials if they are ignitable-capable of burning or causing a fire: corrosive-able to corrode steel or harm organisms because of extreme acidic or basic properties: reactive-able to explode or produce toxic gases such as cyanide or sulfide: or toxic-containing substances that are poisonous to people and other organisms [14]. In U.S., the
regulatory definition of hazardous substances is detailed in the Resource Conservation and Recovery Act (RCRA) [14].

Most hazardous waste is the by-product of industrial or commercial manufacturing processes but significant levels of hazardous substances are also associated with agricultural chemicals such as pesticides. There is a distinction between widely dispersed contaminants such as agricultural pesticides known as non-point sources and point sources such as an industrial site. Even household waste contains substances such as bleach, gasoline, batteries and solvents that qualify as hazardous wastes. Hazardous substance can also be naturally occurring substances, such as heavy metals like mercury, cadmium, and lead that are brought into much higher than normal exposure concentrations by anthropogenic processes.

1.5.2. Heavy metal

Our environment contains countless numbers of toxic metal ions e.g. arsenic, antimony, mercury, lead, cadmium, etc., and platinum group elements (PGEs) e.g. Pt, Pd etc., and compounds which influence on natural components of the environment e.g. soil, water and air. The pollution of environment with metal ions represents one of the most serious environmental problems because of their high stability in contaminated site and complexity of mechanism in biological toxicity. Now a day, the contamination of water by toxic metal ions through the discharge of industrial and municipal wastewater is a worldwide environmental problem. The term “heavy metal” refers to the metallic elements having density greater than or equal to 6.0 g/mL. Heavy metals are introduced into environment through dumping wastes, effluents leading to heavy metals runoff of terrestrial system and geological weathering [15, 16].
Arsenic, mercury, bismuth, lead, cadmium, antimony, copper, and others have the ability to accumulate in bottom sediments. Due to various processes of remobilization, these metals may be released and moved into the biological or food chain and concentrate in fish and other edible organisms, thereby, reaching humans and causing chronic or acute diseases [16]. This class of chemicals occurs in a minute concentration in natural biological systems and exerts a beneficial or harmful effects on plant, animal and human life. Moreover, bio magnifications, i.e. the tendency of some chemicals e.g. heavy metals to pass through the food chain resulting in progressive increase of its levels at each tropic level may occur and enter into the environment [17]. The toxicity and the bioavailability of heavy metals in water depend on its pH, conductivity, and dissolved substances. Moreover, it is found that the edges, feeding habits of fish or aquatic animals and their retention time in polluted water affect the accumulation of the heavy metal ions such class of organisms [18, 19]. Therefore, the subsequent survey will briefly discuss occurrence, toxicity, determination methods of toxic pollutants understudy e.g. Hg and cyanide. Pollution with heavy metals, toxic anions and others has been a matter of great concern for human health and animals [20-24]. Mercury, arsenic (III, V), chromium (VI), lead, cadmium, bismuth (III, V), and antimony (III, V) species are one of the most elements affecting the environment. Thus, recent years have seen an upsurge of interest in monitoring and controlling environmental pollution from trace elements [20, 21]. Therefore, great attention has been oriented towards developing precise and low cost methods for removal and determination of heavy metal ions in various matrices including industrial water effluents [23, 24].

Water pollution occurs when pollutants are discharged into water bodies without adequate treatment to remove harmful compounds [25]. There are many causes for water
pollution but two general categories exist: direct and indirect contaminant sources. Direct sources include effluent outfalls from factories, refineries, mining and waste treatment plants. Indirect sources include contaminants that enter the water supply from soils/groundwater systems and from the atmosphere via rain water. Soils and ground waters contain the residue of human agricultural practices and improperly disposed of industrial wastes [25, 26]. Atmospheric contaminants are also derived from human practices (such as gaseous emissions from automobiles and factories) [25, 26]. Heavy metal ions toxicity is in significant in human body and is capable of causing ecological risk to aquatic organisms. Heavy metal ions could also gradually accumulate in human body through food chain and cause damage to human health [27]. Thus, the determination of trace metals in the environmental samples including food materials has been continuously performed in order to designate the level of pollution as the number of ecological and health problems associated with environmental contamination continue to rise. Direct instrumental analysis of these samples is difficult because of complex formation and significant matrices, which invariably influence normal instrumental analysis. In addition, some metals have low concentrations, which are near or below the limit of detection of the instrument. hence effective preconcentration step can solve the above two problems and leads to simple determination of heavy metal ions in complicated matrices [28].

