

MONITORING OF SULPHUR DIOXIDE, NITROGEN OXIDES, PM₁₀ AND TSP PRESENT IN THE AMBIENT AIR OF NIT ROURKELA

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF TECHNOLOGY
IN
CIVIL ENGINEERING

BY

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UNDER THE GUIDANCE
OF

**Prof. Somesh Jena
AND
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DEPARTMENT OF CIVIL ENGINEERING
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CERTIFICATE

This is to certify that the thesis entitled, "Monitoring of sulphur dioxide, Nitrogen oxides, PM₁₀ and TSP present in the ambient air of NIT Rourkela" submitted by Sri Anil Kumar Singhdeo and Sri Nilamadhab Suna in partial fulfillment of the requirements for the award of Bachelor Of Technology Degree in Civil Engineering at the National Institute Of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/institute for the award of any Degree or Diploma.

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ABSTRACT

The project investigates the concentration of the pollutants sulphur dioxide, nitrogen oxides, particulate matter (PM₁₀) and total suspended particulate (TSP) generated from various sources like automobiles, industries over the ambient air quality of the NIT Rourkela campus. As such Rourkela is a big city and it is not possible to measure the concentration of these major pollutants in all areas, so we have restricted our study to our institute campus. The major pollutants as suggested by the Central pollution control board (CPCB) in an industrial area are sulphur dioxide, oxides of nitrogen (NO_x) , particulate matter (PM₁₀) and total suspended particulate (TSP) .

The rate of emission and concentration of these gases in the ambient air is studied by the following laboratory methods – (a) Modified West and Gaeke method for determination of sulphur dioxide in ambient air, (b) Modified Jacob and Hochheiser method for determination of nitrogen oxides in ambient air, (c) High volume method for determination of TSP in the ambient air, (d) Cyclonic flow technique for the measurement of PM₁₀.

The results will show the concentration of emissions of the above cited gaseous and suspended solid pollutants and will be compared with the permissible concentrations as per the standards given by CPCB for an industrial area and major precautions can be taken to reduce the concentration level of these pollutants.

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

The air we breathe is a mixture of gases and small solid and liquid particles. Some substances come from natural sources while others are caused by human activities such as our use of motor vehicles, domestic activities, industry and business. Air pollution occurs when the air contains substances in quantities that could harm the comfort or health of humans and animals, or could damage plants and materials. These substances are called air pollutants and can be either particles, liquids or gaseous in nature (Alias M. et al, 2007). Keeping the air quality acceptable has become an important task for decision makers as well as for non-governmental organizations. Particulate matter and gaseous emissions of pollutant emission from industries and auto exhausts are responsible for rising discomfort, increasing airway diseases and deterioration of artistic and cultural patrimony in urban centers (Rao M. et al, 2003).

As many cities around the world become more congested, concerns increase over the level of urban air pollution being generated and in particular its impact on localized human health effects such as asthma or bronchitis. The more this relationship is understood, the better chance there is of controlling and ultimately minimizing such effects. In the majority of the developed world, legislation has already been introduced to the extent that local authorities are required by law to conduct regular Local Air Quality Reviews of key urban pollutants such as SO₂, NO_x or Ozone - produced by industrial activity and/or road transport (Ghanem M. et al ,unknown).

In most European countries, industrialization and high volumes of traffic mean that anthropogenic sources predominate, especially in urban areas, and sources of anthropogenic particles are similar throughout Europe. The most significant of these are traffic, power plants, combustion sources (industrial and residential), industrial fugitive dust, loading/unloading of bulk goods, mining activities, human-started forest fires and, in some local cases, non-combustion sources such as building construction and quarrying. The main natural sources of airborne particulates in Europe are sea spray and soil resuspension by the wind. In addition, in the Mediterranean basin and the Atlantic archipelagos (eg Canaries, Azores), Saharan dust and volcano emissions can also be important natural sources of particles (Unknown, 1997).

In the UK, local authorities are now required to improve air quality in their respective area. In most urban areas, emissions from traffic are a major contributor of harmful pollutants such as nitrogen oxides (NO_x) and particulate matter (PM) (Lim Ling L., 2005).

In India, pollution has become a great topic of debate at all levels and especially the air pollution because of the enhanced anthropogenic activities such as burning fossil fuels, i.e. natural gas, coal and oil-to power industrial processes and motor vehicles. Among the harmful chemical compounds, this burning puts into the atmosphere, are carbon dioxide (CO₂), carbon monoxide (CO), nitrogen oxides (NO_x), sulphur dioxide (SO₂), and tiny solid particles-including lead from gasoline additives-called particulates (Goyal P. et al., 2003).

In India, outdoor air pollution is restricted mostly to urban areas, where automobiles are the major contributors, and to a few other areas with a concentration of industries and thermal power plants. Apart from rapid industrialization, urbanization has resulted in the emergence of industrial centers without a corresponding growth in civic amenities and pollution control mechanisms. In most of the 23 Indian cities with a million-plus population, air pollution levels exceed World Health Organization's (WHO) recommended health standards. In every city, the levels are getting worse because of rapid industrialization, growing number of vehicles, energy consumption, and burning of wastes. Several cities face severe air pollution problems, with annual average levels of total suspended particulates (TSP) at least three times as high as the WHO standards. A study conducted by the World Bank indicates premature deaths of people in Delhi owing to high levels of air pollution (Review of air quality management system in India).

Rourkela is one of the most important industrial cities in the state of Orissa. The entire Industrial Complex is divided by a hill range and the hill is virtually a separation boundary between the localities of the steel township and the "Old Rourkela". Steel Township contains various residential sectors and very well planned to protect the inhabitants from environmental pollution. On the other side of the hill range lies Bondamunda area, Civil township, the Giant Steel Plant, several medium industries, like cement, refractories, sponge iron plant, explosive and chemicals and many more small scale industries. For the Steel plant, the raw materials like coal, hematite, limestone, dolomite etc. are available within a short radius of the plant itself. Besides these, bulk of raw materials comes from its own captive mines. A survey from the regional transport office revealed that more than 1.5 lakh registered small and heavy vehicles are in the industrial complex (Naik S. ,2005)

From the discussion of the scope of present study, i.e. motor vehicles, large population density and industries present in this area produce huge amount of pollutant which pollute the environment. Thus, the ambient air quality of the city Rourkela is needed to be studied in detail as it is a major concern to care for the health of the people residing in Rourkela resulting due to

air pollution. But since we are concerned about the pollution level in NIT Rourkela, we have considered the monitoring sites inside the institute campus.

1.2 WORLDWIDE STRATEGY FOR AIR POLLUTION

Potential health hazards due to particulate air pollution are a significant concern in both urban areas and rural areas in the United States. Several air sheds are currently classified by United States Environmental Protection Agency (US EPA) as non attainment areas for airborne particulate matter with an aerodynamic diameter of less than 10 μm (PM_{10}). Non-attainment areas are identified based on National Ambient Air Quality Standards (NAAQS) set by the Clean Air Act Amendments (CAAA) of 1990 (Pulugurtha Srinivas S. et al., 2006).

Lombardia is a densely inhabited and industrialized region located in Po Valley (Northern Italy) which is often affected by high ozone levels during summer months and by elevated PM_{10} and NO_x concentrations during the cold season. The major urbanized and industrial conglomeration within the Region is the “Milanoe-Comoe-Sempione critical area”, for which local authorities have designed, during last years, different emission abatement strategies (use of cleaner fuels for domestic heating, limitation of the circulation for non-catalyzed vehicles during colder seasons, etc.) (Silibello et al., 2008).

In the 1990s, WHO updated its Air quality guidelines (AQG) for Europe, to provide detailed information on the adverse effects of exposure to different air pollutants on human health. The prime aim of these guidelines was to provide a basis for protecting human health from effects of air pollution. The guidelines were in particular intended to provide information and guidance for authorities to make risk management decisions. The European Union (EU) used the WHO guidelines as a basis to set binding air quality limit values and target values for all EU member states for several pollutants (World Health Organization, 2003)

Kathmandu Metropolitan City (KMC) has put forward many efforts for the air quality management of the city and as a whole controlling the valley’s air pollution. Realizing the need to address Kathmandu's pollution problems, in 1998, KMC established an Environment Department and an Urban Environment Section within the Department to initiate activities to reduce air and water pollution. The Urban Environment Section got together with various NGOs involved in air quality improvement and formed a Citizens Monitoring Group to co-ordinate activities, interact with one another and monitor Kathmandu's environment quality. In 1999,

when citizen groups raised their voices against polluting diesel three-wheelers, KMC supported the campaign. Previously, KMC had also taken the initiative to introduce electric vehicles in Kathmandu (Shrestha Rabin M. et al, 2002).

In accordance with Executive Yuan's National Environmental Protection Project, Taipei Municipal Government has been improving urban air quality in the city. After undertaking air quality surveys and providing guidance for, and inspection of, air pollution sources, a reduction in the concentration of urban air pollutants has been achieved. These pollutants include particulate matter (PM₁₀), sulphur dioxide (SO₂), and nitrogen dioxide (NO₂). (Wang Dah J, unknown).

Standard gas mixtures are an accurate and cost effective method for calibrating air quality monitoring instruments. They are stable and provide a repeatable reference concentration that can be used for regular calibrations. Each air quality standard contains one or more component mixed with nitrogen or air. At present there is no agency in the country which has the capability and authorization to certify gas standards. Central Pollution Control Board has undertaken the study to develop standard gas mixtures, under a sponsored project by Department of Science and Technology (DST), CPCB will qualify as a centre for traceability of all gas measurements. Traceability of gases is necessary if the standards are applied to analysers and methods. By applying standards which are directly traceable to national primary gases, not only do the quality of measurement increases but at the same time measurements performed in different laboratories can be compared (CPCB,2002).

Various other countries throughout the world are making strategies to deal with the increase in air pollution especially due to sulphur dioxide, nitrogen oxides, TSP and PM₁₀. Our project deals with the monitoring of these pollutants in the study area(NIT campus) and aims to come up with a result that can be referred if a strategy is to be made now or in the near future for the area under study, to combat the increase in air pollution.

1.3 AIR POLLUTANTS

The air pollutants can be classified as primary or secondary pollutants. The primary air pollutants are harmful chemicals which directly enter the air due to natural events of human activities. A secondary air pollutant is a harmful chemical produced in the air due to chemical reaction between two or more components. That is primary pollutant combines with some component of the atmosphere to produce a secondary pollutant (Naik S., 2005).

Among the most common and poisonous air pollutants are sulphur dioxide (SO₂), formed when fossil fuels such as coal, gas and oil are used for power generation; suspended particulate matter (SPM), solid and liquid particles emitted from numerous man-made and natural sources such as industrial dust, volcanic eruptions and diesel-powered vehicles; and nitrogen oxides (NO_x), from natural sources such as lightning, fires (Hayatham A. Ahmed, 1999).

Central Pollution Control Board initiated National Ambient Air Quality Monitoring (NAAQM) programme in the year 1984 with 7 stations at Agra and Anpara. Subsequently in 1998-99 the programme was renamed as National Air Monitoring Programme (NAMP). The number of monitoring stations under NAMP has increased, steadily, to 295 by 2000-01 covering 98 cities/towns in 29 States and 3 Union Territories of the country. Under NAMP, four air pollutants viz., Sulphur Dioxide (SO₂), Oxides of Nitrogen as NO₂, Total Suspended Particulate (TSP) and Respirable Suspended Particulate Matter (RSPM/PM₁₀), have been identified for regular monitoring at all the locations (CPCB, 2002).

The pollutants those are under study, in this project are:-

- (i) Sulphur dioxide
- (ii) Nitrogen oxides
- (iii) TSP
- (iv) PM₁₀

(i) Sulphur dioxide: It is a colourless gas with a pungent and suffocating odour. The gas is produced by the combustion of fossil fuels (Naik S.,2005). Sources include industrial activities such as flaring at oil and gas facilities and diesel power generation, commercial and home

heating and vehicle emissions. The amount of SO₂ emitted is directly related to the sulphur content of the fuel (Air Quality Monitoring Network, 2008).

(ii) Nitrogen oxides (NO_x): NO_x represents the sum of the various nitrogen gases found in the air, of which Nitric Oxide (NO) and Nitrogen Dioxide (NO₂) are the dominant forms. The emission sources are varied but tend to result from high temperature combustion of fuel for industrial activities, commercial and residential heating, and vehicle use. Forest fires can be a large natural source of NO_x (Air Quality Monitoring Network, 2008).

(iii) Total suspended particulate (TSP): TSP refers to particles ranging in size from the smallest to a generally accepted upper limit of 50-100 microns in diameter (1 micron = 1 millionth of a metre). TSP is dominated by the larger sized particles commonly referred to as “dust” and is associated with aesthetic and environmental impacts such as soiling of materials or smothering of vegetation (Air Quality Monitoring Network, 2008). The entire domain of particulate matter is known as *Total Suspended Particulate*, TSP (IPCC, 2001). This includes all airborne solid and liquid particles, except pure water, ranging in size from approximately 0.005mm to 100mm in diameter (Balaceanu C. et al., 2004).

(iv) PM₁₀: Particulate matter is a ubiquitous pollutant, reflecting the fact that it has both natural and anthropogenic sources. Natural sources of primary PM include windblown soil and mineral particles, volcanic dust, sea salt spray, biological material such as pollen, spores and bacteria and debris from forest fires (National Ambient Air Quality Objectives for Particulate matter, 1998). PM₁₀ refers to particulate matter that is 10 µm or less in diameter. PM₁₀ is generally subdivided into a fine fraction of particles 2.5 µm or less (PM_{2.5}), and a coarse fraction of particles larger than 2.5 µm (National Ambient Air Quality Objectives For Particulate matter, 1998). In the atmosphere the particulate matters (PMs) may be classed as either *primary* or *secondary*. *Primary particles* are those such as carbon particles from combustion, mineral particles derived from stone abrasion, and sea salt. *Secondary particles* are those that are formed in the atmosphere by the chemical reaction of the gases, which combine to form less volatile compounds that then condense into particles (Balaceanu C. et al, 2004).

1.4 EFFECTS OF AIR POLLUTION:

Air pollution is a basic problem in today's world. Exposure to ambient air pollution has been linked to a number of different health outcomes, starting from modest transient changes in the respiratory tract and impaired pulmonary function, continuing to restricted activity/reduced performance, emergency room visits and hospital admissions and to mortality. There is also increasing evidence for adverse effects of air pollution not only on the respiratory system, but also on the cardiovascular system (WHO, 2004).

Physical damage functions relating health (mortality and morbidity) to air pollution levels have been estimated over a number of years in different countries. Although the net effect of pollutants on health is unclear, the Committee of the Medical Effects of Air Pollution (COMEAP), set up by the UK government has found the strongest link between health and pollution to be for particulates (PM_{10}), sulphur dioxide (SO_2) and ozone (O_3) (Powe Neil A., et al, 2002).

The major air pollutants discussed here are sulphur dioxide, nitrogen oxides, TSP and PM_{10} . The harmful effects of these pollutants are discussed here in detail:

(i) Sulphur dioxide: Elevated concentrations of SO_2 can be indicated by an odor of 'burning matches' and are associated with human health impacts, including respiratory (breathing) effects, especially asthma. Environmental effects include acid deposition and formation of $PM_{2.5}$. Vegetation, especially lichens, can be very sensitive to SO_2 at relatively low concentrations (Air Quality Monitoring Network, 2008). The gas irritates airways and eyes and is known to cause longer-term heart diseases, other cardiovascular ailments, and bronchitis. It also readily causes shortness of breath and coughing amongst asthma sufferers. SO_2 is also a major contributor to acid rain, which damages the environment and upsets ecosystems (Chan Wai-Shin et al, 2007).

