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Air Pollution: A Case Study of Ilorin and Lagos Outdoor Air

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1. Introduction

Air pollutants are continuously released from numerous sources into the atmosphere. Several studies have been carried out on the quantification of pollutants and analyzing their consequences on public health. It has been estimated that each year between 250 and 300 million tons of air pollutants enter the atmosphere above the United States of America [Dara, 2004; Onianwa, 2001; Stephen and Spencer, 1992]. Tropospheric pollution causes degradation of crops, forests, aquatic systems, structural materials, and human health. It was reported recently, that NO_x air pollution is becoming a far reaching threat to USA National Parks and Wilderness Areas as these areas are suffering from harmful effects of oxides of nitrogen pollution [EDFS, 2003]. It has also been confirmed that NO_x contributes to ground - level ozone (smog) pollution which can cause serious respiratory problems, especially young children and the elderly, as well as healthy adults that are active outdoors. Furthermore, the same report confirmed worsening ozone concentration in nearly all the national parks over the last ten years [EDFS, 2003]. Towards this, an assessment of new vehicles emission certification standards was carried out in metropolitan area of Mexico city and the results show that light duty gasoline vehicles account for most carbon (II) oxide and NO_x emissions [Schifter *et al*, 2006]. The European Environmental Agency also reported very recently that more than 95% contribution to nitrogen oxides emission to the air comes from fuel combustion processes from road transport, power plants and industrial boilers [EEA, 2006]. There is reported evidence of average chronic damage to the human lung from prolonged ozone exposure [EEA, 2006]. Sulphur in coal, oil and minerals are the main source of the Sulphur (IV) oxide in the atmosphere. Moreover, peak concentrations above European Union limit still occur, especially close to point sources in the cities. Asian cities have some of the highest levels of air pollution in the world. In Asia, hundreds of thousands of people in urban areas get sick just by breathing the air that surrounds them. However, the WHO 2006 estimates that dirty air kills more than half a million people in Asia each year of which burden falls heaviest on the poor as reported by Ogawa, 2006. The worsening of the situation has been attributed to cumulative effects of rapid population growth, industrialization and increased use of vehicles. The ozone primary tropospheric pollutants (SO_2 , NO_x , HC_s , and CO) often react in the atmosphere to form secondary pollutants which are acidic compounds (H_2CO_3 , H_2SO_4 and HNO_3) and photochemical oxidants. Environmental damage frequently results from several primary and secondary pollutants

acting in concert rather than from a single pollutant. Tropospheric oxidants such as ozone, PBN, PAN illustrate the complexity of atmospheric chemistry and processes. They help to form acidic compounds thereby contributing to green house warming and hence, damage to human health, animal, plant life and materials [USEPA, 1998; Dara, 2004]. Significant changes in stratospheric ozone, high above the troposphere, can affect tropospheric oxidants level [USEPA, 1998]. If increased UV-B radiation penetrates a depleted ozone shield, the photochemical formation of ground level oxidants may be enhanced [Stoker and Seager, 1972]. Green house warming could amplify this effect: A study carried out in three U.S. cities; Nashville, Philadelphia, and Los Angeles showed that a large depletion of stratospheric ozone, coupled with the green house warming, could increase smog formation by as much as 50% [Adelman, 1987]. The study also showed that NO_2 concentration might increase more than ten folds. There is however progress towards the reduction of anthropogenic emissions of NO_x , CO, volatile organic compounds in Europe and North American [Jonson *et al*, 2001]. However, the concentration of air pollutants emitted into the atmosphere is on the increase in the Southeast Asia and other parts of the World [Jonson *et al*, 2001]. It is therefore expected that the emissions from Africa and other parts of the Worlds that are yet to take strict and effective controlling measures on emissions will influence the free tropospheric levels in most of the Northern Hemisphere.