1.5.3. Mercury

The toxicity of mercury species is highly dependent on its chemical form. The determination of organic and inorganic Hg in addition to total Hg is important for quality control taking into account the risk for human health (e.g. ingestion of Hg contaminated food like fish practically all organic mercury content is found as methyl mercury (a highly toxic species). In natural water, Hg concentrations are typically in the low-ng/L range [29]. The well-known
concentration ranges of mercury species in various natural and contaminated water samples are summarized in Table 1.1 [30, 31]. Trace concentration ranges of mercury species makes their reliable determination is a major analytical challenge. In fresh waters e.g. lake water about 94–99% of inorganic Hg and 72–97% of organic Hg are complexed by dissolved matter [32] whereas, in seawater, the proportion of Hg bound to matter is very low due to high chloride-ion concentrations that stabilize Hg species in solution by ionic interactions. Furthermore, the proportion of organic Hg species in marine waters is typically less than 5% of the total Hg concentration [33] although Mediterranean waters show an ‘‘Hg anomaly’’ with an organic Hg content of up to 30% of total Hg [34]. while, in freshwater systems, the organic Hg fraction is typically 30% of the total Hg, which is in the range of 1–5 ng Hg/L [28].

Table 1.1. Concentration ranges of total mercury in different natural waters [30, 31]

<table>
<thead>
<tr>
<th>Natural water</th>
<th>Concentration of total Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open ocean water</td>
<td>Below 1 ng/L</td>
</tr>
<tr>
<td>Estuarine water</td>
<td>0.5–5 ng/L</td>
</tr>
<tr>
<td>Humic lakes and particle-rich river water</td>
<td>10-20 ng/L</td>
</tr>
<tr>
<td>Contaminated natural water</td>
<td>Up to 1 g/L</td>
</tr>
</tbody>
</table>

In natural waters, the most common and well known three main mercury species found in the dissolved phase are: (i) inorganic mercury \( \text{Hg}^{2+} \) and its \( \text{Hg}^{\text{2+}} \) complexes; (ii) organic mercury e.g. monomethyl mercury and dimethyl mercury and finally (iii) elemental mercury (Hg 0). All of these mercury species are highly mobile by the biogeochemical cycle of mercury as demonstrated in Fig. 1.8 [35, 36].
1.5.4. Silver

Silver ion, like other heavy metals cadmium, chromium, copper and mercury etc., is one of the poisonous categories of toxic ions. Excessive intake and long-term accumulation of Ag$^+$ ions can lead to insoluble precipitates in skin and eyes [37]. Ag$^+$ ions have also been widely used commercially in the electrical, photographic imaging and in the pharmaceutical industry [38]. Hence, Ag$^+$ ions also get accumulated in the environment, which may lead to toxicity upon overexposure [39]. On the other hand, Ag$^+$ ions play important roles, such as microelements in the human tissue, antimicrobial activity [40], possible roles in biological systems [41]. Owing to the fact that Ag$^+$ ions have moderate coordination ability, it is quite difficult to be discriminated from other chemically similar heavy metal ions.

![Biogeochemical cycle of mercury.](image)
Silver is not used in any known physiological process in the human body. It is treated by the body as a toxic heavy metal, chelated and removed extremely slowly by proteins called metallothioneins. This removal process can easily be overwhelmed, leading to argyria. Silver has an affinity to cell membranes, including those of nerve cells, where it deposits permanently as silver sulfide. This is a typical pattern of heavy metal toxicity. The Ag⁺ ions are highly toxic to aquatic organisms and may accumulate in the human body through the food chain [42, 43]. When absorbed in the human body, silver ions can displace essential metal ions such as Ca²⁺ and Zn²⁺ ions in hydroxyl apatite in bone. Moreover, the bioaccumulation and toxicity of Ag⁺ ions through binding with various metabolites such as amine, carboxyl groups, and inactivates sulfhydryl enzymes have also been disclosed [44]. Therefore, the analysis of Ag⁺ ions in water and food resources is of great importance. The Ag⁺ ions in high concentration is damaging to the environment because it accumulates in the body through the food chain and can lead to a variety of adverse health effects, brain damage and damage to the nervous and immune systems.

