INTRODUCTION

1.1 Inspiration of the work
Environmental pollution is the most undesirable ecological crisis to which the plants, animals and mankind are subjected today in various forms. Among them, atmospheric pollution is a major problem of vital interest. The motivation behind the air pollution study is to implement effective control measures [1]. According to Engineer’s joint council of USA, the term “air pollution” is defined as the “presence in the outdoor atmosphere of contaminants such as dust, fumes, gas mist, odour, smoke or vapor in such quantities or characteristics and duration, such as to be injurious to plant, animal or mankind which are unreasonably interfere with the comfortable enjoyment of life and property” [2]. Substantial evidence has accumulated to show that air pollution affects the health of mankind and animals, damage vegetation, deteriorate materials, affects climate, reduces visibility and contributes to health hazards [3]. The magnitudes of these problems are best appreciated when it is realized that some of them are able to cause damage even when they are present in ppm or ppb levels.

1.2 Nitrogen in nature as an element
Nitrogen is an incredibly versatile element and is extremely important to living systems. The main source of nitrogen is the atmosphere and it is found in the earth's crust as part of organic matter. Nitrogen exists as a colorless, odorless and nontoxic gas which can appear in both inorganic and organic forms. Nitrogen and its compounds in which nitrogen may exist in different oxidation states and is an essential component of DNA, RNA and proteins the building blocks of life. Although the majority of the air that we breathe is nitrogen, most of the nitrogen in the atmosphere is unavailable for use by organisms due to strong triple bond between the N atoms in nitrogen molecule. In order to its utility the nitrogen gas must be converted to chemically available forms such as ammonium (NH₄⁺), nitrate (NO₃⁻), nitrite (NO₂⁻) or organic nitrogen (urea - (NH₂)₂CO) [4].

The soil nitrogen is the most important constituent for plant development. It is required in large quantities and must be added to the soil to avoid deficiency. Nitrogen is responsible for lush, vigorous growth and the development of a dense, attractive lawn in our house premises. Although nitrogen is the most abundant element in our atmosphere, plants cannot use it until
it is naturally processed in the soil or added as fertilizer. An excess of nitrogen caused by fertilizer over application can result in rapid lush growth and a diminished root system. In extreme cases too much quick release of nitrogen can cause burning of the leaf tissue and plant death. A lawn with a nitrogen deficiency will lose its green color and begin to turn yellow [5]. However nitrogen compounds are found in foods, fertilizers, poisons and explosives. The compounds of nitrogen are formed by the decomposition of organic matter as sodium nitrate and potassium nitrate. Other inorganic nitrogen compounds are nitric acid, ammonia; the oxides of nitrogen (NO, N₂O, NO₂, N₂O₃, N₂O₅) and cyanides (CN⁻) etc. and these salt peters are used as fertilizers [6]. Ammonia is the most important commercial compound and basic gas of nitrogen in the atmosphere. This colorless gas with a pungent odor is easily liquefied and is used as a nitrogen fertilizer. It comes mainly from agriculture both from the storage of animal wastes and from fertilizer use. In atmosphere it reacts with acid species like nitric acid to form aerosol particles. It is also used in the production of urea as a fertilizer [7].

Nitrogen fixation is a process where nitrogen is converted into ammonium and is essential because it is the only way that organisms can take up nitrogen directly from the atmosphere. The only bacteria which fix nitrogen through metabolic processes are rhizobium [8]. Nitrogen fixing bacteria often form symbiotic relationships with host plants. This symbiosis is well known to occur in the legume family of plants (beans and peas). In this relationship nitrogen fixing bacteria inhabit legume root nodules and receive carbohydrates and a favorable environment from their host plants in exchange for some of the nitrogen they fix. There is also nitrogen fixing bacteria that exist without plant hosts known as free living nitrogen fixers. In addition to nitrogen fixing bacteria, high energy natural events such as lightning, forest fires and hot lava flows can cause the fixation of smaller but significant quantity of nitrogen. The high energy prevailing in these natural phenomena can break the triple bond of N₂ molecules, thereby making individual N atoms available for chemical transformation in nature [9]. The ammonia produced by nitrogen fixing bacteria is usually gets incorporated into protein and other organic nitrogen compounds either by a host plant, the bacteria itself, or another soil organism [10].

After nitrogen’s incorporation into organic matter, it is often converted back into inorganic nitrogen by a process called nitrogen mineralization. When organisms die, decomposers such
as bacteria and fungi consume the organic matter and lead to the process of decomposition. During this process, a significant amount of the nitrogen contained within the dead organism is converted into ammonium form. In this form nitrogen is available for use by plants or for further transformation into nitrate through the process called nitrification. Nitrification has two steps both are carried out by bacteria that live in the soil. Common sources of ammonium in the soil results from decaying of plants and organic matter or ammonium can come from the application of manure or nitrogen fertilizers [11]. Denitrification is an anaerobic process that is carried out by denitrifying bacteria which converts nitrate to dinitrogen in the following sequence [12].

\[
\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2
\]

Nitric oxide and nitrogen dioxide are both environmentally important gases and they contribute towards smog and global climate change respectively [13]. Once converted to dinitrogen, nitrogen is unlikely to be reconverted into biological form, because it is a gas and is rapidly lost into the atmosphere. Denitrification is the only nitrogen transformation that removes nitrogen from ecosystems and it roughly balances the amount of nitrogen fixed by the nitrogen fixers. Natural biological processes carried out by microorganisms in the soil which converts organic nitrogen into inorganic forms which are having ability to be used as fertilizers. Organic nitrogen is a common component in plant residues and organic matter. Most of the nitrate is in the form of nitrogen and is used by plants for growth and development. Nitrate regardless of its source is the form of nitrogen that can get into ground water [14].