During a five-day period marked by temperature inversion and fog in London in 1952, between 3,500 and 4,000 deaths in excess of normal occurred with 1.3 ppm SO_2 level recorded [O'Neill, 1993; ACGIH, 1991]. SO_2 is oxidized to SO_3 in the atmospheric air by photolytic and catalytic processes involving ozone, oxides of nitrogen (NO_x), and hydrocarbon (HC), giving rise to the formation of photochemical smog [Dara, 2004].

In contrast to NO_2 , SO_2 is deleterious to plant life [Haagen-Smith, 1952; Molski and Dmuchowski, 1986]. Air pollution causes the decline in Eastern Europe [Nihlgard, 1985; Schutt and Cowling, 1985]. Area with extensive large-scale forest decline correlate with the areas where SO_2 concentration were elevated [ECE, 1984; Molski and Dmuchowski, 1986], therefore If the concentration of SO_2 is higher along with other gaseous pollutants (NO_x , O_3 , HC, organic and inorganic peroxides etc) in the troposphere and continues to accumulate over time, the overall concentration can have a negative effect on health, vegetation and structures [Abdul Raheem, 2007; Abdul Raheem *et al.*, 2009^a].

Surface concentration of ozone has been reported to be on the increase in the last decades in northern hemisphere [Vautard *et al.*, 2007] and in Southeast Asia [Jaffe, 1999]. A rise of about 26% in the ambient concentration of ozone has been reported in Taiwan between 1994 and 2003 [Chou *et al.*, 2006]. High levels of ambient air ozone can cause serious damage to health. The health hazards include shortness of breath, nausea, eye and throat irritation, and lung damage [Menezes and Shively, 2001]. Identification of air pollution source characteristics is an important step in the development of regional air quality control strategies. Receptor modeling, using measurements of pollutant concentrations at one or more sample sites, is often a reliable way to provide information regarding source regions for air pollution [Watson, 1984]. One of such receptor-modeling technique is principal component analysis (PCA) [Einax and Geiss, 1997; Jackson, 1991; Norman, 1987]. This is often combined with multiple linear regression (MLR), principal component regression (PCR), and partial least square regression, which have been demonstrated as powerful tools for handling several environmental problems, especially source apportioning [Otto, 1999; Timm, 1985; Vogt, 1989].

In recent years, certain statistical techniques that incorporate the influence of meteorological variables have been applied to assess the trend in ozone levels in the ambient air [Bakken et al., 1997]. One common approach is the use of a parametric regression model to link some characteristics of ozone, such as the mean level of ozone to meteorological variables. Other scientists have equally used PCA to pattern the spatial and temporal variations of ozone and to identify the important factors influencing ozone concentration [Klaus et al., 2001; Lengyel et al., 2004; Pissimanis et al., 2000]. Different subregions have, however, been identified where ozone concentration exhibited characteristic spatial and temporal patterns based on the differences arising from the interaction of their respective meteorological conditions with anthropogenic effects [Alvarez et al., 2000]. More specifically, Bloomfield et al., (1996) established a nonlinear regression model for hourly ozone data in the Chicago area in which meteorological variables, seasonality, and a trend term were all implicated. Cox and Chu (1992), on their part, proposed a model for the daily maxima of hourly ozone concentrations based on the Weibull distribution in which the scale parameter is allowed to vary as a function of meteorological conditions. On the other hand, Menezes and Shively (2001) used a multivariate approach to estimate the long-term trend in the extreme values of tropospheric ozone in Houston and Texas. They found that there is a downward trend in the probability of an exceedance followed by a relative flat trend. Shively and Sager (1999) extended the work of Cox and Chu (1992) as well as Bloomfield et al., (1996) by using nonparametric regression models to model ozone. The use of multivariate methods was further supported by Lengyel et al., (2004) who analyzed air quality data of which the hidden structure was uncovered by factor analysis and modeled ozone concentration using MLR, PLS, and PCR. While PCA is a very useful tool for selection of properties and different qualities processes leading to a linear model of the data, MLR and PCR or PLS can predict ozone concentration with an error below 2, 5, and 1ppb levels, respectively.