1.5.5. p-Nitrophenol

Anthropogenic and natural sources of p-Nitrophenols

Water pollution, especially the industrial wastewater containing aromatic compounds, is one of the most urgent environmental problems. Phenolic compounds are pollutants of great concern because of the high toxicity and possible accumulation in the environment. Most of these compounds are recognized as organic contaminants in environmental systems [45, 46]. p-Nitrophenol (pNP) is one of the most thoroughly studied toxic environmental pollutants: it has been widely used in industries for chemical synthesis of dyes and plastics, resulting in high levels of pNP contaminations.
The presence of nitrophenols in the environment is related to both natural processes and anthropogenic activity. Nitrophenols, particularly p-Nitrophenol, is formed in the reaction of phenol with nitrite ions in water. The reactions proceed under the influence of UV irradiation (sunlight) and in the wide range of pH values [47, 48]. Environmental reactions also lead to the formation of nitrophenols in the atmosphere. The reaction of phenol, nitrite ions and hydroxyl radical leads to the formation of 2-nitrophenol and other nitrated compounds [49]. Nitration of phenols substituted mainly in ortho and para positions also proceeds at the participation of enzymes present in plant tissues. Peroxidases and lipoxygenases in the presence of nitric ions and hydrogen peroxide catalyze phenol nitration to form nitrophenols. It is considered that this phenomenon may considerably affect the presence of nitrophenols in soil environment [50]. Nitrophenols in the atmosphere are usually determined in low concentrations of some ng/dm³, however strong pollution of air due to industrial emissions lead to increase of nitrophenols concentrations up to 320 ng/dm³ [51]. The concentrations were of 0.04 to 10 μg/L. 2-nitrophenol levels in rainwater and snow are between 0.03 to 5.7 μg/L. Nitrophenols are formed by man during production and degradation of pesticides like 2-buthyl-4,6- dinitrophenol (Dinoseb) and 4,6-dinitro-2-methylphenol (DNOC). Those compounds are also used as components and precursors in polymers and drug production [52], and employed as photographic developers and preservatives. Moreover, nitrated phenols are used in dyes, solvents, plastics and explosives production [53] and formed due to electric, electronic and metallurgic industrial activity. Mononitrophenols, 3-methyl-4-nitrophenol and 4-nitro-3-phenylphenol reach the environment in regards to vehicular emissions [54]. In the United States exposure to nitrophenols related with exceeded and illegal use of methylparathion has led to the accumulation of the main metabolite of this pesticide (4-nitrophenol) in tissues. The analysis of samples obtained from 16,000 people
revealed the increased concentration of 4-nitrophenol and its concentration were correlated with the amount and frequency of methylparathion usage in homes [55]. Exposure of the general population to nitrophenol isomers is mainly through ambient air and drinking water. A daily uptake by inhalation of nitrophenols was calculated to be of 0.06 μg/kg per body weight. The uptake via drinking water for 2- and 4-nitrophenols is calculated to be about 0.02 μg/kg of body weight [56]. Workers are usually exposed to high (toxic) concentrations of nitrophenols via inhalation and skin contact during production and processing (mainly in the manufacturing of pesticides).

1.5.6. Hydrazine

Hydrazine is a highly reactive base and reducing agent. Its primary uses are as a high-energy rocket propellant, as a reactant in military fuel cells, in nickel plating, in the polymerization of urethane, for removal of halogens from wastewater, as an oxygen scavenger in boiler feedwater to inhibit corrosion, and in photographic development [57]. Hydrazine was historically used experimentally as a therapeutic agent in the treatment of tuberculosis, sickle cell anemia, and non-specific chronic illnesses [57, 58]. The annual statewide industrial emissions from facilities reporting under the Air Toxics Hot Spots Act in California based on the most recent inventory were estimated to be 1664 pounds of hydrazine.

1.5.7. Effects of human exposure of hydrazine

One person was occupationally exposed to hydrazine at unknown levels once per week for a period of 6 months [59]. The worker showed symptoms of conjunctivitis, tremors, and lethargy for 1-2 days following each exposure. Vomiting, fever, and diarrhea developed on the last day of exposure and progressed to abdominal pain and incoherence. The previously healthy
59-year old individual died three weeks after the last exposure. Evidence of tracheitis, bronchitis, heart muscle degeneration, and liver and kidney damage was found at autopsy. A single case report cannot prove a cause and effect relationship between hydrazine exposures and the noted symptoms and death, but the repeated association between exposures and symptoms is highly suspicious. Liver toxicity is also associated with acute exposure to hydrazine.

1.5.8. Nitrite

Sodium nitrite is a water soluble, inorganic salt. Nitrite and nitrate are readily interconverted in the body by means of oxidation-reduction reactions. Hence the pharmacokinetics and metabolism of nitrite cannot appropriately be considered in complete isolation from nitrate. Nitrite and, by extension, nitrate, can also serve as precursors for the in vivo formation of carcinogenic N-nitroso compounds. Both nitrite and nitrate occur naturally in many foods, particularly vegetables. Both compounds also have food additive uses in the production of cured meat products. Both nitrite and nitrate can be found as contaminants of drinking water.