Nitrogen is one of the important macro nutrients for the growth of plants and vegetation. Atmospheric nitrogen cannot be used by plants; hence it must be converted into other forms before it can be used by the plants and vegetation. Organic forms of nitrogen make up a very high percentage of the total nitrogen found in the soil. However plants are able to use only very specific inorganic forms of nitrogen. The most common forms of nitrogen found in the soil used by the plants are shown in (Table 1.1) [15]. The utility of all these forms of nitrogen with respect to animals, plants and vegetation are described in terms of environmental pollution point of view [16].
Table 1.1 Different forms of nitrogen and their utility in nature

<table>
<thead>
<tr>
<th>Nitrogen entity</th>
<th>Chemical symbol</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dinitrogen (atmospheric nitrogen)</td>
<td>N$_2$</td>
<td>It is the most common and stable form which contributes nearly 78% of the atmospheric composition but cannot be used by plants. It is taken into the soil by bacteria, some algae, lightning and other means.</td>
</tr>
<tr>
<td>Nitrate</td>
<td>NO$_3^-$</td>
<td>Nitrate is the most stable form of oxyanion of nitrogen used by plants for the growth and development.</td>
</tr>
<tr>
<td>Nitrite</td>
<td>NO$_2^-$</td>
<td>Nitrite is another stable form of nitrogen and most of it is used as a food additive, mainly as a preservative, antimicrobial agent and color fixative. It is mainly used in foods such as cheese and its products, raw and processed meats, edible casings, processed fish and its products.</td>
</tr>
<tr>
<td>Ammonium nitrogen</td>
<td>NH$_4^+$</td>
<td>Ammonium ion is taken by plants and is used directly in proteins. It is the most stable form of nitrogen in soil.</td>
</tr>
<tr>
<td>Organic nitrogen</td>
<td>C-NH$_2$</td>
<td>Organic nitrogen exists in different forms. It is changed into ammonium, then into nitrates, by microorganisms. Both of these inorganic forms can be used by the plant.</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>NO</td>
<td>It is highly reactive gas that is produced naturally within the body. It has only a short life of a few seconds. But within its miniscule lifespan, nitric oxide plays the role of the human body’s most important “messenger”.</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>NO$_2$</td>
<td>Nitrogen dioxide has been used as a catalyst in certain oxidation reactions, as an inhibitor to prevent polymerization of acrylates during distillation, as a nitrating agent for organic compounds, as an oxidizing agent, as a rocket fuel, as a flour bleaching agent and in increasing the wet strength of paper.</td>
</tr>
</tbody>
</table>
1.3 Nitrogen Cycle

The nitrogen cycle represents one of the most important nutrient cycles found in terrestrial ecosystems which describes the series of processes by which the element nitrogen make up about 78% of the earth’s atmosphere. The gaseous form of dinitrogen is converted into usable forms by living organisms, occurs as a consequence of atmospheric processes such as lightning but most its fixation takes place through free living and symbiotic bacteria. Plants and bacteria participate in symbiosis such as the one between legumes and rhizobia or contribution through decomposition and other soil reactions. Bacteria like rhizobium or the actinomycete frankia which modulates members of the plant families’ rosaceous and betulaceae utilize atmospheric nitrogen and convert it into inorganic form usually ammonium and is used by plants. The plants then use the fixed nitrogen to produce vital cellular products such as proteins. The plants are then eaten by animals which also need nitrogen to make amino acids and proteins. Decomposers acting on plant and animal materials and waste return nitrogen back to the soil. Chemical fertilizers are another source of nitrogen in the soil along with pollution and volcanic emissions which release nitrogen into the air in the form of ammonium and nitrate gases. The gases react with water in the atmosphere and are absorbed by the soil with rain water. Other bacteria in the soil are key components in this cycle converting nitrogen containing compounds to ammonia, nitrates and nitrites. The process of denitrification involves the metabolic reduction of nitrate to nitrogen (N$_2$) or nitrous oxide (N$_2$O) gases. Both of these gases then diffuse into the atmosphere. Various forms of nitrogen and their transformation into other species and its cycling have been described in the form of cycle called nitrogen cycle as shown in the fig.1.1 [17-18].
Fig. 1.1 Nitrogen Cycle [19].
1.4 Toxicity

1.4.1 Environmental and health effects

1.4.1.1 Nitrogen oxides

Nitrogen oxides (NO\textsubscript{x} ≡ NO + NO\textsubscript{2}) are released into earth's atmosphere by both natural sources (lightning and microbiological processes) and anthropogenic sources (fossil fuel combustion and biomass burning) play important roles in tropospheric ozone chemistry and secondary aerosol formation [20]. These two gaseous nitrogen oxides are significant pollutants of the lower atmosphere [21 - 22]. Nitric oxide is a colorless, tasteless, flammable gas with a slight odor and is the predominant among the nitrogen oxides and it readily converts to much more harmful nitrogen dioxide by the reaction with ozone present in the atmosphere. Since the meteorological and climatic conditions that favour the production of ozone. It has the potential to cause large economic losses by lowering the crop yields [23]. Nitrogen dioxide is a yellowish orange to reddish brown gas with a pungent, irritating odour and is highly toxic in nature but it is not flammable. It along with aerosols is responsible for the reddish brown color of smog. Nitrogen dioxide in the atmospheric air can combine with moisture to form nitric acid and ammonium salts under suitable conditions [24]. Oxides of nitrogen significantly contribute air pollution and play a major role in the formation of both acid rain and photochemical smog which are mainly responsible and interfere in the plant growth [25 - 26]. Since nitric acid is responsible for hydrogen ion concentration in wet and dry acid depositions, the contribution of nitrogen oxide emissions to acid deposition could be more significant. It is nitrogen oxides that absorbs sunlight, initiating the photochemical processes and to produce nitric acid. Approximately 90 - 95 % of the nitrogen oxides emitted from power plants is nitric oxide; this slowly converts to nitrogen dioxide in the presence of ozone [27]. The extent and severity of the damage attributable to acid depositions is difficult to estimate, since impacts vary according to soil type, plant species, atmospheric conditions, insect populations and other factors that are not well understood. Human exposure to nitrogen oxides varies from indoors to outdoors, from cities to the countryside and with the time of day and season. Nitric oxide does not significantly affect on human health. On the other hand it readily gets oxidized to nitrogen dioxide and per oxidation then occurs [28], the elevated levels of nitrogen dioxide cause damage to the mechanisms that protect the human
respiratory tract and can increase a person's susceptibility to and the severity of, respiratory infections and asthma. Long term exposure to high levels of nitrogen dioxide can cause chronic lung disease [29]. It may also affect sensory perception by reducing a person's ability to smell an odor. Nitrogen dioxide in reaction to textile dyes can cause fading or yellowing of fabrics. Exposure to nitrogen dioxide can also weaken fabrics or reduce their affinity for certain dyes [30]. Nitrogen oxides (NOₓ) also contribute to acid deposition, which damages trees at high elevations and increases the acidity of lakes and streams, which results in severe damage to aquatic life. NOₓ emissions can also contribute to increased levels of particulate matter by changing into nitric acid in the atmosphere and forming particulate nitrate. It inflames the lining of the lungs and reduces immunity to lung infections. This can cause problems such as wheezing, coughing, cold, flu and bronchitis. Increased levels of nitrogen dioxide can have significant impacts on people with asthma because it can cause more frequent and more intense attacks. Children with asthma and older people with heart disease are most at risk.