(ii) Nitrogen oxides (NO_x): It causes severe respiratory problems, especially in children. When combined with water, it forms nitric acid and other toxic nitrates. NO_2 is also a main component in the formation of ozone at the surface level. The gas irritates the lungs and has been known to lower the immune system (Chan Wai-Shin et al, 2007). It may cause acidification and eutrophication harmful to health (mainly the respiratory system),

materials, cultural artifacts , vegetation and crops (Sida ,unknown) . Elevated concentrations of NO_2 can also affect visibility through creation of a 'reddish brown' haze. However, the effects of NO on vegetation is coming under increasing investigation in Europe, while NO_x is also a concern due to the role it plays as a *precursor pollutant* for $\text{PM}_{2.5}$ formation and its association with acid deposition (Air Quality Monitoring Network, 2008).

(iii) Total suspended particulate (TSP): TSP is associated with aesthetic and environmental impacts such as soiling of materials or smothering of vegetation (Air Quality Monitoring Network, 2008). It may pose the greatest threat to human health because, for the same mass, they absorb more toxic and carcinogenic compounds than larger particles and penetrate more easily deep into the lungs (Masitah Alias et al, 2007).

(iv) PM_{10} : The increases in particulate matter have been shown to cause small, reversible decrements in lung function in normal asymptomatic children, and in both adults and children who have some form of pre-existing respiratory condition, particularly asthma. These changes were often accompanied, especially in adults, by increases in symptoms such as chronic bronchitis or cough (National Ambient Air Quality Objectives For Particulate matter, 1998).

CHAPTER 2

LITERATURE REVIEW

The rapid industrialization leading to urbanization, unplanned and excessive exploitation of natural resources have been causing pollution problems in cities and towns of developing countries. Man made and natural sources of emissions have polluted the air with toxic substances.

The national average per capita SO₂ emission was 4.2 kg per person in 1990, which rose to 5 kg in 1995, an increase of almost 20% in 5 yr. In 1990, coal consumption contributed 64% of total SO₂ emissions in India, oil products 29%, biomass 4.5% and non-energy consumption 2.5% (A. Garg et al, 2001). Total SO₂ and NO_x emissions from India were 3542 and 2636 Gg respectively [1990] and 4638 and 3462 Gg [1995] growing at annual rate of around 5.5%. The sectoral composition of SO₂ emissions indicates a predominance of electric power generation sector [46%]. Power and transport sector emissions equally dominate NO_x emissions contributing nearly 30% each (A Garg et al, 2001). The ambient air quality in Madurai City of South India was studied and it was found that the SPM concentration varied from 200 to 500 µg / cu-m, NO_x from 50 to 170 µg / cu-m and SO₂ from 10 to 25 µg / cu-m. The Ambient Air Quality of Jyotivihar, Orissa in terms of TSP, SO₂ and NO_x was studied during December–1994 to November–1995. The minimum and maximum values were 82.995 µg/cu-m and 182.7 µg/cu-m for TSP, 4.62 µg/cu-m and 25.74 µg/cu-m for SO₂ and 4.39 µg/cu-m and 16.89 µg/cu-m for NO_x (Naik S., 2005). A report showed that SPM concentrations in Shanghai, New Delhi, Mumbai, Guangzhou, Chongquin, Calcutta, Beijing and Bangkok exceeded WHO limits (90 µg/cu-m) by three, five, three, three, four, four, four and two times respectively . It also showed that PM₁₀ exceeded the USEPA limit (50µg/cu-m) by several times in a number of cities, most notably by over four times in New Delhi and Calcutta. Data from Tokyo shows that TSP increased rapidly from 40 µg/cu-m in the early 1980s to over 70 µg/cu-m in the early 1990s; after that TSP has been decreasing or stagnating, but it is becoming an increasing challenge to contain TSP and NO_x (Air Pollution Control in the Transportation Sector, 2007).

The Central Pollution Control Board monitors the quality of air at nine stations in Delhi. The latest data published before the field work commenced pertained to 1991(CPCB, 1992). The range of mean annual concentrations across these nine stations were: total suspended particulates (TSP)=255–643 µg/cu-m; nitrogen dioxide (NO₂)=24.2–61.7 µg/cu-m; sulphur dioxide (SO₂)=8.4–51.2 µg/cu-m. The overall mean level of RSP in this micro-environment was 390µg/cu-m. The average level of PM₁₀ as measured at nighttime indoors was found to be comparably very high F 900 µg/cu-m (Saksena et al, 2003). A recent study in middle-income

homes of Delhi found PM₁₀ levels to be as high as 170–810 µg/cu-m even in homes where there was no cooking or smoking activity (Kumar, 2001).

A study for assessment and management of air quality was carried out in the Ib Valley area of the Ib Valley coalfield in Orissa state, India. The 24 h average concentrations of total suspended particulate (TSP), respirable particulate matter (PM₁₀), sulfur dioxide (SO₂) and oxides of nitrogen (NO_x) were determined at regular intervals throughout one year at twelve monitoring stations in residential areas and six monitoring stations in mining/industrial areas. The 24 h average TSP and PM₁₀ concentrations were 124.6–390.3 µg/cu-m and 25.9–119.9 µg/cu-m in residential areas, and were 146.3–845.2 µg/cu-m and 45.5–290.5 µg/cu-m in industrial areas. During the study period, 24 h and annual average TSP and PM₁₀ concentrations exceeded the respective standards set in the Indian national ambient air quality standard (NAAQS) protocol as well as USEPA, EU, WHO and World Bank standards at most of the residential and industrial areas. However, concentrations of SO₂ (annual average: 24.6–36.1 µg/cu-m and 24 h average: 17.0–46.3 µg/cu-m) and NO_x (annual average: 23.6–40.9 µg/cu-m and 24 h average: 18.3–53.6 µg/cu-m) were well within the prescribed limit of the NAAQS and international standards in both residential and industrial areas (Chaulya S. K., 2004).

In one of the project the fine and coarse fractions of PM (PM_{2.5} and PM_{10-2.5} respectively) and volatile organic compounds (benzene, toluene and xylene) were monitored during wet season 2002, dry season 2003, wet season 2003. Monitoring was done for 24 hours in 5 different sites in Chennai city. Regarding PM results in wet season 2002, for coarse fraction (PM_{10-2.5}) the background site, mixed traffic site and industrial sites (Manali and Ambattur) recorded a maximum of 139 µg/cu-m, 206 µg/cu-m, 238 µg/cu-m, 231 µg/cu-m respectively where the prescribed standard for residential areas is 100 µg/cu-m and for industrial area is 150 µg/cu-m. In dry season 2003, for coarse fraction (PM_{10-2.5}) at the background site, mixed traffic site, mixed residential site and industrial sites recorded a maximum of 143 µg/cu-m, 253 µg/cu-m, 121 µg/cu-m, 234 µg/cu-m, and 267 µg/cu-m respectively. In wet season 2003, at the background site and mixed traffic site particulate concentrations showed a maximum of 98 µg/cu-m and 192 µg/cu-m for coarse fraction (PM_{10-2.5}) (Murthy D.V.S et al, 2004).

Available air quality data suggest that pollutant of most concern from the point of view of environmental health risk in South Asia is airborne particulate matter. Average high values have been recorded for PM₁₀ in various cities in South Asia such as 900 µg/cu-m for Lahore; 225, 135 and 126 µg/cu-m for core, sub core and remote part of Nepal. Average values of PM₁₀ and NO₂

were 61 and 22 $\mu\text{g}/\text{cu-m}$ at ambient site and at Kerbsite it was 90 and 25 $\mu\text{g}/\text{cu-m}$ respectively (Kumar R. et al, 2006).

The rural-industrial site at Satna shows significant different from urban, urban-industrial, rural, rural-remote and rural–urban influenced sites. With a minimum of one daily sample at each site, mean PM_{10} concentration at the rural-industrial Satna site varied from 65.5 to 147.5 $\mu\text{g}/\text{cu-m}$, and from 205.0 to 320.3 $\mu\text{g}/\text{cu-m}$ at the urban-industrial Delhi site. With a minimum of one daily sample at each site, the mean TSP concentration at the rural-industrial Satna site varies from 283.9 to 678.0 $\mu\text{g}/\text{cu-m}$, while at the urban industrial Delhi site mean TSP concentration varies from 553.4 to 827.6 $\mu\text{g}/\text{cu-m}$. The maximum TSP concentration in Satna, 678.0 $\mu\text{g}/\text{cu-m}$, was on December 9, 2000. Maximum TSP concentration in Delhi, 827.6 $\mu\text{g}/\text{cu-m}$, occurred on October 23, 2000. Levels of TSP in Ashok Vihar, a residential area in Delhi, reached 10 times the permissible limit in October 2000 (Shandilya Kaushik. K. et al, 2007).

Monitoring of ambient respirable suspended particulate matter or PM_{10} and total suspended particulate (TSP) levels around a large coal-fired power station in India was carried out. Geometric mean values of PM_{10} and TSP concentrations at sites of downwind direction are found in ranges of 74–144 $\mu\text{g}/\text{cu-m}$ (PM_{10}) and 459–647 $\mu\text{g}/\text{cu-m}$ (TSP) in post rainy season, 154–207 $\mu\text{g}/\text{cu-m}$ (RSPM) and 437–610 $\mu\text{g}/\text{cu-m}$ (SPM) in summer season and 180–275 $\mu\text{g}/\text{cu-m}$ (PM_{10}) and 933–1578 $\mu\text{g}/\text{cu-m}$ (TSP) in winter season (Sharma R. et al, 2005).

In a study conducted in the city Kanpur it was found out that average pollution level in the city expressed in PM_{10} was 225.68 $\mu\text{g}/\text{cu-m}$ during the year 2004. One of the monitoring stations i.e., Vikas Nagar registers wild fluctuations in the level of PM_{10} . It varies from 295 to 463 $\mu\text{g}/\text{cu-m}$ during summer and from 42.5 to 122 $\mu\text{g}/\text{cu-m}$ during the monsoon and winter seasons respectively (Gupta U., 2007).

A study conducted on the ambient air quality of the city Lucknow during Diwali festival showed varied concentrations of PM_{10} , SO_2 and NO_x . In this study, PM_{10} , SO_2 , NO_x and 10 trace metals associated with PM_{10} were estimated at four representative locations, during day and night times for Pre Diwali (day before Diwali) and Diwali day. On Diwali day 24 h average concentration of PM_{10} , SO_2 , and NO_x was found to be 753.3, 139.1, and 107.3 $\mu\text{g}/\text{cu-m}$, respectively, and these concentrations were found to be higher at 2.49 and 5.67 times for PM_{10} , 1.95 and 6.59 times for SO_2 and 1.79 and 2.69 for NO_x , when compared with the respective concentration of Pre Diwali and normal day, respectively. On Diwali night (12 h) mean level of PM_{10} , SO_2 and NO_x was

1,206.2, 205.4 and 149.0 $\mu\text{g}/\text{cu-m}$, respectively, which was 4.02, 2.82 and 2.27 times higher than their respective daytime concentrations (Barman S. C. et al, 2008).

In dry, unpolluted atmospheric conditions, it is estimated that the average SO_2 concentration ranges from 0.03 to 0.3 $\mu\text{g}/\text{cu-m}$ (0.01 to 0.1 parts per billion or ppb). In remote areas, SO_2 concentrations range 0.13 to 0.31 $\mu\text{g}/\text{cu-m}$ (0.05 to 0.12 ppb). In urban and industrialized areas, SO_2 concentrations range from 2.6 to 2600 $\mu\text{g}/\text{cu-m}$ (1 to 1000 ppb). A survey by the World Health Organization (WHO) of urban areas showed annual mean SO_2 concentrations ranging from 20 to 60 $\mu\text{g}/\text{cu-m}$ (7 to 21 ppb) and daily means rarely exceeding 125 $\mu\text{g}/\text{cu-m}$ (44 ppb) (WHO, 2000). IARC (1992) presents data for ambient air concentrations of SO_2 in different parts of the world (WBK et al, 2003).

A study of air pollution in the city Taipei reveals that sulphur dioxide and nitrogen oxides are the major contributors for air pollution and are found in abundance in the urbanized city. The emissions of sulphur oxides (SO_x) total 2,658 tonnes per year. Combustion emission accounts for approximately 62 per cent, mostly fuel combustion (44 per cent for commercial activities and 12 per cent for industries). Non-fuel combustion emissions account for some 3 per cent, and road transportation emissions 37 per cent (23 per cent from petroleum vehicles, 8 per cent from diesels and 6 per cent from motorcycles). The NO_x emissions total 22,023 tonnes per year. Road transportation accounts for 81 per cent (diesels 44 per cent; petroleum cars 34 per cent and motorcycles 3 per cent). As for non-road transportation emissions, aircraft account for some 10 per cent. Combustion emissions accounts for some 9 per cent, of which fuel combustion accounts for a major share (approximately 6 per cent) (Wang Din J., unknown).

CHAPTER 3

SITE DESCRIPTION

3.1 MONITORING SITES:

The main concern of the project is to measure the concentration of sulphur dioxide, NO_x, TSP and PM₁₀ taking readings at different stations with the help of respirable dust sampler. These two critical gaseous pollutants and the particulate pollutants are in abundance in Rourkela environment since it is an industrial area and a little change in their concentration in ambient air can make a strong effect on the existing living stock causing many adverse effects on health and skin.

As we are primarily concerned about the environment around us that means inside the NIT campus, mainly the hostel area and the residential colony, so we decided to choose the sampling stations inside the campus area. The stations were so chosen that there can be adequate safety measures as well as reduced interference of the local public with the devices used for the experiment. We investigated the decided sampling stations and found out the possible problems and the possible precautions to be taken while handling and use of the device for the project.

The monitoring stations chosen are:

1. Station-1: M.S. Swaminathan Hall of residence,
Cycle shed roof top
2. Station-2: Residence area inside campus,
Dispensary
3. Station-3: Institute main building roof top

3.2 PROBLEMS FACED DURING OPERATION:

The implementation of the sampling devices at the aforesaid stations was quite difficult to deal with. The following problems were faced during our operation:

Station I: In station-1, that is on the cycle shed roof top, M.S Swaminathan hall of residence everything seemed to be fine about the setting up of the device and connection for electricity except we had to be aware of the students who found it curious enough to touch and handle it. For that we hired a guard of the hostel itself to take care of the device during its working, with the permission of the Hall-5 warden.

Station II:

In residential area i.e. the dispensary we found the same difficulties as in the station-2. Along with that there was also another problem that was to be taken care of. The high school that is in front of the dispensary was of a major concern while setting of the device. We needed to take care of the curious children and they were to be kept away from the instrument. For that in the morning hour we asked a person working in the dispensary to take care of that.