The aim of the present investigation was therefore to analyze environmental data gathered on the daily monitoring of ambient ozone, oxides of nitrogen, and sulfur (IV) oxide at five monitoring sites in Lagos and four monitoring sites in Ilorin, Nigeria. The data were collected between early morning and late evening of the day, and they covered both dry and wet seasons from years 2003 to 2006. The study also included establishment of prediction models on the influence of meteorological parameters on the seasonal variation of concentration of gaseous pollutants in the two Nigerian cities and comparison of measured and modeled concentration values of ozone [Abdul Raheem et al., 2009b].

2. Theoretical background

2.1 Air pollution

Air is all around us, odourless, colourless and essential to all life on earth as it acts as a gaseous blanket, protecting the earth from dangerous cosmic radiation from outer space. It helps in sustaining life on earth by screening the dangerous ultraviolet (UV) radiations (< 300nm) from the sun and transmitting only radiations in the range 300nm to 2500nm, comprising of near UV, visible and near infrared (IR) radiations and radio waves (0.01 to 4×10^5 nm) [Smart, 1998]. The atmosphere also plays a vital role in maintaining the heat balance on the earth by absorbing the IR radiation received from the sun and re-emitted by the earth. In fact, it is this phenomenon, called “the greenhouse effect”, which keeps the earth warm enough to sustain life on the earth. Yet, the air is actually a combination of gaseous

elements that have a remarkable uniformity in terms of their contribution to the totality of life. Thus, oxygen supports life on earth; nitrogen is an essential macro - nutrient for plants; and carbon (IV) oxide is essential for photosynthetic activity of plants. Moreover, atmosphere is a carrier of water from the ocean to land, which is so vital for the hydrological cycle. Any major disturbance in the composition of the atmosphere resulting from anthropogenic activities may lead to disastrous consequences or may even endanger the survival of life on earth [Dara, 2004]. The constituent elements are primarily nitrogen and oxygen, with a small amount of argon. Below 100km, the three main gaseous elements, which account for about 99.9% of the total atmosphere, are N_2 , O_2 and Ar and they have concentration by volume of 78%, 21%, and 0.93% of respectively [Stanley, 1975]. The presence of trace amounts of other gases would account for the remaining 0.07%. These remaining trace gases exist in small quantities and they are measured in terms of a mixing ratio. This ratio is defined as the number of molecules of the trace gas divided by the total number of molecules present in the volumes sampled. For example, ozone (O_3), carbon (IV) oxide (CO_2), oxides of nitrogen ($NO_2 + NO$) as NO_x and chloro fluoro carbons (CFCs) are measured in parts per million by volume (ppmv), parts per billion by volume (ppbv) as well as microgram per cubic meter ($\mu g m^{-3}$), [Dale, 1976]

Air pollution has been defined [World Bank, 1978] as 'the presence in the outdoor atmosphere of one or more contaminants such as dust, fumes, gas, mist, odour, smoke, or vapour in such quantity, characteristics and duration as to make them actually or potentially injurious to human, plant or animal life, or property, or which unreasonably interferes with the comfortable enjoyment of life and property'. Pollution on the whole is caused principally by human activities, though it can also be a natural process. Air pollution arises from people's economic and domestic activities like modern agriculture which requires agrochemicals. Industrial activities are responsible for wide range of pollution. Thermal power station, burning fossil fuel and moving vehicles emit harmful pollutants like sulphur (IV) oxide, nitrogen (II) oxide and carbon (IV) oxide. Some of these emitted gases have been responsible for acid - rain, global warming and malfunctioning of human / animal's haemoglobin [Stanley, 1975]. Other causes arising from human activities include inappropriate solid waste disposal, gas flaring and oil exploration. Air pollution can also arise from natural causes such as volcanic eruption, whirlwind, earthquake, decay of vegetation, pollen dispersal, as well as forest fire ignition by lightning.