1.4.1.2 Nitrite/nitrate

As the whole human population needs drinking water for sustaining life the provision of a safe water supply is a high priority issue for safeguarding the health and well-being of humans. The production of adequate and safe drinking water is the most important factor contributing to a decrease in mortality and morbidity in developing countries. The WHO [31] reported that nearly half of the population in these countries suffer from health problems associated with lack of drinking water or the presence of microbiologically contaminated water [32]. In the developing countries more than 60 percent population has no access to pure drinking water [33]. The basic question in the production of drinking water is how to rid drinking water of potentially dangerous microorganisms and chemical without introducing new hazards that might pose new and different threats to human health. Water treatment and distribution system, if not properly operated and maintained can be a source of disease outbreak affecting large populations. Therefore, the monitoring and surveillance of quality of raw water sources as well as treated water need to be enhanced [34]. Water is a very good solvent, hence it dissolves some toxic and hazardous substances, producing water pollution
problem posing many public parameters of interest for water quality assessment and nitrates and nitrites are out of them. Furthermore, turbidity and nitrate concentrations peak during heavy rain episodes [35]. Nitrate and nitrite are considered hazardous and there are legal limits to their concentration in food and drinking water. Nitrate from fertilizer accumulates in vegetables and fruit and large-scale livestock production yields huge amounts of manure rich in nitrate that seeps into groundwater. Therefore, keeping nitrate concentrations below legal limits is a struggle for farmers. Many food components are beneficial at low and harmful at high intakes. Nitrate toxicity is sometimes a lethal problem for livestock especially during the fall. The amount of nitrate accumulated within the plant depends on two factors: the rate of uptake by the plant from the soil and the rate the plant reduce it. If uptake exceeds the rate of reduction, large amounts of nitrate can accumulate. If the rate of reduction equals the rate of uptake, there is no accumulation. Nitrate accumulation usually results from plant stress such as drought and is accentuated by excessive soil nitrogen. Most nitrates accumulate in plant stems rather than leaves and concentration tends to be highest in immature forage. A characteristic symptom of nitrate toxicity is a chocolate brown color to the blood. The contamination of water with nitrates associated with fertilizer use has human health risks related mainly to three processes [36].

1) Drinking water or eating food contaminated with nitrates.

2) Changes in the dynamics of some human diseases (like malaria).

3) Harmful algal blooms in rivers, lakes or coastal areas which can produce poisonous toxins and affect humans.

Ingested nitrites and nitrates from polluted drinking waters can induce methemoglobinemia (blue baby syndrome) in humans particularly in young infants by blocking the oxygen carrying capacity of hemoglobin. It is a potentially fatal condition that occurs when the hemoglobin (Fe^{2+}) in an infant's red blood cells is oxidized to methemoglobin (Fe^{3+}). Because methemoglobin is unable to transport oxygen, the condition produces symptoms of cyanosis. Affected infants develop an unusual blue-gray or lavender skin color and are often described as irritable or lethargic, depending on the severity of their illness. Methemoglobin
levels > 50% in blood can quickly lead to coma and death if the condition is not recognized and treated immediately [37]. A variety of risk factors including inherited enzyme deficiencies, infectious and inflammatory conditions, drug reactions and chemical exposures can also increase the methemoglobin levels. Ingested nitrites and nitrates also have a potential role in developing cancers of the digestive tract through their contribution to the formation of nitrosamines [38]. In addition some scientific evidences suggest that ingested nitrites and nitrates might result in mutagenicity, teratogenicity and birth defects which contribute to the risks of non Hodgkin's lymphoma, bladder and ovarian cancers. These symptoms play a role in the etiology of insulin dependent diabetes mellitus and in the development of thyroid hypertrophy or cause spontaneous abortions and respiratory tract infections. Indirect health hazards can occur as a consequence of algal toxins, causing nausea, vomiting, diarrhea, pneumonia, gastroenteritis, hepatocenteritis, muscular cramps and several poisoning syndromes (paralytic shellfish poisoning, neuro toxic shell fish poisoning, amnesic shell fish poisoning). Other indirect health hazards can also come from the potential relationship between inorganic nitrogen pollution and human infectious diseases (malaria, cholera). It is concluded that levels of total nitrogen lower than 0.5 - 1.0 mg TN/L in water could prevent aquatic ecosystems (excluding those ecosystems with naturally high N levels) from developing acidification and eutrophication at least by inorganic nitrogen pollution. Those relatively low TN levels could also protect aquatic animals against the toxicity of inorganic nitrogenous compounds due to the absence of eutrophication in surface waters [39].

1.5 Sources
1.5.1 Oxides of nitrogen

NOx is a collective noun used to represent both nitric oxide and nitrogen dioxide which are quite stable and prevalent in the atmospheric air. Nitrogen oxides play an important role in the chemistry of atmosphere. Among these NO and NO2 are generally present in highest concentrations in the lower troposphere. Nitrogen dioxide is a reddish-brown gas and strong oxidant, soluble in water and can be oxidized within the atmosphere to form nitric acid which along with sulphuric acid falls as acid precipitation or "acid rain". Other NOx derived
compounds that are polluting air include nitrates, nitrates, nitrogen acids and nitroso compounds [40].

The main source of nitrogen dioxide resulting from human activity is the combustion of fossil fuels [41]. Nitrogen oxides are formed in the atmosphere mainly from the breakdown of nitrogen gas (N₂). The natural sources of nitrogen oxides are volcanoes and bacteria [42]. Both NO and NO₂ are generated during high temperature combustion in the atmosphere when oxygen combines with nitrogen. Automobile exhausts are another major source of nitrogen oxides and emissions from electrical power generation plants also contribute a major share in this [43 - 44]. Automobile exhausts have more NO concentration than NO₂ but once the NO is released into the atmosphere it quickly combines with oxygen in the atmosphere to form NO₂. Transportation automobiles alone contribute about 80 % of ambient nitrogen dioxide. Nitrogen oxides are partially responsible for several types of air pollution. About 50 % of emissions from anthropogenic sources come from fossil fuel fired heat and electricity generating plants [45]. Other sources include industrial boilers, incinerators, nitric acid plants, other nitrogenous chemicals manufacturing, electric arc welding processes, use of explosives in mining and farm soils [46].