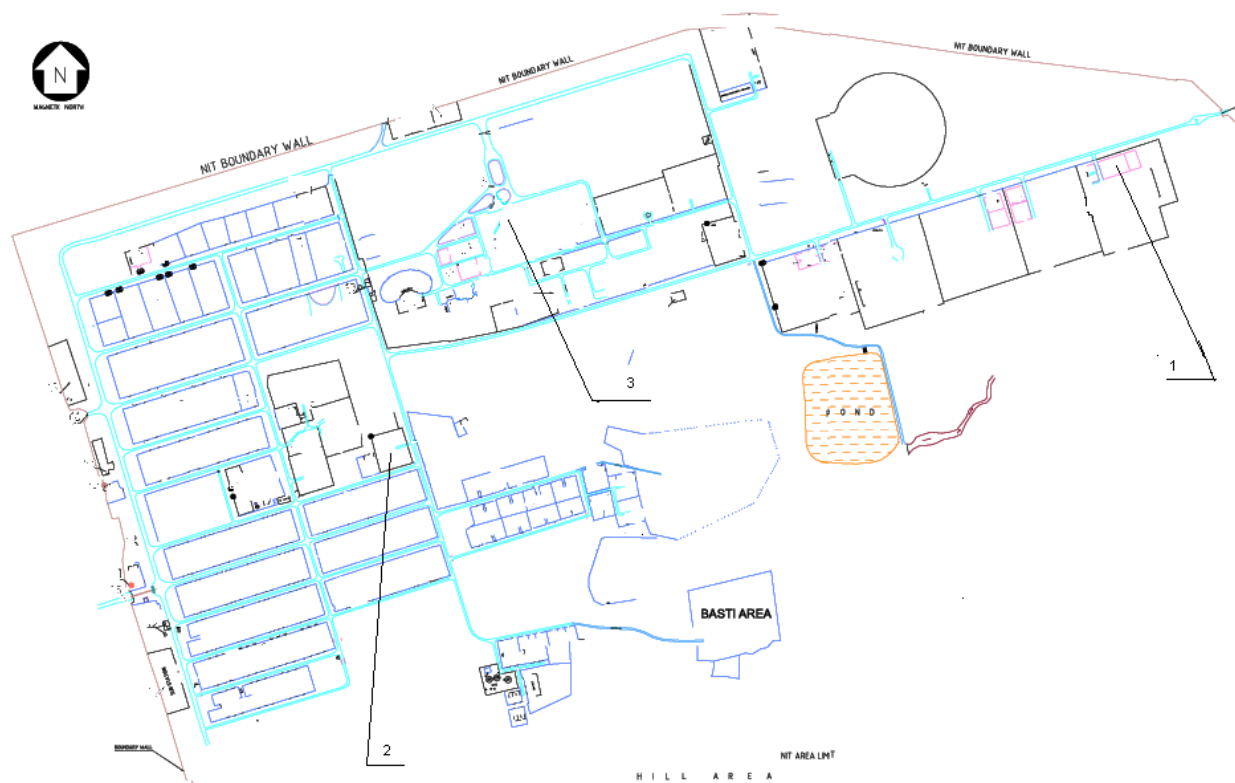
Station III:

(1) It is the most crowded part among the four stations (chosen) during the college hour. So, here serious precautions were preferred. We had to make sure that no students were there to handle it with utter curiosity.

(2) While the machine was running, some construction works were also going on there. So we found laborers inside the institute premises, particularly in that area. It was made sure that they were not to handle or touch the device.

3.4 SITE MAP:

The monitoring sites chosen are given in Figure-3.1.



- 1- M.S. Swaminathan Hall of residence, cycle shed roof top
- 2- Residence area inside campus, Dispensary
- 3- Institute main building roof top

Figure-3.1: NIT campus map along with the monitoring sites.



Figure-3.2: M.S. Swaminathan Hall of Residence, Cycle shed roof top.



Figure-3.3: Residence area inside campus, Dispensary (photographic view)



Figure-3.4: Institute main building roof top (photographic view)

3.4 MONITORING CRITERIAS

The monitoring stations chosen should be free from any interference from the surrounding living stock. Sampling is usually done at 1.5 m height. It was ensured that filter is parallel to the ground. To obtain a representative sample the sample should not be placed under a tree, near a wall or other obstructions that would prevent free air flow from the ambient atmosphere.

During inclement weather (including high winds), the entire sample is moved to a protected location for servicing when practical. Before the new filter is installed, loose particles from the inside surfaces of the sampler were removed and the surfaces around the filter holder by wiping with a clean cloth. The clean installed filter was protected when returning the sampler to the shelter.

In our case sampling was done generally at the roof tops of the respective sites so it was well above the prescribed height that is 1.5 m and was free from any obstructions to flow of air.

CHAPTER 4

METHODOLOGY

4.1: VARIOUS EXPERIMENTAL METHODS FOR THE POLLUTANTS

According to the CPCB (Central pollution control board) the methods prescribed for the pollutant gases and the particulate pollutants are very sensitive ones yet percentage of errors are very less. The methods prescribed for the gases SO₂, NO_x and the particulate pollutants TSP, PM₁₀ are respectively:

- (i) Modified West and Gaeke method
- (ii) Modified Jacob Hochheiser method
- (iii) High Volume method
- (iv) Cyclonic flow technique

The purpose is to lay down an uniform and reliable method for sampling and analysis of SO₂ and NO_x in the ambient air and also to lay down an uniform and reliable method for measurement of TSP and PM₁₀ in the ambient air of NIT Rourkela.

4.2 DESCRIPTION OF THE METHODS

The methods are laid down here as prescribed by the CPCB.

4.2.1 MODIFIED WEST AND GAEKE METHOD FOR MEASUREMENT OF SO₂

4.2.1.1 TITLE:

Method for determination of Sulphur Dioxide in Air (Modified West and Gaeke Method).

4.2.1.2 PURPOSE:

The purpose is to lay down an uniform and reliable method for determination of sulphur dioxide (SO₂) in ambient air.

4.2.1.3 PRINCIPLE:

Sulphur dioxide from air is absorbed in a solution of potassium tetrachloromercurate (TCM). A dichlorosulphitomercurate complex, which resists oxidation by the oxygen in the air, is formed.

Once formed, this complex is stable to strong oxidants such as ozone and oxides of nitrogen and therefore, the absorber solution may be stored for some time prior to analysis. The complex is made to react with pararosaniline and formaldehyde to form the intensely colored pararosaniline methylsulphonic acid. The absorbance of the solution is measured by means of a suitable spectrophotometer.

Concentration of sulphur dioxide in the range of 25-1050 $\mu\text{g}/\text{cu-m}$ can be measured under the conditions given are measure concentration below 25 $\mu\text{g}/\text{cu-m}$ by sampling larger volumes of air, but only if, the absorber efficiency of the particular system is first determined and found to be satisfactory. Higher concentration can be analyzed by using smaller gas samples of a suitable aliquot of the collected sampler. Beer's law is followed through the working range from 0.03 to 1.0 absorbance unit. This corresponds to 0.8-27 μg of sulfite ion in 25 ml of final solution calculated as sulphur dioxide. The lower limit of detection of sulphur dioxide in 10 ml absorbing reagent is 0.75 μg based on twice the standard deviation, which represent a concentration of 25 $\mu\text{g}/\text{cu-m}$ in an air sample of 30 litres.

4.2.1.4 SCOPE:

This method is applicable for the measurement of concentration of sulphur dioxide present in ambient air.

4.2.1.5 INTERFERENCES:

The effects of the principal known interferences have been minimized or eliminated. Interferences by oxides of nitrogen are eliminated by sulphamic acid. Ozone is made to decompose by allowing the solution to stand for some time prior to analysis. The interference of trace metals may be eliminated by the addition of ethylenediamine tetra acetic acid (EDTA) to the absorbing solution prior to sampling. At least 60 μg iron (III), 10 μg manganese (II), and 10 μg chromium (III) in 10 ml absorbing reagent can be tolerated in the procedure. No significant interference was found from 10 μg copper (II) and 22 μg vanadium (V). Ammonium, sulphide, and aldehydes do not interfere.

4.2.1.6 Analysis:

A spectrophotometer suitable for measurement of absorbance at 560 nm with an effective spectral band width of less than 15 nm is required. Reagent blank problems may occur with spectrophotometer having greater spectral bandwidths. The wavelength calibration of the instrument should be verified. If, transmittance is measured, this can be converted to absorbance by the formula:

$$A = 2 - \log_{10} T$$

4.2.1.7 REAGENTS:

4.2.1.7.1 Sampling:

(i) Water - High quality water must be used. It must be free from oxidants, particularly chlorine, which may not be removed by distillation. This criterion must be observed whether water is prepared by distilling or deionizing or by using a combination of both techniques.

(ii) Absorbing Reagents, 0.04 M Potassium Tetrachloro mercurate (TCM) – Dissolve 10.86 g, mercuric chloride, 0.066 g EDTA, and 6.0 g potassium chloride or sodium chloride 4.68 gm in water and bring to the mark in a 1 litre volumetric flask. CAUTION: HIGHLY POISONOUS IF SPILLED ON SKIN, FLUSH OFF WITH WATER IMMEDIATELY. The pH of this reagent should be approximately 4.0 but, it has been shown that there is no appreciable difference in collection efficiency over the range of pH 5 to pH 3. The absorbing reagent is normally stable for six months. If, a precipitate forms, discard the reagent after recovering the mercury.

4.2.1.7.2 Analysis:

(i) Sulphamic Acid (0.6%) - Dissolve 0.6 g sulphamic acid in 100 ml distilled water. Prepare fresh daily.

(ii) Formaldehyde (0.2%) - Dilute 5 ml formaldehyde solution (36-38%) to 1 litre with distilled water. Prepare fresh daily.

(iii) Stock Iodine Solution (0.1 N) - Place 12.7 g iodine in a 250 ml beaker, add 40 g potassium iodide and 25 ml water. Stir until all is dissolved, then dilute to 1 litre with distilled water.

(iv) Iodine Solution (0.01 N) - Prepare approximately 0.01 N iodine solution by diluting 50 ml of stock solution to 500 ml with distilled water.

(v) Starch Indicator Solution - Triturate 0.4 gm soluble starch and 0.002 g mercuric iodide preservative with a little water and add the paste slowly to 200 ml boiling water. Continue boiling until the solution is clear, cool, and transfer to a glass stopper bottle.

(vi) Stock Sodium Thiosulfate Solution (0.1 N) - Prepare a stock solution by placing 25 g sodium thiosulfate pentahydrate in a beaker, add 0.1 g sodium carbonate and dissolve using boiled, cooled distilled water making the solution up to a final volume of 1 litre. Allow the solution to stand one day before standardizing.

To standardize, accurately weigh to the nearest 0.1 mg, 1.5 g primary standard potassium iodate dried at 180⁰C, dissolve, and dilute to volume in a 500 ml volumetric flask. Into a 500 ml Iodine flask, transfer 50 ml of iodate solution by pipette. Add 2 g potassium iodide and 10 ml of N hydrochloric acid and stopper the flask. After 5 min, titrate with stock thiosulfate solution to a pale yellow. Add 5 ml starch indicator solution and continue the titration until the blue color disappears. Calculate the normality of the stock solution.

(vii) Sodium Thiosulphate Titrant (0.01 N) - Dilute 100 ml of the stock thiosulfate solution to 1 litre with freshly boiled and cooled distilled water.

(viii) Standardized Sulphite Solution for Preparation of Working Sulphite-TCM Solution

Dissolve 0.30 g sodium metabisulphite (Na₂S₂O₅) or 0.40 g sodium sulphite (Na₂SO₃) in 500 ml of recently boiled, cooled, distilled water. Sulphite solution is unstable; it is, therefore, important to use water of the highest purity to minimize this instability. This solution contains the equivalent of 320-400 µg/ml of SO₂. The actual concentration of the solution is determined by adding excess iodine and back-titrating with standard sodium thiosulfate solution. To back-titrate, measure, by pipette, 50 ml of the 0.01 N iodine solutions into each of two 500 ml iodine flasks A and B. To flask A (blank) add 25 ml distilled water and into flask B (sample) measure

25 ml sulphite solution by pipette. Stopper the flasks and allow to react for 5 minutes. Prepare the working sulphite-TCM solution at the same time iodine solution is added to the flasks. By means of a burette containing standardized 0.01 N thiosulfate, titrate each flask in turn to a pale yellow. Then add 5 ml starch solution and continue the titration until the blue color disappears.

(ix) Working Sulphite-TCM Solution - Measure 2 ml of the standard solution into a 100 ml volumetric flask by pipette and bring to mark with 0.04 M TCM. Calculate the concentration of sulphur dioxide in the working solution in micrograms of sulphur dioxide per milliliter. This solution is stable for 30 days if kept in the refrigerator at 5°C. If not kept at 5°C, prepare fresh daily.

(x) Purified Pararosaniline Stock Solution (0.2% Nominal)

(xi) Dye Specifications - The pararosaniline dye must meet the following specifications:

(a) The dye must have a wavelength of maximum absorbance at 540 nm when assayed in a buffered solution of 0.1 M sodium acetate - acetic acid.

(b) The absorbance of the reagent blank, which is temperature sensitive to the extent of 0.015 absorbance unit/ °C, should not exceed 0.170 absorbance unit at 22°C with a 1 cm optical path length, when the blank is prepared according to the prescribed analytical procedure and to the specified concentration of the dye.

(c) The calibration curve should have a slope of 0.030 ± 0.002 absorbance unit/ $\mu\text{g SO}_2$ at this path length when the dye is pure and the sulphite solution is properly standardized.

Pararosaniline Stock Solution - Dissolve 0.500 gm of specially purified pararosaniline (PRA) in 100 ml of distilled water and keep for 2 days (48 hours). Pararosaniline Working Solution - 10 ml of stock PRA is taken in a 250 ml volumetric flask. Add 15 ml conc. HCL and make up to volume with distilled water.

4.2.1.8 PROCEDURE:

4.2.1.8.1 Sampling and Analysis

(i) Sampling - Procedures are described for short-term (30 minutes, 1 hour, 4 hours) long-term (8 hours, 24 hours) sampling. Here we have taken 8 hours for gaseous as well as particulate sampling. Sample volumes should be adjusted, so that linearity is maintained between absorbance and concentration over the range in question.

(ii) 8 Hours Sampling - Insert a midgett impinger into the sampling system. Add 10 ml TCM solution to the impinger (30 ml TCM solution for 4 hours sampling). Collect sample at 1 litre/minute for 30 minutes, 1 hour or 4 hours using either a rotameter, or a critical orifice, to control flow. Shield the absorbing reagent from direct sunlight during and after sampling by covering the impinger with aluminum foil to prevent deterioration. Determine the volume of air sampled by multiplying the flow rate by the time in minutes and record the atmospheric pressure and temperature. Remove and stopper the impinger. If, the sample must be stored for more than a day before analysis, keep it at 5⁰C in a refrigerator; during hot weather, sampling is not recommended unless it is possible to refrigerate the samples as taken.

(iii) Sample Preparation - After collection, if a precipitate is observed in the sample, remove it by centrifugation.

(iv) 8 Hours Samples - Transfer the sample quantitatively to a 30 ml volumetric flask using about 5 ml distilled water for rinsing. Delay analyses for 20 minutes to allow any ozone to decompose.

4.2.1.8.2 Sample Preservation

After sample collection, the solutions must be stored at 5⁰C in a refrigerator. At 22⁰C losses of sulphur dioxide occur at the rate of 1% per day. When samples are stored at 5⁰C for 30 days, no detectable losses of sulphur dioxide occur. The presence of EDTA enhances the stability of sulphur dioxide in solution, and the rate of decay is independent of the concentration of sulphur dioxide.