2.2 Pollutants

These are substances introduced into the environment in an amount sufficient to cause adverse measurable effects on human beings, animals, plant, vegetation or materials. Pollutants are referred to as primary pollutants, if they exert the harmful effects in the original form in which they enter the atmosphere e.g. CO , NO_x , HC_s , SO_x , particulate matter and so on. On the other hand, secondary pollutants are products of chemical reactions, among primary pollutants are ozone, hydrogen peroxide, peroxyacetyl nitrate (PAN) and peroxybenzoyl nitrate (PBN). Classification of pollutants can also be according to chemical compositions i.e. organic or inorganic pollutants or according to the state of matter i.e. gaseous or particulate pollutants. Air pollution is basically made up of three components and these are source of pollutants, the transporting medium, which is air and target or receptor which could be man, animal, plant and structural facility.

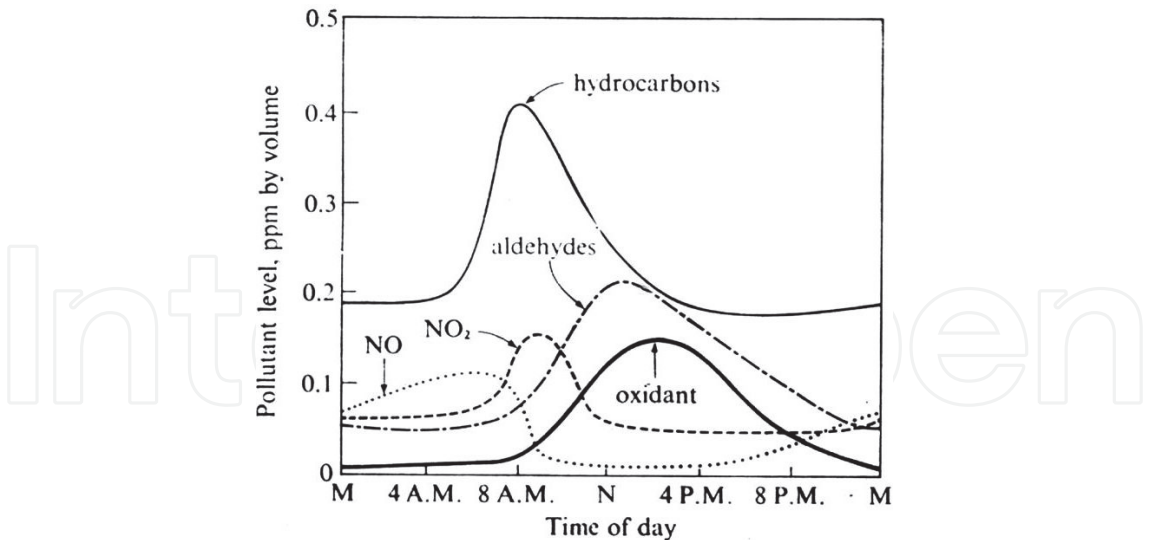


Fig. 1. Generalized Plot of Atmospheric Concentrations of Species Involved In Smog Formation As A Function of Time of The Day

3. Atmospheric photochemical reaction

The various chemical and photochemical reactions taking place in the atmosphere mostly depend upon the temperature, composition, humidity and the intensity of sun light. Thus the ultimate fate of chemical species in the atmosphere depends upon these parameters. Photochemical reactions take place in the atmosphere by the absorption of solar radiations in the UV region. Absorption of photons by chemical species gives rise to electronically excited molecules. These reactions are not possible under normal laboratory conditions except at higher temperature and in the presence of chemical catalysts [Hansen *et al*, 1986]. The electronically excited molecules spontaneously undergo any one or combination of the following transformations: Reaction with other molecules on collision; Polymerization; Internal rearrangement; Dissociation; De - excitation by fluorescence or De - activation to