A series of chemical reactions transform volatile organic compounds (VOCs) into substances that combine with nitrogen dioxide to produce PAN (peroxyacylt nitrate) which is responsible in photochemical smog formation which is an undesirable phenomenon in nature [47]. Nitrogen dioxide in the air reacts with water vapor to produce nitric acid one of the constituent of acid rain. Nitric acid is not only a major contributor to acid rain but also the main way in which nitrogen oxides are removed from the air either by dry deposition of the acid directly or by its removal through rain [48]. Only 10 % of all NOₓ emissions come from anthropogenic sources and the rest is produced naturally by anaerobic biological processes in soil as well as water by lightning and volcanic activity [49]. Photochemical destruction of nitrogen compounds in the upper atmosphere by sun light produces nitric oxide and ozone in the troposphere which is another component of smog. Worldwide annual emissions of anthropogenic nitrogen oxides are estimated at approximately 50 million metric tons [50]. United States alone generate about 20 million metric tons of nitrogen oxides per year in which about 40 % is emitted from mobile sources. Of the 11 million to 12 million metric tons
of nitrogen oxides that originate from stationary sources about 30 % is the result of fuel combustion in large industrial furnaces and 70 % is from electric utility furnaces [51]. Annual mean concentrations of nitrogen dioxide in urban areas throughout the world are in the range of 20 - 90 μgm⁻³ of air. Maximum half hourly and 24 hourly values of nitrogen dioxide may reach 850 and 400 μgm⁻³ respectively. Hourly averages near very busy roads often exceed 1000 μgm⁻³. Urban outdoor levels of nitrogen dioxide vary according to time of day, season and meteorological conditions. Typically in urban areas the peak concentrations prevail during morning and afternoon rush hours. These levels are also higher in winter seasons in cold regions of the world than in other seasons because of the increased use of heating fuels. The conversion of nitrogen dioxide from nitric oxide depends on solar light intensity and concentrations are often greater on warm sunny days. Concentrations of nitrogen oxides in rural areas without major sources are typically close to background levels. However nitrogen oxides can travel long distances in the upper atmosphere contributing to elevated ozone levels and acidic depositions far from sources of emissions. Concentrations of nitrogen dioxide in houses may considerably exceed outdoor levels and may therefore be more important for human health. Large sources of indoor nitrogen dioxide include cigarette smoke, gas fired appliances and space heaters. Nitrogen dioxide concentrations in kitchens with unvented gas appliances may exceed 200 μgm⁻³ of air over a period of several days. Maximum 1 h concentration during cooking may reach 500 - 1900 μgm⁻³ and 1000 - 2000 μgm⁻³ where a gas fired water heater is also in use [52].

1.5.2 Nitrite/nitrate

Nitrate and nitrite are naturally occurring oxyanions of nitrogen and part of the nitrogen cycle and are ubiquitous in the environment. Both are products of the oxidation of nitrogen by microorganisms in plants, soil or water. Nitrate is the more stable form of oxidized nitrogen but can be reduced by microbial action to nitrite which is moderately chemically reactive; Nitrogen is one of the macronutrient applied in the largest quantities for lawn and garden care and crop production. In addition to fertilizer, nitrogen can also occur naturally in the soil as in organic forms by the decay of plant and animal remains. In soil several bacterial processes dominate in the conversion of nitrogen to nitrate or nitrite [53].
1.5.2.1 Water

Most of the studies have been reported in the literature reveal that the presence of nitrite/nitrate in water and its characterization as one of the water quality parameter throughout the world. Hence the studies have been focused on the areas where waters were affected by specific sources of contamination. Groundwater is the main source of nitrate/nitrite concentration throughout the world [54]. Nitrate is not bound to the soil but when it starts soluble, the soluble nitrate leaches into groundwater or rivers. This occurs when the transit of water through soil is rapid due to its geological composition (sandy soils). The main diffuse sources of contamination of surface water are agricultural run-off, road drainages, suburban lawns and the transportation of nitrogen by rain [55]. Nitrite is a relatively unstable form of nitrogen and is rapidly converted to nitrate by bacteria thus the concentration of nitrite in environmental media such as water is usually very low even when the concentration of nitrate is high [56 - 57]. As the majority of the nitrogen used by plants is absorbed in the form of nitrate and is highly leachable and readily moves with water through the soil. Due to excessive rainfall or over-irrigation, nitrate may leach below the plant's root zone and may eventually reach ground water [58]. Nitrate nitrogen (NO$_3$-N) in ground water may result from point sources such as sewage disposal system and livestock facilities and non-point sources such as fertilized cropland, parks, golf courses, lawns and gardens are the naturally occurring sources of nitrogen. Nitrate is the more stable form of oxidized nitrogen but it can be reduced by microbial action to nitrite which is moderately reactive. Nitrates are used widely as inorganic fertilizers, in explosives, as oxidizing agents in the chemical industries, as food preservatives especially in cured meats. Because of the relative stability of the nitrate ion, most of the nitrogenous materials in environmental media tend to be converted to nitrates. Therefore, all sources of nitrogen (including organic nitrogen, ammonia and fertilizers) should be considered as potential sources of nitrates. Sources of nitrates in water (particularly groundwater) include decay of plant or animal remains, agricultural fertilizers, manure, domestic sewage or geological formations containing soluble nitrogen compounds. Nitrites may be produced from excess ammonia in drinking water distribution systems that use chloramines, formed in situ from chlorine and ammonia which are used as disinfectants.
Chapter 1

The sources of nitrate/nitrite in soil mainly results from microbial oxidation of ammonia. These are derived from organic nitrogenous materials such as plant proteins, animals and animal excreta [59]. The concentration of nitrate/nitrite found at higher concentrations in contaminated sources especially in groundwater [60]. Intensive use of nitrogen fertilizers in agricultural field is the main source of water contamination. Other anthropogenic sources of nitrate/nitrite are the disposal of municipal effluents by sludge spreading on fields [61 - 62]. Public water supplies are rarely heavily contaminated with nitrate/nitrite concentration. In private wells the quality of water is not usually regulated, in particular shallow wells that are located in agricultural areas are at greater risk of nitrite/nitrate contamination [63]. Nitrate is the major cause of eutrophication in stagnant surface waters which lead to abundant growth of algae and aquatic plants. As a result, the concentration of nitrate in surface water is usually lower than that in groundwater [64 - 65]. The treatment of contaminated groundwater is very expensive and the recharge process can often take a prolonged period [66].

1.5.2.2 Food products

The sources of nitrite/nitrate in food products are mainly based on the anthropological activities. The following are the important processes which may cause for nitrite/nitrate existence in food chain.

1) Use of nitrates as food preservatives
2) Use of nitrogen based fertilizers in the agricultural industry and its run offs [67].
3) Use of colorants in food packaging industry [68].

The presence of nitrate and nitrite in vegetables mainly depends on the type of vegetable, the method of production, the use of fertilizer and the season. Nitrate and nitrite are also used as food additives in processed food as preservatives and colour fixatives in meat, poultry, fish and cheese.

1.5.2.2.1 Dairy products

In the total diet study the average concentration of nitrate in dairy products was found to be 27 mgkg⁻¹ and that in milk was 3.9 - 5.3 mgL⁻¹ [58]. The Concentration of nitrate in cow’s
milk is generally below 5 mgL⁻¹ [62 - 63]. In cheese without nitrate additives, the concentration of nitrates was found to be in the range of 1-8 mgkg⁻¹ [69].