Determination:

For each set of determinations prepare a reagent blank by adding 10 ml of unexposed TCM solution to a 25 ml volumetric flask. Prepare a control solution by measuring 2 ml of working sulphite-TCM solution and 8 ml TCM solution into a 25 ml volumetric flask by pipette. To each flask containing either sample, control solution, or reagent blank, add 1 ml 0.6% sulphamic acid and allow to react 10 minutes to destroy the nitrite resulting from oxides of nitrogen. Measure by pipette and add 2 ml of 0.2% formaldehyde solution and 2 ml pararosaniline solution. Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with freshly boiled and cooled distilled water and mix thoroughly. After 30 minutes and before 60 minutes, determine the absorbance of the sample, A , reagent blank, A_0 , and the control solution at 560 nm using cells with a 1 cm path length. Use distilled water; not the reagent blank, as the optical reference. This is important because of the color sensitivity of the reagent blank to temperature changes which may be induced in the cell compartment of a spectrophotometer. Do not allow the colored solution to stand in the absorbance cells, because a film of dye may be deposited. Clean cells with alcohol and clean pipe cleaner after use. If, the temperature of the determinations does not differ by more than 2°C from the calibration temperature, the reagent blank should be within 0.03 absorbance unit of the y-intercept of the calibration curve. If, the reagent blank differs by more than 0.03 absorbance unit that found in the calibration curve, prepare a new curve.

4.2.1.8.3 Absorbance Range

If, the absorbance of the sample solution lies between 1.0 and 2.0, the sample can be diluted 1:1 with a portion of the reagent blank and read within a few minutes. Solutions with higher absorbance can be diluted up to six fold with the reagent blank in order to obtain on-scale readings within 10% of the true absorbance value.

4.2.1.8.4 Calibration and Efficiencies

(i) Calibration Curve - Procedure with Sulphite Solution - Measure by pipette graduated amounts of the working sulphite-TCM solution (such as 0, 0.5, 1, 2, 3 and 4 ml) into a series of 25 ml volumetric flasks. Add sufficient TCM solution to each flask to bring the volume to approximately 10 ml. Then add the remaining reagents as described in previous sections. For

maximum precision use a constant-temperature bath. The temperature of calibration must be maintained within $\pm 1^{\circ}\text{C}$ and within the range of $20\text{-}30^{\circ}\text{C}$. The temperature of calibration must be maintained within two degrees. Plot the absorbance against the total concentration in micrograms sulphur dioxide for the corresponding solution. The total micrograms sulphur dioxide in solution equals the concentration of the standard in micrograms sulphur dioxide per milliliter times the milliliter of sulphite solution added ($\mu\text{g SO}_2 = \mu\text{g/ml/SO}_2 \times \text{ml added}$). A linear relationship should be obtained, and the Y-intercept should be within 0.03 absorbance unit of the zero standard absorbance. For maximum precision determine the line of best fit using regression analysis by the method of least squares. Determine the slope of the line of best fit, calculate its reciprocal, and denote as B, the calibration factor. See previous section for specifications on the slope of the calibration curve. This calibration factor can be used for calculating results provided there are no radical changes in temperature or pH. At least one control sample containing a known concentration of SO_2 for each series of determinations is recommended to ensure the reliability of this factor.

(ii) Sampling Efficiency - Collection efficiency is generally above 98%; efficiency may fall off, however, at concentrations below $25 \mu\text{g/cu-m}$.

4.2.1.9 CALCULATION:

4.2.1.9.1 Normality of Thiosulfate Solution

The normality of this solution N is calculated as follows:

$$N = \frac{W \times 10^3 \times 0.1}{V \times 35.67}$$

Where:

V - Volume thiosulfate used, ml

W - Weight of potassium iodate, g

35.67 - Equivalent weight of potassium iodate

4.2.1.9.2 Concentration of Sulphite Solution

The amount of sulphur dioxide per milliliter in the standard solution, is calculated as follows:

$$C = \frac{(V_1 - V_2) \times N \times K}{V}$$

Where:

- C - SO₂ concentration in µg/ml
- V₁ - Volume of thiosulfate for blank, ml
- V₂ - Volume of thiosulfate for sample, ml
- N - Normality of thiosulfate
- K - 32000 (Milliequivalent weight SO₂/µg)
- V - Volume of standard sulphite solution, ml

4.2.1.9.3 Sulphur Dioxide Concentration at the Reference Conditions

When sulphite solutions are used to prepare calibration curves, compute the concentration of sulphur dioxide, C, in micrograms per cubic metre, in the sample as follows:

$$C = \frac{(A - A_0) (10^3) (B)}{V} \times D$$

Where:

- A - Sample absorbance
- A₀ - Reagent blank absorbance
- 10³ - Conversion of litres to cubic metres
- V - Volume of air in litres
- B - Calibration factor, µg/absorbance unit
- D - Dilution factor

4.2.1.9.4 The Concentration of SO₂ in µg/cu-m in the sample is calculated as follows:

$$C (\text{SO}_2 \mu\text{g}/\text{cu-m}) = \frac{(A - A_0) \times 10^3 \times B}{V}$$

Where:

A - Sample absorbance

A₀ - Reagent blank absorbance

10³ - Conversion litres to cubic meters

B - Calibration factor, µg/absorbance

V - Volume of air sampled in liters

4.2.1.9.5 Conversion of Micrograms per Cubic Metre to Parts per Million

If desired, the concentration of sulphur dioxide may be calculated as parts per million of sulphur dioxide at reference conditions as follows:

$$\text{ppm SO}_2 = \mu\text{g SO}_2/\text{cu-m} \times 3.82 \times 10^{-4}$$

4.2.1.9.6 Precision and Accuracy: Relative standard deviation at the 95% level is 4.6% for the analytical procedure using standard samples.

4.2.2 MODIFIED JACOB AND HOCHHEISER METHOD FOR DETERMINATION OF NO_x IN THE ATMOSPHERE

4.2.2.1 TITLE:

Method for determination of Nitrogen Dioxide in the Atmosphere (Sodium Arsenite method).

4.2.2.2 PURPOSE:

The purpose is to lay down a uniform and reliable method for sampling and analysis of nitrogen dioxide in ambient air.

4.2.2.3 PRINCIPLE:

4.2.2.3.1 Ambient nitrogen dioxide (NO₂) is collected by bubbling air through a solution of sodium hydroxide and sodium arsenite. The concentration of nitrite ion (NO₂⁻) produced during sampling is determined colorimetrically by reacting the nitrite ion with phosphoric acid, sulfanilamide, and N-(1-naphthyl)-ethylenediamine dihydrochloride (NEDA) and measuring the absorbance of the highly colored azodye at 540 nm.

4.2.2.3.2 The nominal range of the method is 9 to 750 µg NO₂/cu-m (0.005 to 0.4 ppm). The range of the analysis is 0.04 to 2.0 µg NO₂/ml, following Beer's Law throughout this range (0 to 1.0 absorbance units). Under the specified conditions of 50 ml of absorbing reagent, a sampling rate of 200 cu-cm/min for 24 hours, and a sampling efficiency of 0.82, the range of the method is, therefore, 9 to 420 µg/NO₂/cu-m (0.005 to 0.22 ppm). Nitrogen dioxide concentrations in the range of 420 to 750 µg/cu-m (0.22 to 0.4 ppm) are accurately measured by 1:1 dilution of the collected sample.

4.2.2.3.3 Based on results from a collaborative study, the within laboratory standard deviation is 8 µg/cu-m (0.004 ppm) and the between laboratory standard deviation is 11 µg/cu-m (0.006 ppm) over the range of 50 to 300 µg NO₂/cu-m (0.027 to 1.16 ppm).

4.2.2.3.4 Based on results from a collaborative study, the method has an average bias of -3% over the range of 50 to 300 µg NO₂/cu-m (0.027 to 0.16 ppm).

4.2.2.4 SCOPE:

This method is applicable to 8 hours and 24 hours integrated sampling of NO₂ in ambient air.

4.2.2.5 INTERFERENCES:

4.2.2.5.1 Nitric oxide (NO) is a positive interferant and carbon dioxide (CO₂) is a negative interferant. The average error resulting from normal ambient concentrations on NO and CO₂ is small for most monitoring situations and does not necessitate applying a correction to measurements obtained with the method.

4.2.2.5.2 Potential interference from sulfur dioxide (SO₂) is eliminated by converting any SO₂ to sulfate with hydrogen peroxide during analysis.

4.2.2.6 SAMPLE PRESERVATION:

Collected samples are stable for at least six weeks at room temperature. Stored samples should be tightly sealed to prevent absorption of NO₂ from the atmosphere.

4.2.2.7 ANALYSIS:

4.2.2.7.1 Volumetric Flasks - 100, 250, 500, 1,000 ml.

4.2.2.7.2 Pipets - 1, 2, 5, 10, 15, 20, 50 ml volumetric; 2 ml, graduated in 1/10 ml intervals.

4.2.2.7.3 Test Tubes - Approximately 150 mm long x 20 mm diameter.

4.2.2.7.4 Spectrophotometer - Capable of measuring absorbance at 540 nm; equipped with 1 cm optical path length cells.

4.2.2.8 REAGENTS:

All reagents should conform to ACS specifications for reagent grade materials unless otherwise specified.

4.2.2.8.1 Sampling:

4.2.2.8.1.1 Distilled Water - Must be reagent water as defined by ASTM procedure 1193-66 part 6.3 (consumption of potassium permanganate test).

4.2.2.8.1.2 Sodium Hydroxide.

4.2.2.8.1.3 Sodium Arsenite - CAUTION: Arsenic compounds are highly toxic and should be handled with extreme care. Avoid contact with skin and especially with eyes. Avoid generating dust or breathing dust. Keep away from food. Wash hands after handling it. Do not take internally.

4.2.2.8.1.4 Absorbing Reagents - Dissolve 4.0 g of sodium hydroxide in distilled water, add 1.0 g of sodium arsenite, and dilute to 1,000 ml with distilled water.

4.2.2.8.2 Analysis

4.2.2.8.2.1 Sulfanilamide - Melting point 165 to 167°C.

4.2.2.8.2.2 N-(1-Naphthyl)-ethylenediamine Di-hydrochloride (NEDA) - A 1% aqueous solution should have only one absorption peak at 320 nm over the range of 260-400 nm. NEDA showing more than one absorption peak over this range is impure and should not be used.

4.2.2.8.2.3 Hydrogen Peroxide, 30%.

4.2.2.8.2.4 Phosphoric Acid, 85%.

4.2.2.8.2.5 Sulfanilamide Solution - Dissolve 20 g of sulfanilamide in 700 ml of distilled water. Add, with mixing, 50 ml of 85% phosphoric acid and dilute to 1,000 ml. This solution is stable for one month, if refrigerated.

4.2.2.8.2.6 NEDA Solution - Dissolve 0.5 g of NEDA in 500 ml of distilled water. This solution is stable for one month, if refrigerated and protected from light.

4.2.2.8.2.7 Hydrogen Peroxide Solution - Dilute 0.2 ml of 30% hydrogen peroxide to 250 ml with distilled water. This solution may be used for one month, if, refrigerated and protected from light.

4.2.2.9 PROCEDURE:

4.2.2.9.1 Preparation of Calibration Graph.

4.2.2.9.2.1 Sodium Nitrite - Assay of 97% NaNO₂ or greater.

4.2.2.9.2.2 Sodium Nitrite Stock Solution (1000 µg NO₂/ml) - Dissolve 1.5 g of desiccated sodium nitrite in distilled water and dilute to 1,000 ml such that a solution containing 1000 µg NO₂/ml is obtained. The amount of NaNO₂ to be used if, the assay percent is less than 100%, is calculated as follows:

$$G = \frac{1.500}{A}$$

Where:

G = Amount of NaNO₂, grams

1.500 = Gravimetric conversion factor

A = Assay, percent (should be 97 or greater)

This stock solution can be stored for six weeks, if refrigerated.

4.2.2.9.2.3 Sodium Nitrite Working Standard (1.0 µg NO₂/ml)

4.2.2.9.2.3.1 Solution A - Pipette 5 ml of the stock solution into a 500 ml volumetric flask and dilute to volume with distilled water. This contains 10 µg NO₂/ml.

4.2.2.9.2.3.2 Solution B - Pipette 25 ml of solution A into a 250 volumetric flask and dilute to volume with absorbing solution. This contains 1 µg NO₂/ml. Prepare fresh daily.

4.2.2.9.3 Calibration

4.2.2.9.3.1 Flowmeter - Calibrate the flowmeter against a calibrated flow measurement standard, such as a wet test meter, bubble flowmeter, or other reliable volume measurement standard. Calibrate in units of standard cm³/min (i.e., corrected to 25⁰C and 760 torr).

4.2.2.9.3.2 Absorber - Calibrate the polypropylene absorber pipeting 50 ml of water or absorbing reagent into the absorber. Scribe the level of the meniscus with a sharp object, mark over the area with a felt-tip marking pen, and rub off the excess.

4.2.2.9.3.3 Spectrophotometer

4.2.2.9.3.3.1 Prepare calibration curve using 1 µg/ml working standards

4.2.2.9.3.3.2 In accordance with the analytical procedure given in, measure and record the absorbance for each calibration standard (0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20 µg NO₂).

4.2.2.9.3.3.3 Plot absorbance (y-axis) versus the corresponding concentration in µg NO₂/50 ml final solution (x-axis). Draw or compute the straight line best fitting the data to obtain the calibration curve.

4.2.2.9.4 Sample Collection

4.2.2.9.4.1 8-Hourly Sampling

4.2.2.9.4.1.1 Assemble the sampling apparatus at the sampling site. Components upstream from the absorber may be connected, where required, with Teflon tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joints with Teflon or polypropylene.

4.2.2.9.4.1.2 Add exactly 30 ml of absorbing reagent to the calibrated absorber.

4.2.2.9.4.1.3 Disconnect the funnel, connect the calibrated flowmeter, measure the flow rate before sampling and record as F₁. If, the flow rate before sampling is not 0.2 Lpm, replace the

flow control device and/or check the system for leaks. Start sampling only after obtaining an initial flow rate of 0.2 Lpm.

4.2.2.9.4.1.4 Sample for 8 hrs. Record the exact sampling time in minutes at t_s .

4.2.2.9.4.1.5 Measure the flow rate after the sampling and record as F_f .

4.2.2.9.4.2 24-Hourly Sampling

4.2.2.9.4.2.1 Assemble the sampling apparatus at the sampling site. Components upstream from the absorber may be connected, where required, with Teflon tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joints with Tygon, Teflon, or polypropylene.

4.2.2.9.4.2.2 Add exactly 30 ml of absorbing reagent to the calibrated absorber.

4.2.2.9.4.2.3 Disconnect the funnel, connect the calibrated flowmeter, measure the flow rate before sampling and record as F_1 . If, the flow rate before sampling is not between 180 and 220 cu-cm/min, replace the flow control device and/or check the system for leaks. Start sampling only after obtaining an initial flow rate in this range.