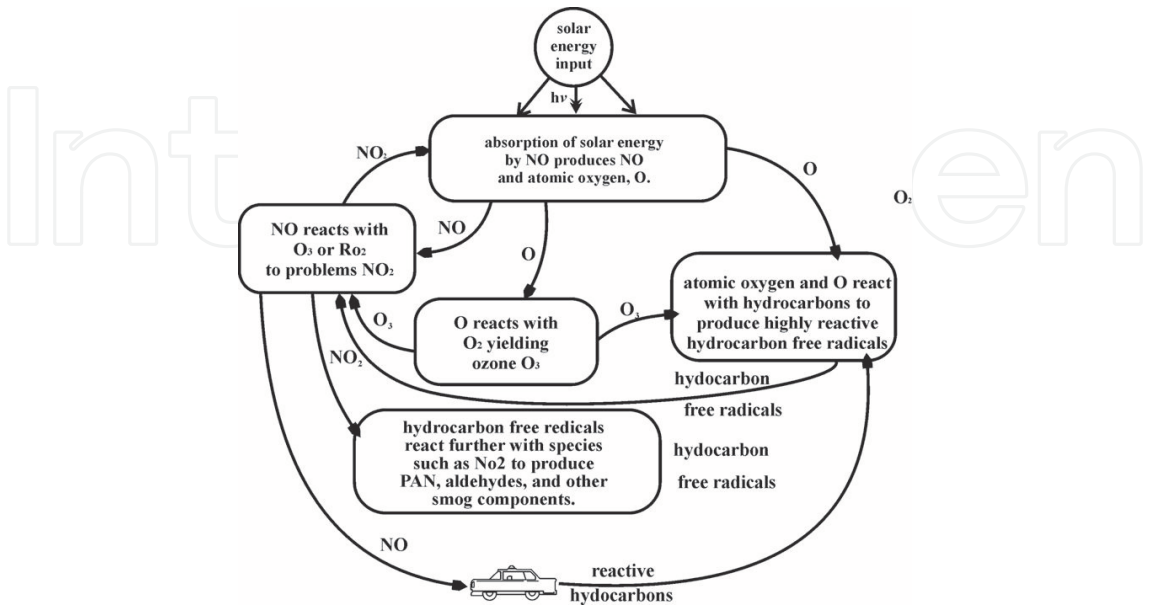


Fig. 2. Generalized Scheme For The Formation Of Photochemical Smog

return to the original state [Dara, 2004]. Any of these transformation pathways may serve as an initiating chemical step or a primary process. The three steps involved in an overall photochemical reaction are Absorption of radiation, Primary reactions and Secondary reactions.

Smoggy atmosphere show characteristics variations with time of the day in levels of NO, NO₂, hydrocarbons, aldehydes and oxidants. A generalized plot showing these variations is shown in Figure 1. This shows that shortly after dawn the level of NO in the atmosphere decreases markedly, a decrease which is accompanied by a peak in the concentration of NO₂. During the mid - day the levels of aldehydes and oxidants become relatively high, however, the concentration of total hydrocarbons in the atmosphere peaks sharply in the morning, then decreases during the remaining daylight hours. The variations in species concentration shown in the above Figure 1 may be explained by a generalized reaction scheme in Figure 2. This is based on the photochemically initiated reactions which occur in an atmosphere containing oxides of nitrogen, reactive hydrocarbons, and oxygen. The various chemical species that can undergo photo - chemical reactions in the atmosphere include NO₂, SO₂, HNO₃, N₂, ketones, H₂O₂, organic peroxides and several other organic compounds and aerosols; the time - variations of which are explained in a group of overall reactions first proposed by Friedlander and Seinfeld (1974)

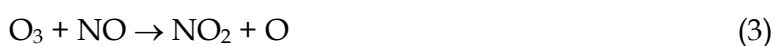
* Primary photochemical reaction:



* Reactions involving oxygen species



(M is an energy absorbing third body)



* Production of organic free radicals from hydrocarbons,

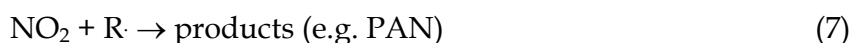


R[·] is a free radical, which may or may not contain oxygen

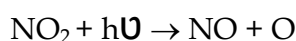
* Chain propagation, branching and termination