1.5.2.2 Meat products

The nitrate/nitrite levels have been found to be 380 mgkg⁻¹ in meat products due to the use of nitrite based salts as food additives in some countries [69]. Based on the total diet study, the concentration of nitrate in meat products was found to be 45 mgkg⁻¹ (range 14 - 101 mgkg⁻¹). The average concentration of nitrate in egg was found to be in the range 4.4-5.4 mgkg⁻¹ [58]. The concentration of nitrate in fish samples was generally found to be below 2.5 mgkg⁻¹ and it varies from place to place as well as the extent of water pollution in that locality.

1.5.2.3 Vegetables and fruits

The concentration of nitrate in vegetables varies due to the soil nature and water quality. The literature values of nitrate concentration in fruits and vegetables varied in a wide range from 30 to 6000 mgkg⁻¹ [69 - 71]. Based on such a wide concentration, the vegetables can be grouped into three categories according to their nitrate concentration [72].

(a) high nitrate content   - -- > 1000 mgkg⁻¹
(b) medium nitrate content --- 100 - 1000 mgkg⁻¹
(a) low nitrate content    --- < 100 mgkg⁻¹

In the first category the leafy vegetables such as lettuce, spinach, celery and beetroot have the highest nitrate concentration (above 1000 mgkg⁻¹). In the republic of Korea [73], the concentrations of nitrate were found to be 4259 mgkg⁻¹ in spinach while an average level of 1800 mgkg⁻¹ was reported in radishes and cabbage. In Singapore the concentration of nitrate in salad, lettuce and spinach were found to be 1360, 1470 and 4570 mgkg⁻¹ respectively [74]. In Italy the concentration of nitrate in leafy vegetables such as salad and chicory were found to be 80 and 3232 mgkg⁻¹ respectively [75]. In France, the concentration of nitrate in spinach and lettuce was found to be 1135 mgkg⁻¹ and 1221 mgkg⁻¹ respectively [76]. In Poland, the concentration of nitrate in lettuce was found to be up to 3500 mgkg⁻¹ [77].
The average concentration of nitrate in lettuce was produced in glasshouses was 2382 and 3124 mgkg\(^{-1}\) in the summer and winter seasons respectively, whereas the concentration of nitrate in lettuce produced in outdoors was 1085 mgkg\(^{-1}\). In the same study, the concentration of nitrate in spinach was 1900 mgkg\(^{-1}\) [78]. The recent survey on an average concentration nitrate in UK in lettuce produced in glasshouses in summer was 2999 mgkg\(^{-1}\) and in winter, the average was 3617 mgkg\(^{-1}\) respectively. Whereas the average concentration of nitrate in lettuce produced at outdoors during the summer and winter season was found to be 1140 mgkg\(^{-1}\); (range 181 - 2656 mgkg\(^{-1}\)) and in winter 1997 mgkg\(^{-1}\) (range 810 - 3100 mgkg\(^{-1}\)) [79]. In second category the concentration of nitrate in vegetables such as potatoes, cabbage and spring greens was found to be in the range between100 and 1000 mgkg\(^{-1}\). In Singapore, the concentration of nitrate, in cabbage, green beans, ladies finger and potatoes were found to be 930, 340, 150 and 140 mgkg\(^{-1}\) respectively [74]. In Poland, the concentration of nitrate in green beans was found to be up to 800 mgkg\(^{-1}\) [77]. In France, the concentration of nitrate in carrots for both conventional and organic products was found to be 113 and 394 mgkg\(^{-1}\) respectively [76]. In the same study, the French beans were found to contain 711 and 561 mgkg\(^{-1}\) nitrate for both conventional and organic products.

In third category the concentration of nitrate in vegetables such as asparagus or onions and fresh fruits of tomatoes were found the lowest concentrations (\(\leq 100\) mgkg\(^{-1}\)). In United Kingdom, the average concentration of nitrate in fresh fruits of tomatoes was found to be 27 mgkg\(^{-1}\)(range 12 - 46 mgkg\(^{-1}\)) [80]. In Singapore, the concentrations of nitrate in tomatoes, asparagus, onions and mushrooms were found to be 60, 55, 35 and 15 mgkg\(^{-1}\) respectively [74]. In the Republic of Korea, the concentrations of nitrate in onions, soya bean sprouts and green peppers were found to in the range between 23 and 76 mgkg\(^{-1}\) [73]. In France, the concentration of nitrate in tomatoes was found to be 19 and 1 mgkg\(^{-1}\) in conventional and organic products respectively [76]. In Poland, the concentration of nitrate in various fruits (currants, gooseberries, raspberries and cherries) range between 1.3 and 36 mgkg\(^{-1}\), while the concentration of nitrate in strawberries was found to be 58.7 mgkg\(^{-1}\) [77].
1.5.2.6 Conversion of nitrate to nitrite and vice versa during storage

The transformation of nitrate to nitrite during storage, especially in home-made food, is known to occur. Evidence from the studies on methaemoglobinemia support the contention that the nitrate contained in vegetables is converted to nitrite before consumption [81]. Levels of nitrite up to 400 mg kg\(^{-1}\) have been reported in vegetables that have been damaged, poorly stored or stored for extended periods and in pickled or fermented vegetables [56, 82]. In contrast, levels of nitrite in cured meat appear to decrease during storage as it is converted into nitric oxide due to its reactivity [83].

1.6 Ambient air standards and guidelines

The main objective of specifying air quality standards by the major national and international agencies are to protect the ambient air quality and guidelines to keep these contaminants well within specified limits. These limits have been prescribed in order to prevent any untoward incidents caused due to the exposure of these toxic pollutants by human beings. Some countries have also produced guidelines and standards for nitrogen oxides to protect vegetation and sensitive ecosystems such as wetlands. Table 1.2 and 1.3 provides threshold limit values of ambient nitrogen dioxide levels in atmospheric air prescribed by various agencies of several countries.

<table>
<thead>
<tr>
<th>Agency</th>
<th>NO(_2) (µg/m(^3))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>USEPA</td>
<td>50</td>
<td>[84]</td>
</tr>
<tr>
<td>WHO</td>
<td>50</td>
<td>[85]</td>
</tr>
<tr>
<td>EU</td>
<td>40</td>
<td>[86]</td>
</tr>
</tbody>
</table>
USEPA: United States Environmental Protection Agency
WHO: World Health Organization
EU: European Union

According to Central Pollution Control Board (CPCB), New Delhi, the Indian standards for ambient nitrogen dioxide levels has been classified based on different areas as given below.