4.2.2.9.4.2.4 Sample for 24 hrs. Record the exact sampling time in minutes at t_s .

4.2.2.9.4.2.5 Measure the flow rate after the sampling period and record as F_f .

4.2.2.9.4.2.6 Seal the collected samples and transport to the laboratory for analysis.

4.2.2.9.5 Analysis

4.2.2.9.5.1 Replace any water lost by evaporation during sampling by adding distilled water up to the calibration mark on the absorber. Mix thoroughly.

4.2.2.9.5.2 Pipette 10 ml of the collected sample into a test tube. Pipette in 1 ml of hydrogen peroxide solution, 10 ml of sulfanilamide solution, and 1.4 ml of NEDA solution, with thorough mixing after the addition of each reagent and make up to 50 ml with distilled water.

4.2.2.9.5.3 Prepare a blank in the same manner using 10 ml of unexposed absorbing reagent.

4.2.2.9.5.4 After a 10 min color development interval, measure and record the absorbance at 540 nm against the blank.

4.2.2.9.5.5 Determine $\mu\text{g NO}_2$ from the calibration curve.

4.2.2.9.5.6 Samples with an absorbance greater than 1.0 must be reanalyzed after diluting an aliquot of the collected samples with an equal quantity of unexposed absorbing reagent.

A randomly selected 5-10% of the samples should be reanalyzed as apart of an internal quality assurance program.

4.2.2.9.6 Sampling Efficiency

4.2.2.10 CALCULATION:

4.2.2.10.1 Air Volume - Calculate the volume of air samples as follows:

$$V = \frac{F_1 + F_f}{2} \times t_s \times 10^{-3}$$

Where:

V = Volume of air sample, cu-m

F₁ = Air flow rate before sampling, litre/min

F_f = Air flow rate after sampling, litre/min

t_s = Sampling time, min

10⁻³ = Conversion of lpm to cubic-m.

If, the temperature and pressure conditions at the time of the initial and final air flow rate measurements are substantially different from the conditions under which the flowmeter was calibrated, appropriate corrections to the flow rate measurements may be made to improve the accuracy of the resultant NO₂ concentration measurement. The mathematical form of these corrections depends on the type of flowmeter used; consult an appropriate reference for guidance.

4.2.2.10.2 NO₂ Concentration in Analyzed Sample - Determine µg NO₂/ml graphically from the calibration curve or compute from the slope and intercept values.

4.2.2.10.3 NO₂ Concentration in Air Sample - Calculate as µg of NO₂ per cubic meter of air as follows:

$$\mu\text{g NO}_2/\text{cu-m} = \frac{\mu\text{g NO}_2 \times V_s}{V_a \times 0.82} \times D$$

Where:

µg/ NO₂ = NO₂ concentration in analyzed sample

V_a = Volume of air sample, cu-m

0.82 = Sampling efficiency

D = Dilution factor (D = 1 for no dilution; D = 2 for 1:1 dilution).

V_s = Volume of sampling solution

4.2.2.10.4 The NO₂ concentration may be calculated as ppm using:

$$\text{ppm NO}_2 = (\mu\text{g NO}_2/\text{cu-m}) \times 5.32 \times 10^{-4}$$

4.2.3 HIGH VOLUME METHOD FOR DETERMINATION OF TOTAL SUSPENDED PARTICULATE MATTER IN THE ATMOSPHERE

4.2.3.1 TITLE:

Method for determination of Total suspended particulate (TSP) or Suspended Particulate Matter (SPM) in the Atmosphere (High Volume Method).

4.2.3.2 PURPOSE:

The purpose is to lay down an uniform and reliable method for measurement of Total Suspended Particulate Matter (TSP) in the ambient air.

4.2.3.3 PRINCIPLE:

Air is drawn through a size-selective inlet and through a 20.3 X 25.4 cm (8 X 10 in) filter at flow rate which is typically 1132 L/min (40 ft³ /min). Particles with aerodynamic diameters less than the cut-point of the inlet are collected by the filter. The mass of these particles is determined by the difference in filter weights prior to and after sampling. The concentration of suspended particulate matter in the designated size range is calculated by dividing the weight gain of the filter by the volume of air sampled.

4.2.3.4 SCOPE:

This method is applicable for determination of suspended particulate matter in the ambient air.

4.2.3.5 INTERFERENCES:

4.2.3.5.1 Passive Deposition - Passive deposition occurs when windblown dust deposits on a filter both prior to and after sampling.

4.2.3.5.2 Inlet Loading and Re-Entrainment - Material collected in size-selective inlets can become re entrained in the sample flow. Controlled studies are insufficient to quantify this interference. It can be minimized by greasing or oiling inlet impaction surfaces, though this may change the size selective properties.

4.2.3.5.3 Re-circulation - Re-circulation occurs when the blower exhaust, which contains carbon and copper particles from the armature and brushes, is entrained in the samples air. Positive biases of $0.15\mu\text{g}/\text{cu-m}$ have been measured, which are insignificant mass interferences but which may affect carbon and copper measurements. Recirculation can be minimized by assuring a tight seal between the blower and the sampler housing or by ducting blower exhaust away from the sampler.

4.2.3.5.4 Filter Artifact Formation - Sulfur dioxide, nitrogen oxides, nitric acid and organic vapors can be absorbed on the filter medium along with the suspended particles thereby causing positive biases. Samples taken in the presence of high SO_2 concentrations have been shown to yield up to $10\mu\text{g}/\text{cu-m}$ of excess sulfate on glass fiber filters.

4.2.3.5.5 Filter Conditioning - Filter conditioning environments can result in different mass measurements as a function of relative humidity (RH). Soluble particles take on substantial quantities of water as RH increases, especially above the deliquescence point of approximately 70% RH. Increased mass deposits of 50% or more have been observed as RH increases to 100%. Twenty-four hours at a constant temperature and RH is considered adequate for sample equilibration.

4.2.3.5.6 Shipping Losses - Particle loss during transport occurs when filters are heavily loaded with large dry aerosols. It is more prevalent on membrane than on glass fiber filters. Particle loss is minimized by shorter sample duration in heavily polluted environments, use of fiber as opposed to membrane filters, folding the filter prior to transport, and careful shipping procedures.

4.2.3.5.7 Precision and Accuracy

4.2.3.5.7.1 Mass of the filter deposit, flow rate through the filter, and sampling time have typical precision of + 2 mg, +5%, and + 1 min, respectively, as determined from performance tests. The accuracy of those measurements can be well within these tolerances when determined with independent standards. These uncertainties combine to yield a propagated precision of approximately + 13% at $10\mu\text{g}/\text{cu-m}$ and approximately + 5% at $100\mu\text{g}/\text{cu-m}$. The filter deposit

mass measurement precision dominates at low concentrations while the flow rate precision dominates at high concentrations.

4.2.3.5.8 APPARATUS

4.2.3.5.8.1 Sampler - It is a compact unit consisting a protective housing, blower, voltage stabilizer, automatic time and time totalizer, rotameter, gaseous sampling assembly, filter holder capable of supporting a 20.3 x 25.4 cm. glass fiber filter.

4.2.3.5.8.2 Size Selective Inlets

4.2.3.5.8.2.1 The peaked roof inlet is the oldest inlet and consists of a right triangular structure with an open hypotenuse placed over the filter. Over 50% of the particles smaller than 30 um to 50 um diameter penetrate this inlet (at 566 to 1698 L/min flow rates) and deposit on the filter. The peaked roof inlet does not have a sharp sampling effectiveness curve and is intended primarily to protect the filter from dust-fall. The sampling effectiveness of this inlet varies depending on its orientation with respect to wind direction and on the wind speed.

4.2.3.5.8.3 Flow Controllers

4.2.3.5.8.3.1 Manual Volume Flow Control - A variable voltage transformer placed in series with the blower controls the blower motor power. The motor speed varies with the voltage supplied, and the flow rate through a filter can be adjusted by increasing or decreasing the voltage to obtain the desired value for the resistance of the filter being used. The flow rate decreases as filter deposit increases, but this change is normally less than 10% and is quantifiable via pre-and post-exposure flow measurements.

4.2.3.5.8.4 Laboratory Equipment

4.2.3.5.8.4.1 Controlled Environment - A clean laboratory environment is required for filter inspection, equilibration, and weighing. A temperature in the range of 15 to 30⁰C with + 3⁰C variability and a relative humidity of 20 to 45% with + 5% variability is recommended.

4.2.3.5.8.4.2 Light Table - A photographic slide viewing table is used for filter inspection.

4.2.3.5.8.4.3 Analytical Balance - The balance must be equipped with an expanded weighing chamber to accommodate 20.3 x 25.4 cm (8 x 10 in) filters and must have a sensitivity of 0.1 mg.

4.2.3.5.9 REAGENTS

4.2.3.5.9.1 Filter Media

A 20.3 x 25.4 cm (8 x 10 in) glass fiber filter is used to collect particles. The choice of filter type results from a compromise among the following filter attributes: (i) mechanical stability, (ii) chemical stability, (iii) particle sampling efficiency, (iv) flow resistance, (v) clogging level, (vi) blank values, (vii) artifact formation, and (viii) cost and availability. EPA filter requirements specify 0.3 μm DOP sampling efficiency in excess of 99%, weight losses or gains due to mechanical or chemical instability of less than a 5 $\mu\text{g}/\text{cu-m}$ equivalent, and alkalinity of less than 25 micro-equivalent/g to minimize sulfur dioxide (SO_2) and nitrogen oxides (NO_x) absorption. The most appropriate filter media for high volume sampling are cellulose fiber, glass fiber, quartz fiber, Teflon coated glass fiber, and Teflon membrane. None of these materials is perfect for all purposes.

4.2.3.5.9.1.1 Glass fiber filters meet requirements in most categories with the exception of artifact formation and blank levels. Sampling efficiency is very high for all particle sizes. Blank levels for several elements of interest are high and variable. Glass fiber filters may exhibit organic carbon artifacts.

4.2.3.5.9.2 Filter Jacket - A smooth, heavy paper folder or envelope is used to protect the filter between the lab and field and during storage. Filter and sampling data are often recorded on the outside of the jacket, but this should not be done while the filter is in the jacket to prevent damage.

4.2.3.5.10 PROCEDURE:

4.2.3.5.10.1 Sub-sections.

4.2.3.5.10.2 Filter Weighing - It is best to weigh filters in groups of ten to fifty. Wear gloves for all filter handling. Stack filter jackets with data forms printed on them in the same order (in ascending order of filter ID numbers, if possible) as the order of filters in the equilibration rack. Adjust the balance tare to read zero with nothing in the weighing chamber and adjust the span to read (or verify that it reads) 3.00000 g with the 3 g standard weight on the weighing pan. Place a filter in the weighing chamber and adjust the balance to its equilibrium position. If, a stable reading cannot be obtained, it may be necessary to neutralize electrostatic charges with a radioactive source prior to and during weighing. Record the weight on the data form in the blank or exposed filter column. Verify the zero and span every ten filters. If, these differ from their normal values by more than + 1.0 mg, read just them and re-weigh the previous ten filters. Place each filter in its filter jacket when weighing is complete, but do not seal the jacket opening. A separate technician randomly selects four filters or ten percent of all filters in the batch (whichever is larger), re-weigh them and subtracts this check-weight value from the corresponding routine weight. If, any check weight differs by more than + 4.0 mg from the routine weight, re-weigh the entire batch of filters. Seal filter jackets and ship blank filters to the field or place exposed filters into storage.

4.2.3.5.10.3 Field Sampling - Tilt back the inlet and secure it according to manufacturer's instructions. Loosen the face-plate wing-nuts and remove the face plate. Remove the filter from its jacket and center it on the support screen with the rough side of the filter facing upwards. Replace the faceplate and tighten the wing-nuts to secure the rubber gasket against the filter edge. Gently lower the inlet. Inertial jet and cyclonic inlets must have their seals in contact with the top of the faceplate. Look underneath the inlet just as it is coming into contact with the faceplate to assure that this contact is being made. It may be necessary to readjust the position of the filter/motor assembly in the sampler housing to obtain such a seal. Excessively windy and wet conditions should be avoided when changing samples. Pre-loading in a filter cartridge assembly, temporary removal of the sampler to a protected area, or a wind or rain shield may be used if the sample must be changed in inclement weather. Set the timer for the desired start and stop time. Replace the chart paper in the flow recorder, if there is one, set the proper time, and mark the time and date on the chart. For a manually flow controlled sampler turn on the motor for five minutes and measure the exhaust pressure with a pressure gauge or rotameter. Read the flow rate corresponding to this exhaust pressure from the calibration curve and record it on the data sheet.

Turn off the motor and assure that the timer is in its automatic mode. For automatically flow controlled units, record the designated flow rate on the data sheet. Record the reading of the elapsed time meter. The specified length of sampling is commonly 8 hours or 24 hours. During this period, several reading (hourly) of flow rate should be taken. After sampling is complete, record the final flow rate and the elapsed time in the same manner. Subtract the initial elapsed time from the final elapsed time to determine the sample duration. Remove the face-plate by removing the wing-nuts. Fold the filter in half lengthwise by handling it along its edge with the exposed side inward. Insert the filter in its jacket. Note the presence of insects on the deposit, loose particles, non-centered deposits, evidence of leaks, and unusual meteorological conditions on the data sheet. Mark the flow recorder chart, if any, and return it with the data sheet.

4.2.3.5.11 CALCULATIONS:

4.2.3.5.11.1 Calculation of Volume of Air Sampled

$$V = QT$$

Where, V = Volume of air sampled in cu-m
 Q = Average flow rate in cu-m/minute
 T = Total sampling time in minute

4.2.3.5.11.2 Calculation of Suspended Particulate Matter in Ambient Air

$$(W_f - W_i) \times 10^6$$

$$\text{SPM} = \frac{\text{-----}}{V}$$

Where:

SPM = Mass concentration of suspended particles in $\mu\text{g}/\text{cu-m}$

W_i = Initial weight of filter in g.

W_f = Final weight of filter in g.

V = Volume of air sampled in cu-m

10^6 = Conversion of g to μg .

4.2.4 MEASUREMENT OF RESPIRABLE SUSPENDED MATTER (PM₁₀) BY CYCLONIC FLOW TECHNIQUE

4.2.4.1 TITLE

Method for measurement of Respirable Suspended Particulate Matter (PM₁₀) in ambient air (Cyclonic Flow Technique).

4.2.4.2 PURPOSE

The purpose is to lay down an uniform and reliable method for determination of PM₁₀ (Particulate matter less than 10µm diameter) in ambient air.

4.2.4.3 PRINCIPLE

Air is drawn through a size-selective inlet and through a 20.3 x 25.4 cm (8 x 10 in) filter at a flow rate which is typically 1132 L/min. Particles with aerodynamic diameter less than the cut-point of the inlet are collected by the filter. The mass of these particles is determined by the difference in filter weights prior to and after sampling. The concentration of PM₁₀ in the designated size range is calculated by dividing the weight gain of the filter by the volume of air sampled.

4.2.4.4 SCOPE: This method is applicable for measurement of PM₁₀ in the ambient air.

4.2.4.5 INTERFERENCES:

4.2.4.5.1 Passive Deposition- Passive deposition occurs when windblown dust deposits on a filter both prior to and after sampling.

4.2.4.5.2 Re-circulation- Re-circulation occurs when the blower exhaust, which contains carbon and copper particles from the armature and brushes, is entrained in the sample air.

Positive biases of 0.15µg/cu-m have been measured, which are insignificant mass interferences but which may affect carbon and copper measurements. Recirculation can be minimized by assuring a tight seal between the blower and the sampler housing or by ducting blower exhaust away from the sampler.