A major concern in considering the toxicology of nitrite is the induction of methemoglobinemia. Nitrite in the circulation leads to formation of methemoglobin (MetHb), which is incapable of transporting oxygen to the body's tissues and organs. Clinical symptoms of oxygen deficiency become apparent at MetHb levels of 10% and above, with coma and death resulting at levels of 60% or more. Neonatal methemoglobinemia, or "blue baby syndrome," is a serious, life-threatening, and well-documented toxic consequence of nitrite overexposure. Also of concern is the potential for nitrite, or the nitrosating species derived from it, to combine with secondary amines or N-alkylamides to form carcinogenic N-nitroso compounds (nitrosamines

24
and nitrosamides). Many foods, beverages, and medicines contain the necessary constituents for formation of N-nitroso compounds. U.S. Department of Agriculture (USDA) Meat Inspection Regulations specify that the use of nitrates and nitrites, singly or in combination, cannot result in more than 200 ppm (calculated as sodium nitrite) in the finished product.

Sodium nitrite causes conversion (oxidation) of hemoglobin to methemoglobin. Methemoglobin cannot combine reversibly with oxygen and its formation can cause anemic hypoxia which may lead to intense cyanosis. Infants are particularly susceptible to this effect because of their higher stomach pH, immature enzyme systems, the reduced capacity of newborn erythrocytes to reduce MetHb to hemoglobin, and the increased rate of nitrite-induced oxidation of fetal hemoglobin to MetHb (approximately twice the rate of adult hemoglobin oxidation). Coma and methemoglobinemia/carboxyhemoglobinemia were reported in a human that received sodium nitrite (71 mg/kg) orally. In animal studies, methemoglobinemia was reported in dogs that received an intravenous dose of 30 mg/kg sodium nitrite and in rats administered a 10 mg/kg dose of sodium nitrite subcutaneously.

1.6. Conducting polymers

Conducting polymers (CPs) are polymers with conjugated chain structures [60–62]. The typical conducting polymers include polyacetylene, polypyrrole (PPy), polythiophene (PTh), polyaniline (PANI) and their derivatives. CPs in their neutral state is insulators and is also called conjugated polymers. Conducting polymers contain π-electron backbone responsible for their unusual electronic properties such as electrical conductivity, low energy optical transitions, low ionization potential and high electron affinity. This extended π-conjugated system of the conducting polymers has single and double bonds alternating along the polymer chain. The
higher values of the electrical conductivity obtained in such organic polymers have led to the name ‘synthetic metals’ [63].

Neutral conjugated polymers with a small conductivity, typically in the range $10^{-10}$ to $10^{-5}$ S cm$^{-1}$, can be converted into semi conductive or conductive states with conductivities of 1 to $10^4$ S cm$^{-1}$ through chemical or electrochemical redox reactions [61]. This process is called ‘doping’. After doping, the backbone of CP brings positive (p-doping) or negative charge carriers (n-doping), therefore, counter ions with opposite charges will be entrapped or released from the polymer matrix to maintain the charge neutrality of the polymer. Based on the optical, electrical, electrochemical and mechanical properties, CPs have been widely applied in various organic devices such as sensors [64], actuators [65–67], solar cells [68–70], memory [71, 72] and electrochromic devices [73].

1.7. Carbon Nano Tubes

Since the observation of multi-walled carbon nanotubes (CNTs) by Iijima in 1991, tremendous progress has been made in the research area of CNTs in the last two decades. CNT belongs to a family of quasi one-dimensional tubular structures, which can form by rolling up graphene sheet(s) made up of single layer of sp² carbon atoms that are densely packed in a honeycomb lattice structure. Depending on the layer number of graphene sheets, single-walled or multi-walled CNTs can be obtained. Thoroughly searching the literature, carbon nanotubes (CNTs), owing to their lightweight, high aspect ratio, high mechanical strength, electrical conductivity, morphology and good chemical stability, were found to be attractive platforms for electrode modifications. To achieve effective reinforcement property in polymer composites, the filler must fulfil four requirements: (i) high aspect ratio, (ii) homogeneous dispersion, (iii)
effective interfacial stress transfer, and (iv) good alignment \[74\]. Their application in electrochemical double layer capacitors has been studied in detail \[75, 76\].

![Structure representations of (a) MWCNT and (b) SWCNT.](image)

\textbf{Fig. 1.9. Structure representations of (a) MWCNT and (b) SWCNT.}
1.8. Reference