Table 1.3 Indian threshold limit values (TLV) of nitrogen dioxide in ambient air

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Time weighted average</th>
<th>Concentration of NO₂ in ambient air²</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Industrial area</td>
<td>Residential/rural/other area</td>
</tr>
<tr>
<td>NO₂</td>
<td>Annual average*</td>
<td>80 µg/m³</td>
<td>60 µg/m³</td>
</tr>
<tr>
<td></td>
<td>24 hours**</td>
<td>120 µg/m³</td>
<td>80 µg/m³</td>
</tr>
</tbody>
</table>

²Concentration of nitrogen dioxide in atmospheric air at a height of 10 feet from ground.
*Annual arithmetic mean of minimum 104 measurements in a year taken twice a week 24 hourly at uniform interval.
**24 hourly/8 hourly values should be met 98 % of the time in a year. However 2 % of the time, it may exceed but not on two consecutive days.
According to USEPA, WHO, EU and CPCB the maximum permissible limits of nitrate/nitrite in drinking water are shown in the following table.

**Table 1.4** Threshold limit values (TLV) of nitrate/nitrite in drinking water

<table>
<thead>
<tr>
<th>Agency</th>
<th>$\text{NO}_3^-$ (ppm)</th>
<th>$\text{NO}_2^-$ (ppm)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>USEPA</td>
<td>50</td>
<td>0.1</td>
<td>[88]</td>
</tr>
<tr>
<td>WHO</td>
<td>50</td>
<td>0.2</td>
<td>[89]</td>
</tr>
<tr>
<td>EU</td>
<td>50</td>
<td>0.1</td>
<td>[90]</td>
</tr>
<tr>
<td>CPCB, India</td>
<td>50</td>
<td>0.1</td>
<td>[87]</td>
</tr>
</tbody>
</table>

**1.7 Analytical Methods**

A variety of analytical methods for the determination of nitrate and nitrite have been developed and applied to the analysis of food, water, air, soil, biological samples and other matrices. Many methods have been reported for quantitative determination of nitrite/nitrate in environmental and biological samples including the traditional or classical methods of chemical analysis like gravimetry and volumetry. Quantitative measurements are widely applicable and employed for the quantification of both inorganic and organic forms of nitrogen. Generally classical methods of analysis like titrimetry and gravimetry have been extensively used for the quantification of these analyte species from a variety of sample matrices [91]. However these methods are applicable only when the concentration is substantially high and these methods are prone for severe interferences. Hence wet classical methods like titrimetry and gravimetry are not applicable to measure the analyte concentrations at trace level. Instrumental methods will find wide spread use in the quantification of nitrite/nitrate at low concentrations.
Various instrumental methods based on physicochemical principles rather than on wet chemistry have been shown to possess adequate sensitivity for measuring stationary source emission as well as ambient level of air pollutants. Chromatography is one such technique useful in a majority of cases to separate and determine the various constituents of air samples.

Ion chromatography is widely used for the analysis of nitrogen dioxide, nitrite and nitrate [92]. Michalski and co-workers [93] have developed an ion chromatographic method for the determination of nitrite, nitrate and ammonium ionic species in different environmental and food samples with a detection limit of 0.006 - 25.0 mgL\(^{-1}\). Recently Niedzieski et. al. have reported a speciation method by ion chromatography for the determination of ammonium, nitrite and nitrate ions in rain water samples using diode array detector [94]. A reversed phase HPLC methods have been reviewed by Gennaro et.al. for the separation and determination of inorganic anions [95]. Simultaneous determination of nitrite and nitrate was reported by Butt et. al. by normal phase ion pair chromatography [96]. Zuo et. al. has reported an ion pair HPLC method to determine nitrate/nitrite from dew, rain, snow and lake water samples [97].

Chemiluminescent reactions find widespread use for the determination of nitrogen dioxide, nitrite and nitrate because of their sensitivity and specificity [98]. The main reaction which has been exploited in the detection of oxides of nitrogen is the chemiluminescent reaction between nitric oxide and ozone to produce excited NO\(_2^*\) species. For detection of NO\(_{x}\) \(\equiv (NO + NO_2)\), a prior conversion of nitrogen dioxide to nitric oxide is required. The method was useful to determine NO\(_{x}\) in the concentration range 0.5 - 1000 ppm. However, the analysis should be carried out in a chamber of reduced pressure to avoid the quenching reaction. The NO\(_{x}\) monitors based on chemiluminescent reaction have been extended for the determination of nitrite/nitrate after their complete reduction to nitric oxide at 80\(^{\circ}\)C with vanadium (III) and Molybdenum(VI) + Iron(II) as reducing agents [99]. But these methods suffer from serious interference from the reducing agents.

Spectrofluorimetric methods are widely employed for the determination of nitrogen dioxide after fixing as nitrite in suitable trapping medium [100 - 101]. Nitration of 4-hydroxy
coumarin followed by reduction to 3-amino-4-hydroxy coumarin which produces fluorescent emission was useful for the determination of nitrite [102]. Kinetic spectrofluorimetric methods were also reported for the determination of nitrogen dioxide [103]. Recently a sensitive spectrofluorimetric method for the determination of nitrite in water with a detection limit of 10 µgL⁻¹ has been reported based on the diazotisation of 4-methyl-7-amino coumarin [104]. The formed diazonium salt on hydrolysis gives the corresponding hydroxyl derivative, a fluorescence product with excitation at 325 nm and emission at 380 nm.

1.7.1 Spectrophotometric methods

The determination of low concentrations of nitrogen dioxide in atmospheric air, nitrite/nitrate in various biological and environmental samples by spectrophotometric methods has attracted considerable attention due to their simplicity and reliability. The methods developed for the determination of nitrogen dioxide, nitrite/nitrate is mainly based on diazo coupling reaction because of its sensitivity and selectivity. Some of these methods lack adequate sensitivity for direct determination of nitrogen dioxide in ambient air and nitrite/nitrate in biological and environmental samples.