4.2.4.5.3 Filter Artifact Formation – Sulfur dioxide, nitrogen oxides, nitric acid and organic vapors can be absorbed on the filter medium along with the suspended particles thereby causing positive biases. Samples taken in the presence of high SO₂ concentrations have been shown to yield up to 10 ug/m³ of excess sulfate on glass fiber filters.

4.2.4.5.4 Filter Conditioning – Filter conditioning environments can result in different mass measurements as a function of relative humidity (RH). Soluble particles take on substantial quantities of water as RH increases, especially above the deliquescence point of approximately 70% RH. Increased mass deposits of 50% or more have been observed as RH increases to 100%. Twenty-four hours at a constant temperature and RH is considered adequate for sample equilibration.

4.2.4.5.5 Shipping Losses – Particle loss during transport occurs when filters are heavily loaded with large dry aerosols. It is more prevalent on membrane than on glass fiber filter. Particle loss is minimized by shorter sample duration in heavily polluted environments, use of fiber as opposed to membrane filters, folding the filter prior to transport, and careful shipping procedures.

4.2.4.6 CALCULATIONS:

4.2.4.6.1 Calculation of volume of air sampled

$$V=QT$$

Where,

V=Volume of air sampled in cu-m.

Q= Average flow rate in cu-m/min

T= Total sampling time in min

4.2.4.6.2 Calculation of PM₁₀ in Ambient air

$$PM_{10} = \frac{(W_p+W_f) - (W_i+W_j)}{V} \times 10^6$$

Where,

W_p = Weight of material that was collected on the pan including the weighing paper , gm

W_j = Initial weight of weighing paper, gm.

W_f = Weight of exposed filter, gm

W_i = Tare weight of filter, gm

CHAPTER 5

INSTRUMENTS

5.1 RESPIRABLE DUST SAMPLER AND FILTER PAPER:

5.1.1 Principle: Air is drawn into a covered housing and through a filter by a high flow rate blower at 1.1 to 1.5 cu-m/min that allows suspended particulate matter with diameters $<10\mu\text{m}$ (Stokes equivalent diameter) to collect on the filter surface. Particles with diameters of 0.1 to 10 μm are collected on glass fiber filters.

The mass concentration of PM_{10} $\mu\text{g}/\text{cu-m}$ in ambient air is computed by measuring the mass of PM_{10} collected and the volume of air sampled. The size of the sample collected is usually adequate for further analysis of trace elements.

The sample of air is first drawn into a cyclone separator, which passes only the smaller particles with diameter less than 10 μm . These are then collected on the filter, as before, while the larger “non-respirable” particulates are collected in a removable dust collector cup.

PM_{10} is calculated by measuring the mass collected on the filter and the volume of air sampled, while NRPM is calculated by measuring the mass collected on the dust collector cup and the volume of air sampled.

5.1.2 Range and sensitivity: Sampling at an average of 1.1cu-m/min for 24 hours, given an adequate sample, even in an atmosphere having concentrations of particulates as low as $1\mu\text{g}/\text{cu-m}$. If particulates levels are unusually high, a satisfactory sample may be obtained in 6 to 8 hours or less. For determination of average concentrations of suspended particulates in ambient air, a standard sampling period of 24 hours is recommended.

Weights are determined to the nearest milligram, air flow rate are determined to the nearest 0.05 cu-m/min, times are determined to the nearest 1 minute, and mass concentrations are reported to the nearest microgram per cubic meter ($\mu\text{g}/\text{cu-m}$).

5.1.3 Interferences:

Particulate matter that is oily, such as photochemical smog or wood smoke, may block the filter and cause a rapid drop in airflow at a non uniform rate. Dense fog or high humidity can cause the filter to become too wet and severely reduce the air flow through the filter.

Glass-fiber filters are comparatively insensitive to changes in relative humidity, but collected particulates can be hygroscopic.

5.1.4 Specifications:

Netel's Respirable dust sampler, model NPM-HVS/R (Figure-5.1) consist main part- the control module.

The control module, shown in Figure-5.2 houses all the functional parts required for the collection of particulates and gaseous samples. The gaseous sampling arrangements are shown in details in Figure-5.3.

Detailed specifications are given below:

Heavy duty blower: 1.5 cu-m/min free flow (without resistance)

Blower duty cycle: Continuous/ 24 hours maximum with proper maintenance of carbon brush.

Voltage stabilizer: For rallies blower motor

Input: 145-275 VAC (standard)

Output: 230+/- 10 VAC

Auto shut off timer: 0-24 hours

Timer totaliser: 0-9999 min.

Flow controller: Solid state continuously variable.

Flow measurement: U tube manometer with pitot tube and calibration curve.

Filter holder assembly: Fiber with EPDM gasket.

Filter paper: 25 cm × 20 cm (overall)

Dimensions: 23 cm × 18 cm (effective)

Options: Brushless motor, specification 0.5 HP, 3000 RPM, AC single phase motor
1.6 cu-m/min.

Particulate sampling (TSP): From 100 microns to 0.1 microns depending upon the type of filter paper used. Particulates above 10 microns are collected separately in the cup.

Gaseous sampling:

Glass impinger tubes: 4 nos. 35ml capacity

Rotameter: 0-3 lpm, acrylic body.

Dimensions of control module: 85 (H) × 46.5 (W) × 30 (D) cm.

5.1.5 DESCRIPTIONS:

The Respirable dust sampler consist of control module (Figure-5.1) designed to maintain height of air inlet to 1.5 m.

This unit separates particulate matter by size, passing the small respirable particulate to the filter and retaining the large non-respirable particulate matter in a cup. The major parts are described below:

Main housing: The main housing is made of powder coated metal, to withstand corrosive and humid atmospheres. It has one door which gives access to all parts.

Filter holder: The filter holder assembly consist hopper assembly made up of FRP to hold 25 cm × 20 cm filter paper. EPDM gasket helps to make the assembly tight. The effective size of the filter paper for suction is 23 cm × 18 cm knobs are provided for easy replacement of filter paper.

Blower assembly: A heavy duty blower with continuous rating 24 hrs. Max with proper carbon brush maintenance and operating on 230 V AC. 50 Hz is fitted with the hopper assembly. The carbon brushes of the blower can be easily replaced by unscrewing them.

Brushless motor: 0.5 HP, 3000 RPM, AC single phase motor 1.6 cu-m/min.

U tube manometer: The flow rate is monitored by means of U- tube manometer and a pilot tube at the blower exhaust. A factory calibration curve of flow rate, in units of LPM of 25⁰C air, verses manometer ΔP at 30⁰C. In units of water cm, is fixed on the sampler. The horizontal axis of the graph is linear ΔP.

Voltage stabilizer: An automatic voltage stabilizer is provided to keep the voltage output at 230 + 10 V.

Auto shut off timer: The sampler has a on-off timer where sampling time can be set from 0 to 24 hours with auto shut off facility.

Time totaliser: A time totaliser has been provided to indicate the total time of sampling in minutes. It has a maximum range of 9999 minutes. Total time of sampling is calculated by difference of final and initial time in minutes.

Flow controller: To set and adjust the blower flow rate at the time of sampling, a continuously variable type flow is provided.

Impinger tubes with restrictors: For gaseous sampling 4 nos. of graduated impinger tubes

(Midget impingers) having capacity of 35 ml each are supplied. The flow of sampling air through each impinger tubes can be controlled by individual, connected to the manifold.

Inlet & separator unit: Ambient air is drawn into the sampler through a cyclone separator to create a cyclonic flow, Large dust particles impact on the inner wall of the tube and drop down to be collected in the cup. Small dust particles filter with less than 10 microns (Stokes) diameter are assessed along with the air drawn through the filter and collected on it.



Figure-5.1: Respirable dust sampler



Figure-5.2: Control module with view of internal parts



Figure-5.3: Gaseous sampling arrangement for Respirable dust sampler

5.2 SPECTROPHOTOMETER:

(i) A UV visible spectrophotometer was used for analysis of gaseous samples that is SO_2 and NO_x .

(ii) Working principle: The working principle is shown in the Figure-5.4 below:

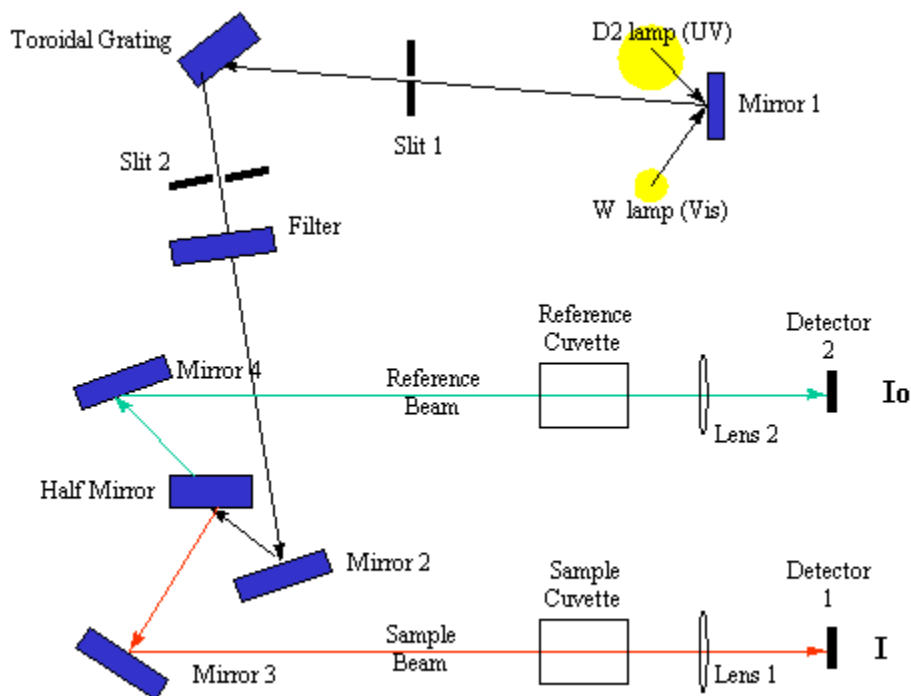


Figure-5.4: Optical system diagram

Optical System Diagram:

The UV-Visible spectrophotometer uses two light sources, a deuterium (D_2) lamp for ultraviolet light and a tungsten (W) lamp for visible light. After bouncing off a mirror (mirror 1), the light beam passes through a slit and hits a diffraction grating. The grating can be rotated allowing for a specific wavelength to be selected. At any specific orientation of the grating, only monochromatic (single wavelength) successfully passes through a slit. A filter is used to remove unwanted higher orders of diffraction. The light beam hits a second mirror before it gets split by a half mirror (half of the light is reflected, the other half passes through). One of the beams is allowed to pass through a reference cuvette (which contains the solvent only), the other passes through the sample cuvette. The intensities of the light beams are then measured at the end.

(iii) When the spectrophotometer was switched on different corrections went on for around 15 minutes. After that the screen showed the different modes and an option was there to change the mode.



Figure-5.5: Monitor

(iv) To scan the sample “mode-1” was selected and to see the variation of absorbance unit spectrum mode was chosen.

(v) The keypad contains different keys like:

- (a) File
- (b) Mode
- (c) Auto zero
- (d) Return
- (e) Return
- (f) Yes
- (g) No
- (h) Copy

- (i) Chart
- (j) Enter
- (k) Start/stop
- (l) Right and Left arrow
- (m) Number pad (0-9)

as shown in Figure-5.6 ,



Figure-5.6: Keypad

(vi) The sample prepared for analysis was taken in the cuvette and another cuvette was left blank for reference. In case of SO_2 , distilled water was taken as the reference rather than the reagent blank. In case of NO_x , blank cuvette was taken as the reference. The assembly is shown in Figure-5.7. The cuvettes are generally held on the hazy side and the transparent side is kept in front of the UV light.



Figure-5.7: Cuvettes during analysis

(vii) The light passes through the cuvette containing sample and the reference cuvette and then after a fraction of a minute the monitor shows the absorbance unit that is actually comparison of the absorbance of the blank and sample. The monitor shows the parameters and values like in Figure-5.8.