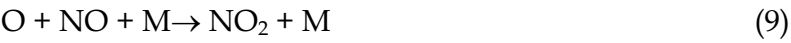
In this case R[·] contains oxygen and oxidizes NO. It is one of many chain propagation reactions, some of which involve NO



A number of specific reactions are involved in the above overall scheme for the formation of photochemical smog, which is smoke and fog [Thomas *et al*, 1974]. The formation of atomic oxygen by the primary photochemical reaction:



This leads to several reactions involving oxygen and nitrogen oxide species. Examples of such reactions are given below:



Pollutant Source	CO	NO _x	HC	SO _x	Particulate	Total
Transportation	111.0	11.7	19.5	1,0	0.7	143.9
Fuel Combustion (Stationary Source)	0.8	10.0	0.6	26.5	6.8	44,7
Industrial Processes	11.4	0.2	5.5	6.0	13.1	36.2.
Solid wastes disposal	7,2	0.4	2.0	0.1	1.4	11.1
Miscellaneous	16.8	0.4	7.1	0.3	3.4	28.0
Total	147.2	22.7	34.7	33.9	25.4	263.9

[Adapted from Thomas *et al*, 1974]

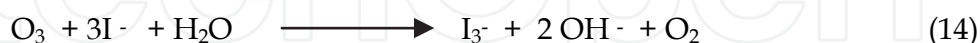
Table 1. Estimates of USA Primary Pollutants Sources in million tons per year (Million Tons/Year)

4. Methodology

The determinations of the concentrations of total oxidants (undertaken as O₃), NO_x and SO₂ in the ambient air were carried out between 2003 and 2006 to cover the two seasons; dry season (November to April) and rainy season (May to October) using standard methods. Total oxidants were determined by buffered potassium iodide solution method proposed by Byers and Saltzman (1958). Determination of oxides of nitrogen concentrations were done using the Intersociety Committee Method of Analysis (1972) which is based on the Griess-Saltzman (1954) colorimetric, azo dye forming reagent while oxides of sulphur were determined by conductivity measurements as proposed by Stanley (1975). The application of these techniques to monitoring required the preparation of the following range of reagents as sampling and absorbing solutions as well as preparation of calibration curves. All the chemicals used in the preparation of sampling and absorbing solutions were of analytical grade. The reagents had been prepared and seen stable for months prior to their use. The validation of all procedures was further confirmed using LaMotte standard air sampler.

4.1 Ozone

The absorbing solution used for trapping ozone was 1% KI buffered at 6.8 ± 0.2 . The standard solution and calibration curve were prepared as follows: 4.09ml of standard 0.001M iodine solution was taken and diluted to 100ml with distilled water. 10ml of this solution was taken and further diluted to 100ml with absorbing reagent and this was labelled solution A. 1ml of A was further diluted to 100ml using absorbing reagent, which gives solution B. This provides a calibrated iodine solution equivalent to $1.92\mu\text{g}$ of ozone per ml [Stanley, 1975 and Dara, 2004] as ozone reacts with iodine ion in neutral buffer solution according to the following equation:



The tri - iodide ion liberated has an intense yellow colour. The standard solution was always prepared freshly when needed. A series of standard solutions prepared from above were used to obtain calibration curve. The absorbance measurement was carried out at 352nm. The calibration curve is shown in Figure 3 and it has regression value of 0.9972