Among all these the widely used spectrophotometric method for the determination of nitrogen dioxide, nitrite/nitrate is based on Griess-Ilosvay reaction [105]. This method is based on the reaction of nitrogen dioxide/nitrite/nitrate with sulphanilic acid to form diazonium ion which subsequently couples with 1-naphthylamine to form an azo dye. The method proposed by Saltzman [106] finds widespread use and it is based on the direct collection of gas in the reagent solution containing sulphanilic acid in glacial acetic acid and N-(1-naphthyl) ethylenediamine dihydrochloride [NEDA]. This method obeys Beer’s law in the concentration range 0 - 20 µg of nitrogen dioxide in 25 mL. However, this method suffers serious interference from sulphur dioxide which slowly bleaches the dye. This difficulty was overcome by the addition of 1 % acetone solution to the absorbing solution. Some of the spectrophotometric methods used for the quantification of ambient nitrogen dioxide, nitrite and nitrate from variety of sample matrices have been detailed in the Table 1.5.
Continuous monitoring techniques require high capital investment and necessitate a permanent monitoring station for installation, so a change of sampling site becomes very difficult. In addition, integrated calibration is always necessary for these instruments. The measurement of the pollutant with the instrument becomes easier than its calibration. The accuracy of calibration procedures depends upon the availability of the standard samples at trace levels. Permeation devices are the reliable sources for the supply of standard gas mixtures for extended periods of time.

Methods based on electrochemical and radiochemical principles though sensitive and sufficiently selective are subject to some operational difficulties. Wet chemical methods still find useful applications when the analysis is less frequent with economic constraints. These methods are reliable and suitable standards can be prepared from salts. Optical methods involving the use of spectrophotometers are suitable alternatives to the online monitoring because they are simple, sensitive and do not emphasize the need for a technical expertise. The review of the existing methods for the spectrophotometric determination of nitrogen dioxide, nitrite/nitrate has pointed out several limitations. Hence, there is a scope for the development of simple, rapid, inexpensive and reliable methods for the determination of these pollutants in various environmental samples.
Table 1.5 Spectrophotometric methods for nitrogen dioxide/nitrate/nitrite determination

<table>
<thead>
<tr>
<th>Reagents</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>working range (µg mL$^{-1}$)</th>
<th>molar absorptivity (L mol$^{-1}$ cm$^{-1}$)</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphanilic acid + NEDA</td>
<td>540</td>
<td>0.002 - 0.8</td>
<td>NA</td>
<td>SO$_2$ interfered</td>
<td>[106]</td>
</tr>
<tr>
<td>Sulphanilamide + NEDA</td>
<td>540</td>
<td>2 - 10</td>
<td>NA</td>
<td>SO$_2$ interfered, interference overcome by H$_2$O$_2$ oxidation</td>
<td>[107]</td>
</tr>
<tr>
<td>Neutral red</td>
<td>530</td>
<td>0 - 20</td>
<td>$2.50 \times 10^4$</td>
<td>Common ions interfered</td>
<td>[108]</td>
</tr>
<tr>
<td>p-nitroaniline + 8-quinolinol</td>
<td>550</td>
<td>0.01 - 0.06</td>
<td>$3.88 \times 10^4$</td>
<td>Tedious extraction into 3-methyl-1-butanol and pH dependent.</td>
<td>[109]</td>
</tr>
<tr>
<td>p-aminoacetophenone + NEDA</td>
<td>545</td>
<td>0.1 - 0.8</td>
<td>$4.6 \times 10^4$</td>
<td>Low detection limit</td>
<td>[110]</td>
</tr>
<tr>
<td>Sulfanilic acid + methyl antranilate</td>
<td>493</td>
<td>0.2 - 8.0</td>
<td>$1.03 \times 10^4$</td>
<td>Temperature dependent and Ce$^{4+}$ and Hg$^{2+}$ ions interfered</td>
<td>[111]</td>
</tr>
<tr>
<td>Reaction</td>
<td>Reaction time</td>
<td>Sensitivity</td>
<td>Reaction time</td>
<td>Sensitivity</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>---------------</td>
<td>-------------</td>
<td>---------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>Sulfadiazine + NEDA</td>
<td>0.08 - 0.4</td>
<td>9.6 × 10⁴</td>
<td>20 min. to develop colour</td>
<td>[112]</td>
<td></td>
</tr>
<tr>
<td>p-aminophenylmercaptocetic acid + NEDA</td>
<td>0.02 - 0.8</td>
<td>4.65 × 10⁴</td>
<td>15 min. to develop colour</td>
<td>[113]</td>
<td></td>
</tr>
<tr>
<td>p-nitroaniline + diphenylamine</td>
<td>0.05 - 0.80</td>
<td>1.45 × 10⁴</td>
<td>Requires high reaction time with low sensitivity</td>
<td>[114]</td>
<td></td>
</tr>
<tr>
<td>phenosafranine</td>
<td>0 - 12</td>
<td>1.03 × 10⁴</td>
<td>Low sensitivity</td>
<td>[115]</td>
<td></td>
</tr>
<tr>
<td>Sulphanilamide + ethyl acetoacetate</td>
<td>0.2 - 3.0</td>
<td>1.22 × 10⁴</td>
<td>Low sensitivity, poor color stability</td>
<td>[116]</td>
<td></td>
</tr>
<tr>
<td>Leucocrystal violet</td>
<td>0.004 - 0.04</td>
<td>1.54 × 10⁴</td>
<td>poor color stability, low detection limit</td>
<td>[117]</td>
<td></td>
</tr>
<tr>
<td>p-rosaniline + phloroglucinol</td>
<td>0.04 - 0.48</td>
<td>NA</td>
<td>Cu²⁺, Mn²⁺, Pb²⁺, Cr⁶⁺, V⁵⁺, Fe³⁺, SO₃²⁻ and S²⁻ interfered</td>
<td>[118]</td>
<td></td>
</tr>
<tr>
<td>4-(1-methyl-1-mesitylcyclobutan-3-yl)-2-aminothiazole + N,N dimethyl- and aniline</td>
<td>0.05 - 2.0</td>
<td>2.03 × 10⁴</td>
<td>pH dependent, high reaction time required, low detection limit</td>
<td>[119]</td>
<td></td>
</tr>
<tr>
<td>Nuclear fast red + potassium bromate</td>
<td>2.0 - 45</td>
<td>NA</td>
<td>less stable</td>
<td>[120]</td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>λ (nm)</td>
<td>ε (M⁻¹ cm⁻¹)</td>
<td>k (s⁻¹)</td>
<td>Interferences</td>
<td>Ref.</td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>--------</td>
<td>--------------</td>
<td>--------------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2-nitroaniline + ethylcyanoacetate in alkali media</td>
<td>465</td>
<td>0.2 - 18</td>
<td>1.21 ×10⁴</td>
<td>Co²⁺, Cu²⁺, Hg²⁺ and Fe³⁺ were interfered</td>
<td>[121]</td>
</tr>
<tr>
<td>Phosphomolybdenum blue</td>
<td>814</td>
<td>0.5 - 2.0</td>
<td>1.1 ×10⁴</td>
<td>Less sensitive, heating required</td>
<td>[122]</td>
</tr>
<tr>
<td>5,10,15,20-tetrakis (4- amino phenyl) porphyrine</td>
<td>434</td>
<td>0.0 - 0.018</td>
<td>2.65 ×10⁵</td>
<td>Less sensitive, high reaction time, requires heating, Fe³⁺ ions interfered.</td>
<td>[123]</td>
</tr>
<tr>
<td>PAA+ Citrazinic acid</td>
<td>495</td>
<td>0.5 - 12</td>
<td>NA</td>
<td>Fe³⁺, Cu²⁺ interfered</td>
<td>[124]</td>
</tr>
<tr>
<td>PNA+ Guaiacol</td>
<td>540</td>
<td>0.03 - 0.15</td>
<td>NA</td>
<td>NO₃⁻, Al³⁺ interfered</td>
<td>[125]</td>
</tr>
<tr>
<td>o-nitroaniline + 1-aminonaphthalene</td>
<td>545</td>
<td>0.08 - 0.68</td>
<td>NA</td>
<td>Low selectivity</td>
<td>[126]</td>
</tr>
<tr>
<td>4-nitroaniline + 1-naphthol</td>
<td>610</td>
<td>0.02 - 0.14</td>
<td>NA</td>
<td>Less sensitivity</td>
<td>[127]</td>
</tr>
<tr>
<td>Compound</td>
<td>λ</td>
<td>Window</td>
<td>Extinction Coefficient</td>
<td>Interference</td>
<td>Reference</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>---</td>
<td>--------</td>
<td>-------------------------</td>
<td>-----------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>p-nitroaniline + acetyl acetone in alkaline medium</td>
<td>490</td>
<td>0.5 - 14</td>
<td>3.2 ×10^4</td>
<td>Cu^{2+}, Fe^{3+}, Co^{2+} and Hg^{2+} interfered</td>
<td>[128]</td>
</tr>
<tr>
<td>p-nitroaniline + 2-methyl-8-quinolinol</td>
<td>585</td>
<td>NA</td>
<td>4.72 ×10^4</td>
<td>Most of cations and anions interfered</td>
<td>[129]</td>
</tr>
<tr>
<td>Sulbutamol sulphate</td>
<td>410</td>
<td>1.84 - 27.6</td>
<td>1.8 × 10^3</td>
<td>Requires heating at 100ºC</td>
<td>[130]</td>
</tr>
<tr>
<td>5,7-dihydroxy-4-imino-2-oxochroman</td>
<td>361</td>
<td>0.1 - 5.0</td>
<td>9.2 × 10^3</td>
<td>Tedious extraction into butanol-ethyl acetate</td>
<td>[131]</td>
</tr>
<tr>
<td>p-nitroaniline + citrazinic acid</td>
<td>530</td>
<td>0.5 - 14</td>
<td>NA</td>
<td>Hg^{2+} and Cr^{6+} interfered</td>
<td>[132]</td>
</tr>
<tr>
<td>p-nitroaniline + ethoxyethylenemaleic ester</td>
<td>439</td>
<td>0.5 - 16</td>
<td>5.04 ×10^4</td>
<td>Hg^{2+}, Cu^{2+}, Co^{2+}, and Fe^{3+} were interfered</td>
<td>[133]</td>
</tr>
<tr>
<td>p-nitroaniline + chromatrophic acid</td>
<td>515</td>
<td>0 - 25</td>
<td>NA</td>
<td>SO_2 interfered</td>
<td>[134]</td>
</tr>
<tr>
<td>p-nitroaniline + dibenzoylmethane</td>
<td>520</td>
<td>0 - 4</td>
<td>NA</td>
<td>SO_2 interfered</td>
<td>[135]</td>
</tr>
</tbody>
</table>