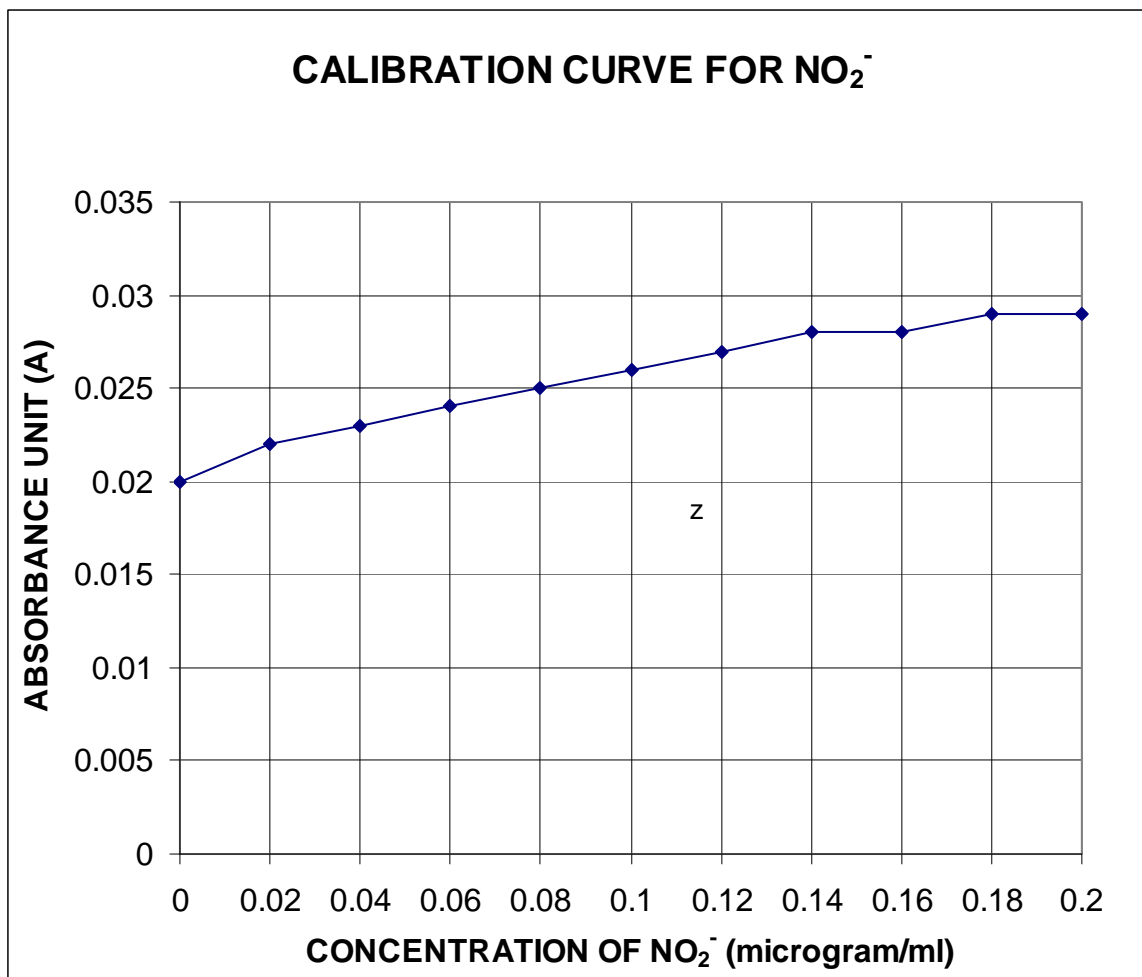


Figure-5.8: Spectrophotometer

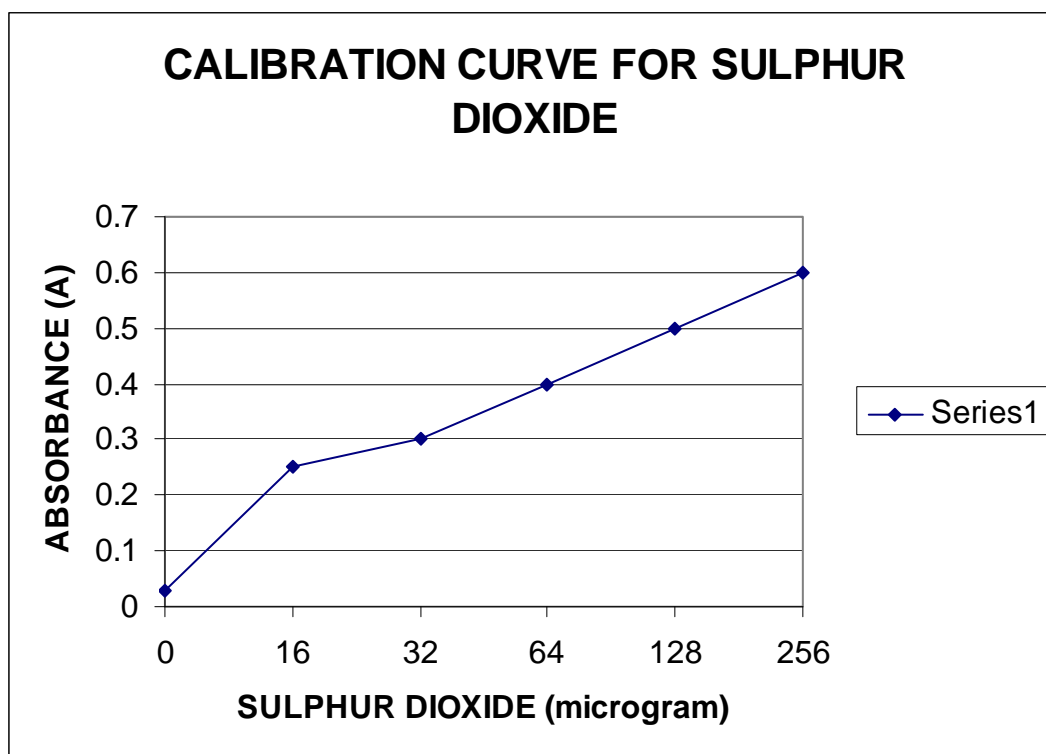
(vii) The absorbance for different samples collected after sampling at different stations were calculated and correspondingly the calibration curves were drawn for SO₂ and NO_x.

5.3 CALIBRATION CURVES:

5.3.1 Calibration curve for NO_2^- :



5.3.2 Calibration curve for SO₂:



CHAPTER 6

RESULTS AND DISCUSSION

Monitoring Stations	Sampling time (minute)	Q _{avg} (m ³)	W _i (gm)	W _f (gm)	W _p (gm)	W _j (gm)	V(m ³)	PM ₁₀	TSP
I	480	0.694	2.7248	2.7543	22.8874	22.8984	333.12	88.56	121.57
I	480	0.705	2.7215	2.7582	22.8809	22.8891	338.64	108.37	132.589
I	480	0.836	2.7428	2.7572	22.8434	22.8482	401.28	36	47.84
I	480	0.794	2.7026	2.7146	22.8357	22.8489	381.33	31.46	66.08
II	480	0.716	2.7415	2.7650	22.8907	22.8987	343.68	68.38	91.65
II	480	0.750	2.7293	2.7591	22.9032	22.9092	360	82.77	107.77
III	480	0.786	2.7359	2.7683	22.9174	22.9182	377.28	85.87	87.99
III	480	0.948	2.7257	2.7468	22.9174	22.9184	455.04	46.36	48.57
III	480	0.903	2.7318	2.7402	22.8428	22.8592	433.71	19.36	57.18
III	480	0.772	2.7298	2.7348	22.8912	22.9162	370.66	40.46	107.91

TABLE-6.1: CONCENTRATION OF PM₁₀ AND TSP IN AMBIENT AIR AT DIFFERENT MONITORING STATIONS IN NIT ROURKELA.

Monitoring stations	F _i (lpm)	F _f (lpm)	V(m ³)	μgNO ₂ / ml	μg/ cu-m
I	0.3	0.1	0.096	0.06	19.05
I	0.2	0.2	0.096	0.06	19.05
I	0.3	0.2	0.12	0.1	25.40
I	0.2	0.2	0.096	0.12	38.10
II	0.2	0.1	0.072	0.06	42.34
II	0.3	0.1	0.096	0.08	25.40
III	0.3	0.2	0.12	0.08	20.32
III	0.3	0.1	0.096	0.1	31.75
III	0.2	0.1	0.072	0.08	33.87
III	0.4	0.2	0.144	0.1	21.17

TABLE-6.2: CONCENTRATION OF NO_x IN AMBIENT AIR AT DIFFERENT MONITORING STATIONS IN NIT ROURKELA

Monitoring Stations	F_i (lpm)	F_f (lpm)	V (m^3)	$\mu g/cu-m$
I	0.3	0.1	0.096	8.20
I	0.2	0.2	0.096	8.20
I	0.3	0.2	0.12	6.56
I	0.2	0.2	0.096	8.20
II	0.2	0.1	0.072	10.94
II	0.3	0.1	0.096	8.20
III	0.3	0.2	0.12	6.56
III	0.3	0.1	0.096	8.20
III	0.2	0.1	0.072	10.94
III	0.4	0.2	0.144	5.47