NA = Not available
1.7.2 Scope of the present work

The use of spectrophotometer involves much simpler and inexpensive instrumentation and this equipment is available in most of the laboratories. Methods based on the use of this technique find wide applicability in the air pollution monitoring. Hence, it was felt that efforts were directed to develop a new set of analytical procedures which would overcome the inadequacies of the existing methods used for the determination of nitrogen dioxide, nitrite/nitrate in various biological and environmental samples. Nitrite is the only ion which causes diazotisation of an aromatic amine in the presence of acid. This property has been utilized for the development of spectrophotometric methods for the estimation of nitrogen dioxide/nitrite/nitrate based on diazocoupling reaction. In wet chemical methods, the pollutant of interest is fixed in a suitable absorbing or trapping solution before its analysis. Hence, development of suitable absorbing solution with good sampling characteristics is equally important. The performances of these absorbing solutions are evaluated using known concentrations of standard gas mixture generated by permeation devices.

The present study is therefore aimed at the development of following methods.

1. To develop a sensitive and selective method for the determination of nitrogen dioxide in air at trace level based on its diazocoupling reaction after it as nitrite ion in suitable trapping solution.
2. To develop a reagent for continuous monitoring of nitrogen dioxide from ambient air.
3. To evaluate a new absorbing solution for fixing nitrogen dioxide with high sampling rate and greater stability of the fixed species.
4. To extend the method developed based on diazocoupling reaction to analyze the nitrite and nitrate levels in various sample matrixes.
5. To develop a speciation method for the analysis of nitrite, nitrate in water and soil samples.

Details of the investigation pertaining to the development and application of these procedures are presented in the following chapters.
1.8 References


[20] Han K.M; Song C.H; Ahn H.J; Park R.S; Woo J.H; Lee1 C.K; Richter A; Burrows J.P; Kim J.Y and Hong J.H, Investigation of NOx emissions and NOx-related chemistry in East Asia using CMAQ-predicted and GOME-derived NO2 columns, *Atmospheric Chemistry and Physics*, 9, 1017 - 1036 (2009).


[23] Last J. A; Sun W.M and Witschi H, Ozone, NO and NOx oxidant air pollutants and more, *Environmental Health Perspectives*, 102, 179 - 184 (1994).


[34] Hamzah A; Abdullah M.P; Sarmani S and Johari M.A, Chemical and bacteriological monitoring of drinking water from and urbanized water catchment drainage basin. *Environmental Monitoring and Assessment*, 44, 327 - 328 (1997).


[63] European Commission, European parliament and council directive on food additives other than colors and sweeteners (1995).


[75] Total diet study, nitrate/nitrate (Food Surveillance Information Sheet No.163), *Food Standards Agency*, UK (1998a).


[84] Primary national ambient air quality standards for nitrogen dioxide; Environmental Protection Agency, rules and regulations (2010).


[99] Fan Y; Eric T; Martin F; Bernard V; Patrick V; Guy C and Gilbert B, Effects of reducing reagents and temperature on conversion of nitrite/nitrate to nitric oxide and detection of NO by chemiluminescence, *Clinical Chemistry*, 43, 657 - 662 (1997).


Chapter 1