TABLE-6.3: CONCENTRATION OF SO_2 IN AMBIENT AIR AT DIFFERENT MONITORING STATIONS IN NIT ROURKELA

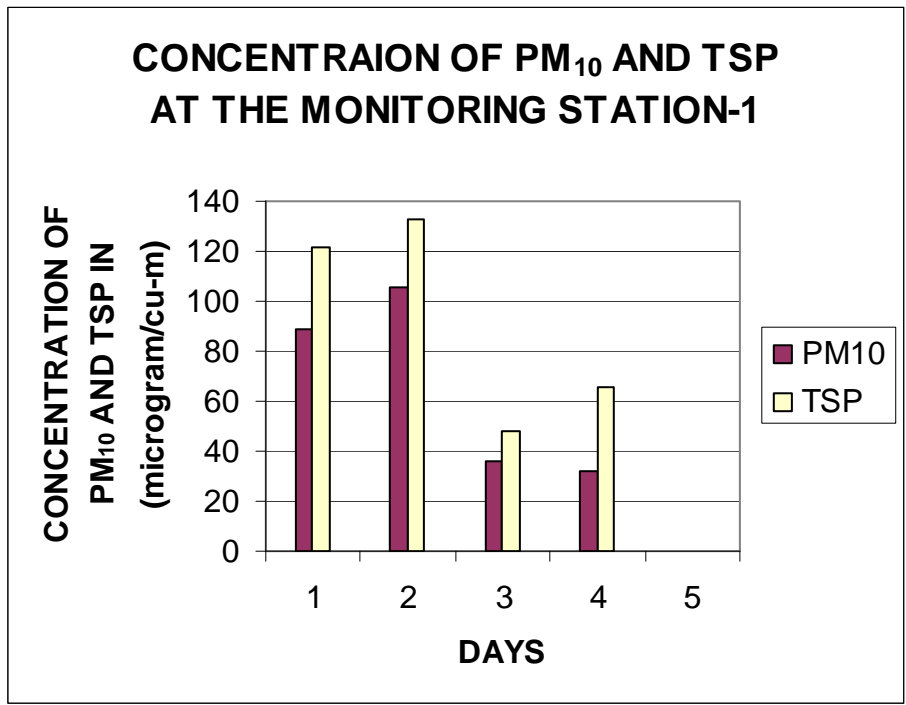


Figure-6.1: Concentration of PM₁₀ and TSP at the monitoring station-1

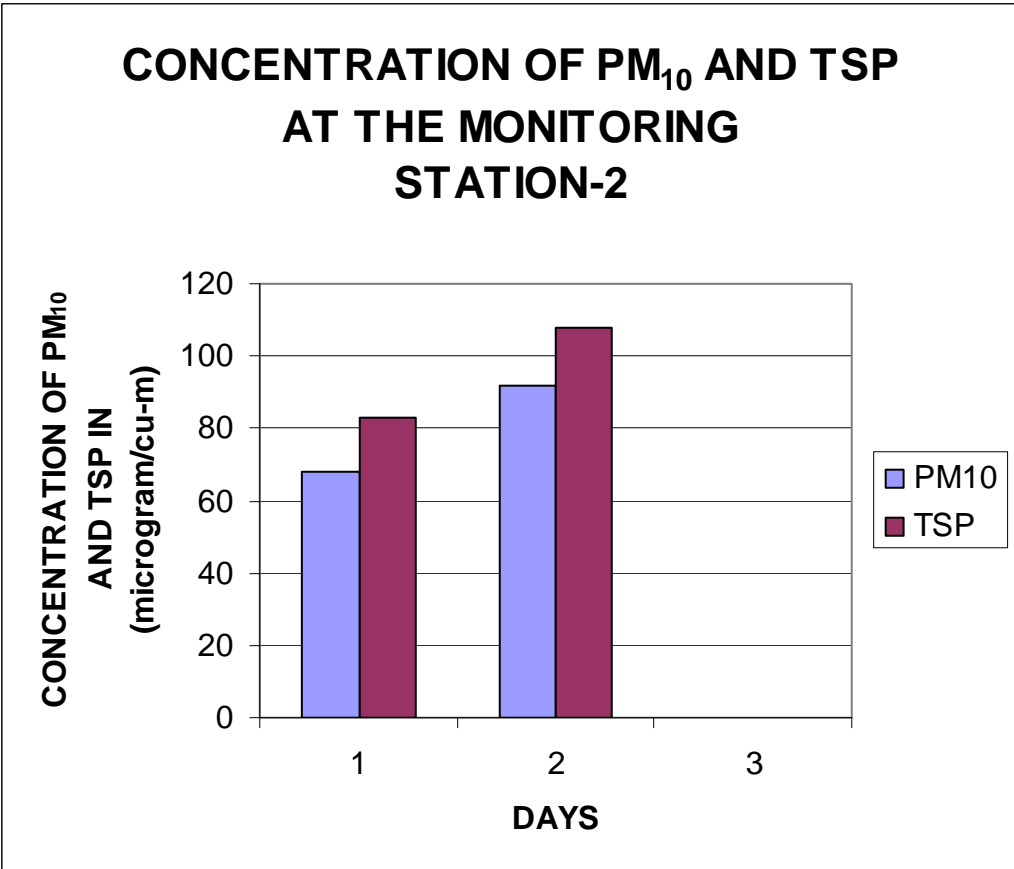


Figure-6.2: Concentration of PM₁₀ and TSP at the monitoring station-2

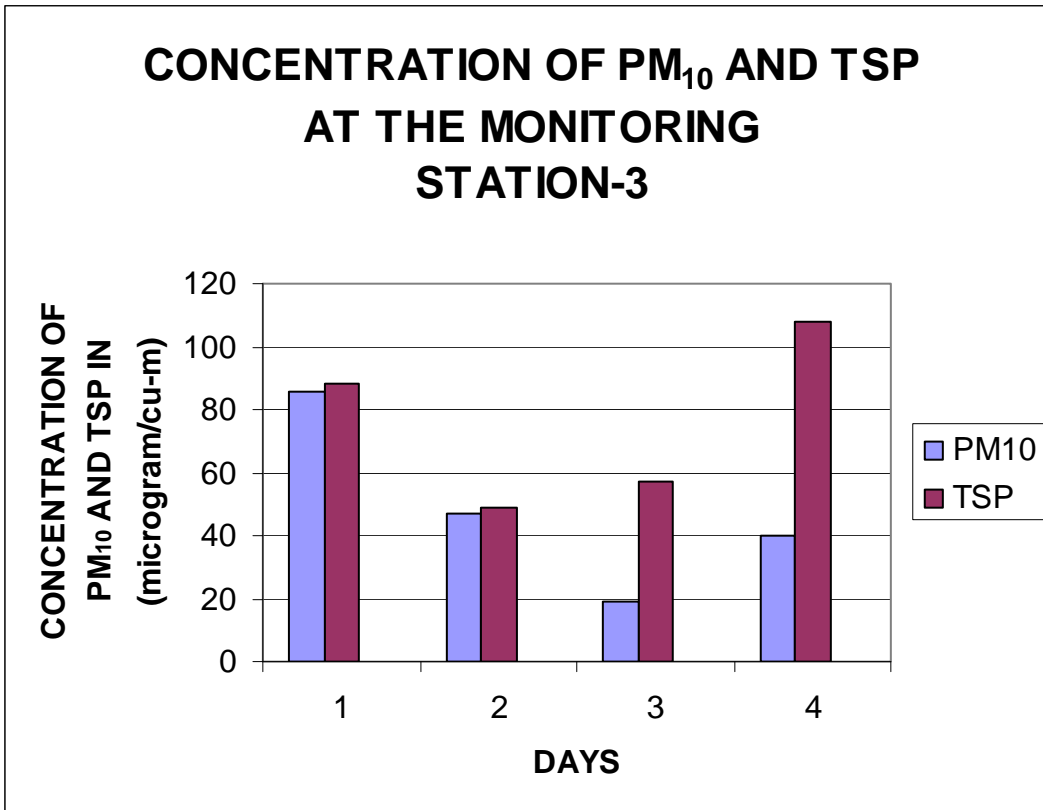


Figure-6.3: Concentration of PM₁₀ and TSP at the monitoring station-3

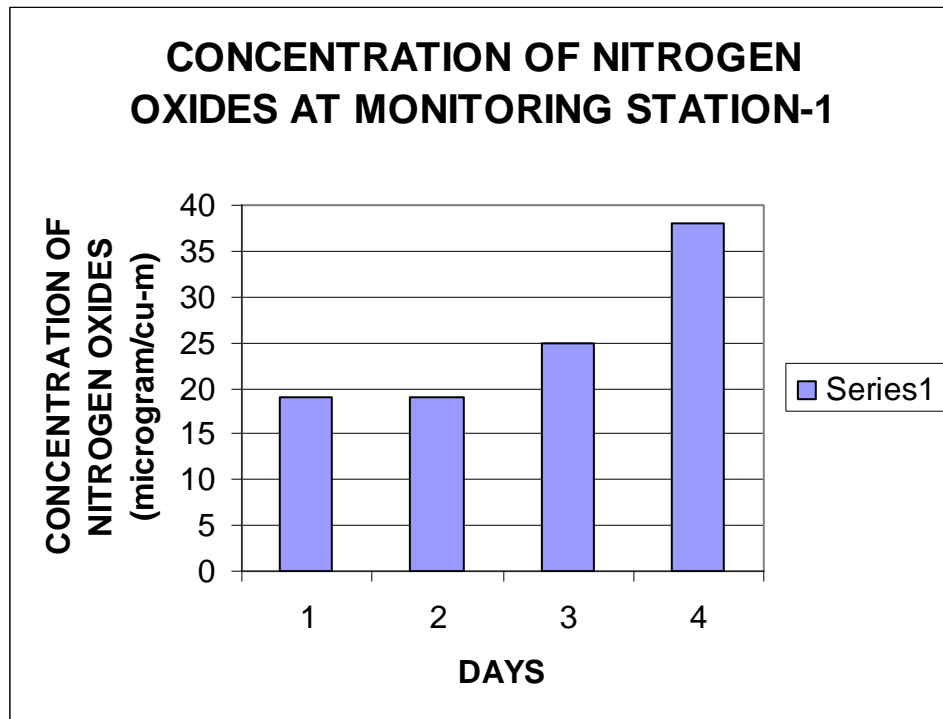


Figure-6.4: Concentration of Nitrogen oxides at the monitoring station-1

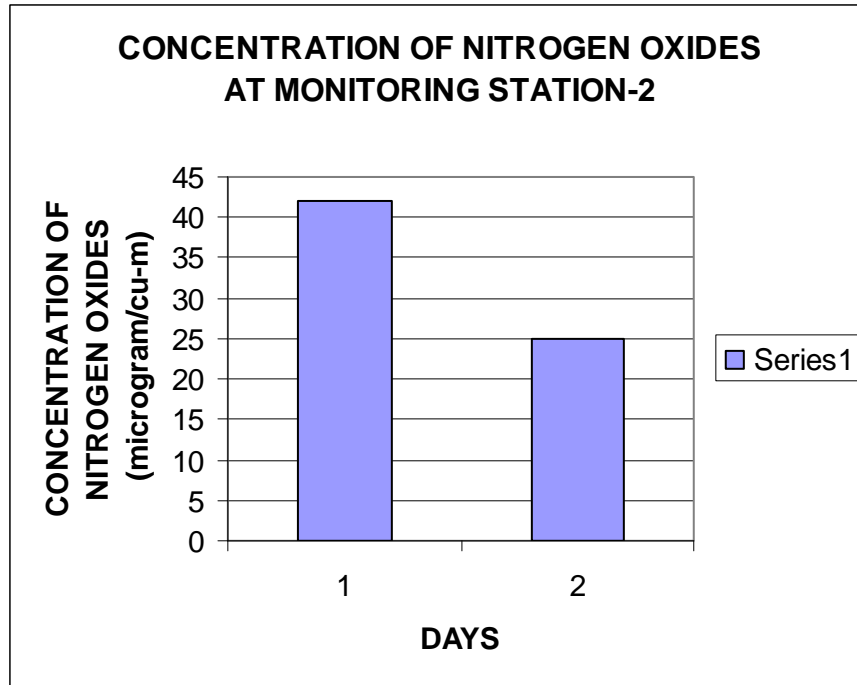


Figure-6.5: Concentration of Nitrogen oxides at the monitoring station-2

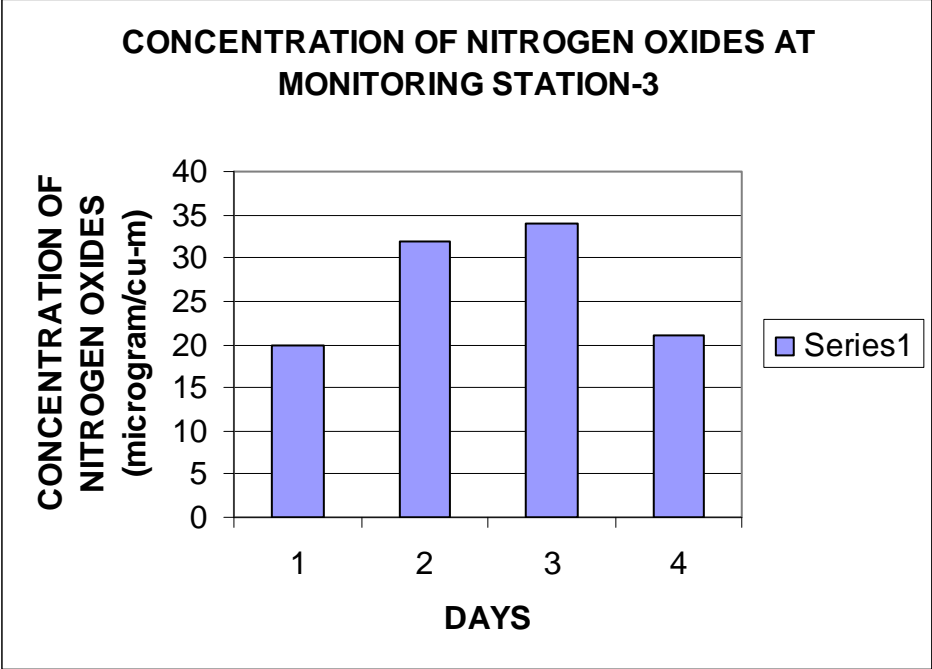


Figure-6.6: Concentration of Nitrogen oxides at monitoring station-3

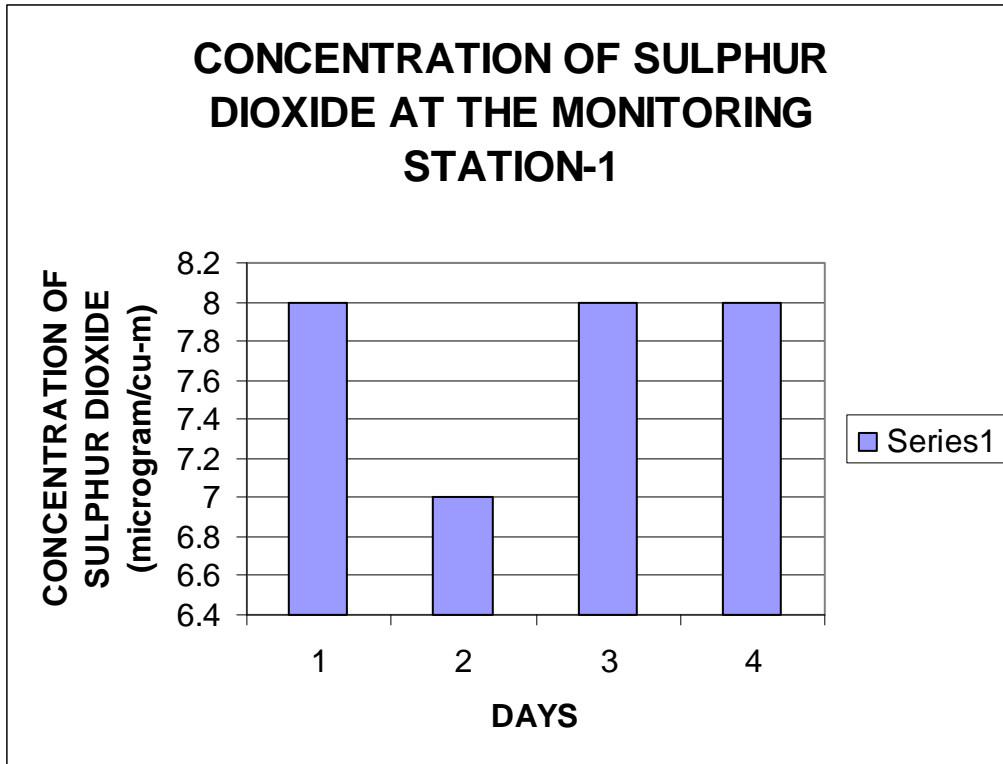


Figure-6.7: Concentration of Sulphur dioxide at monitoring station-1

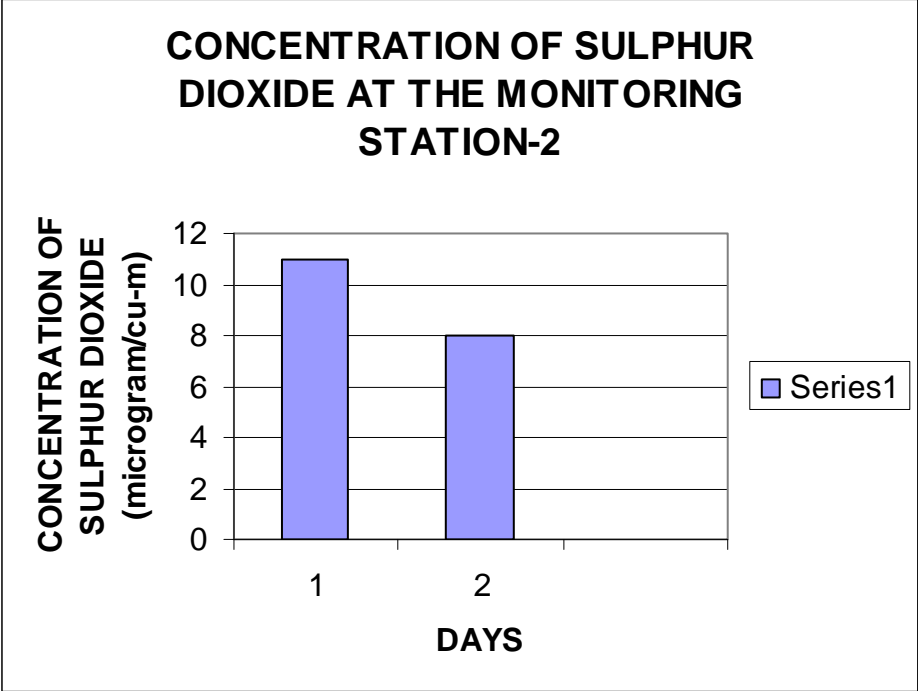


Figure-6.8: Concentration of Sulphur dioxide at monitoring station-2

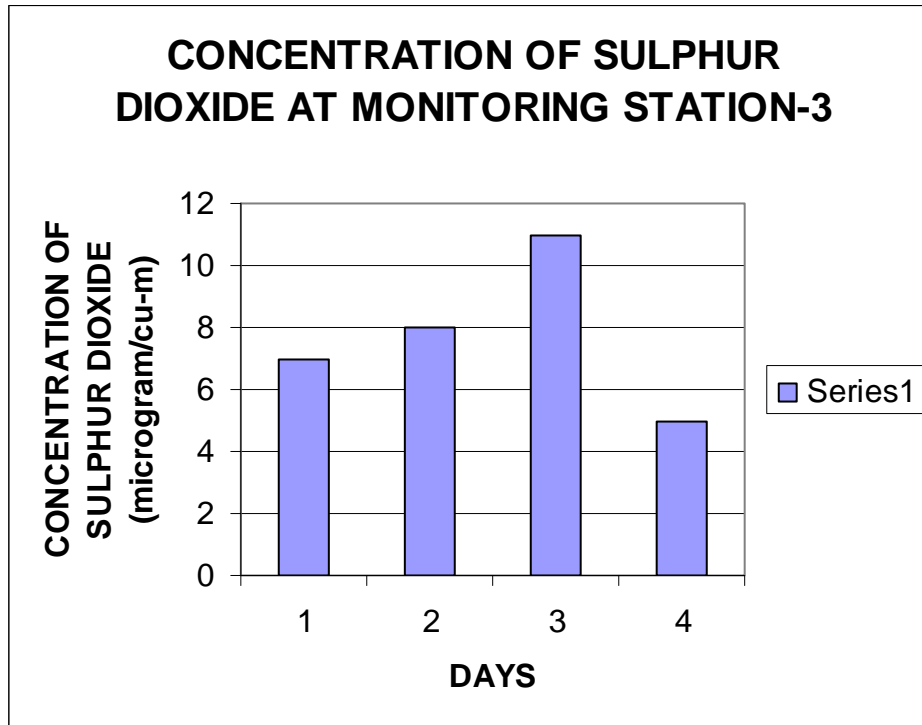


Figure-6.9: Concentration of Sulphur dioxide at monitoring station-3

6.1 Air quality Index calculation:

Vast amount of data that are generated as a result of air quality monitoring program complicates the meaningful interpretation (of data) and demands extensive statistical and computational efforts. Air Quality Index (AQI), although a useful tool devised to simplify interpretation of data, may result in some loss of scientific information. In this research, adaptability of some of the existing AQIs that have been used by various agencies is examined (Rao M. et al, 2003).

The quality of air in the study area can be estimated from the air quality index. The air quality index was calculated from the observed TSP, PM₁₀, NO_x and SO₂ values using the formula;

$$AQI = \frac{1}{4} \times (I_{TSP} / S_{TSP} + I_{PM10} / S_{PM10} + I_{SO2} / S_{SO2} + I_{NOX} / S_{NOX}) \times 100$$

Where:

I_{TSPM} , I_{RSPM} , I_{SO_2} and I_{NOX} = Individual values of suspended particulate matter, respirable particulate matter, sulphur dioxide and oxides of nitrogen respectively.

S_{TSP} , $S_{PM_{10}}$, S_{SO_2} and S_{NOX} = Standards of ambient air quality.

Sampling stations	TSP	PM ₁₀	SO ₂	NO _x
Industrial area	500(8 hr)	120(8 hr)	120(8 hr)	120(8 hr)
	300(24 hr)	150(24 hr)	80(24 hr)	90(24 hr)
Residence area	200(8 hr)	60 (8hr)	80(8 hr)	80(8 hr)
	140(24 hr)	100(24 hr)	60(24 hr)	60(24 hr)
Sensitive area	100(8 hr)	50(8 hr)	30(8 hr)	30(8 hr)
	70(24 hr)	75(24 hr)	20(24 hr)	20(24 hr)

TABLE-6.4: AMBIENT AIR QUALITY STANDARD OF CENTRAL POLLUTION CONTROL BOARD (CPCB)

Category	AQI of ambient air	Description of ambient air quality
I	<10	Very clean
II	Between 10-25	Clean
III	Between 25-50	Fairly clean
IV	Between 50-75	Moderately polluted
V	Between 75-100	Polluted
VI	Between 100-125	Heavily polluted
VII	Beyond 125	Severely polluted

TABLE-6.5: AIR QUALITY CATEGORY BASED ON AIR QUALITY INDEX

Monitoring stations	TSP	PM ₁₀	SO ₂	NO _x	AQI	Ambient air quality
I	92.25	66.25	7.75	25.25	49	Fairly clean
II	100	75.5	9.5	33.5	57	Moderately polluted
III	75.5	26.75	7.75	26.75	31	Fairly clean

TABLE-6.6: AQI AT DIFFERENT MONITORING STATIONS INSIDE NIT ROURKELA

CHAPTER 7

CONCLUSION

Ambient air quality was assessed using three monitoring stations inside NIT Rourkela campus, the studies have clearly revealed the levels of air pollutants for TSP, PM₁₀, NO_x and SO₂. The values of all these pollutants (particulates and gaseous) are observed to be very much below National Ambient Air Quality Standards except the station-2, that is the residential area, dispensary. This increase in AQI at this site is probably due to the increased transportation on the road in front of it and the school that is responsible for this increase in traffic. The air quality is giving the holistic view of air pollution levels. So from the result, it is evident that for the time being, the ambient air inside NIT Rourkela do not need any attention from the policy makers except the residential area, but may be in the future we need to formulate some ways to counteract the increase in air pollution at specific sites as we may never know when the growing urbanization and the traffic will increase the air pollution level inside the campus much more than the maximum permissible limits.

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