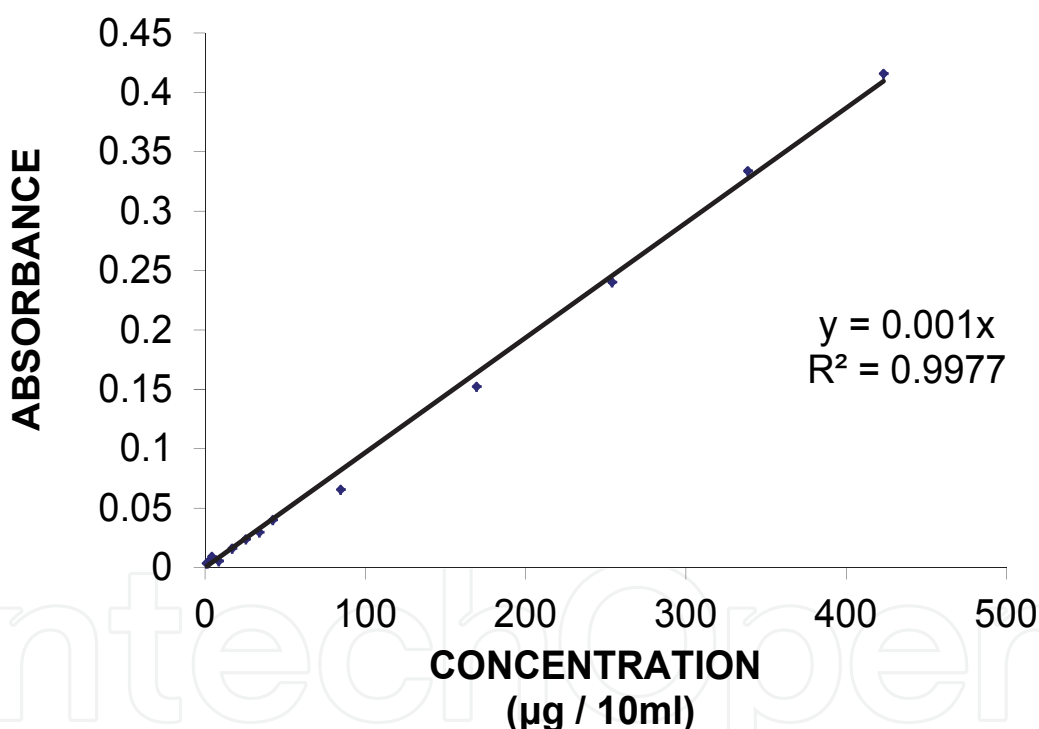


Fig. 3. Total oxidants calibration curve

4.1.1 Sampling procedure

The set-up of the high volume sampler is given in Figure 4. To follow strict guidelines needed when monitoring for criteria pollutants as discussed earlier, our equipment is validated with LaMotte air sampler (Figure 5) purchased from LaMotte & Company, USA, for capability, repeatability and reliability needed to collect accurate data, and operation of the equipment within our established methods. The impinger used is a big boiling tube of capacity 250cm^3 with 42mm diameter. Teflon tubing's used as delivery tubes along with



Fig. 4. Picture of The Sampling train

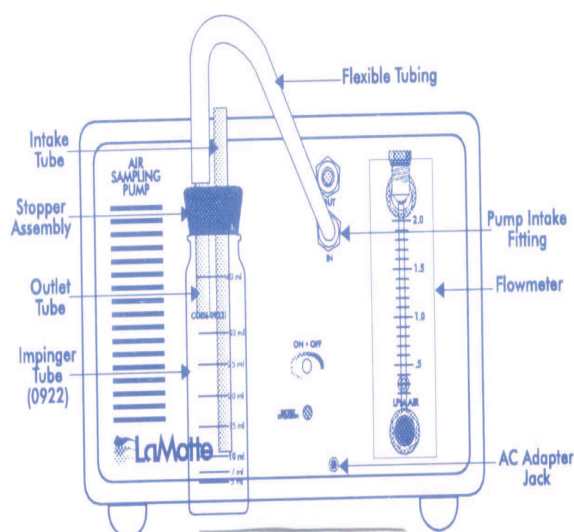


Fig. 5. Lamotte Air- Sampler

glass tubing that serves as inlet for the ambient air sampled. Silicone grease was used to make the set up airtight by its application to all necessary joints. The air was sampled at the rate of $1 \text{ dm}^3 \text{ min}^{-1}$ with absorbing solution fixed at 30 cm^3 as found appropriate and used [Abdul Raheem et al., 2009c], after each sampling for one hour, the impinger was carefully removed and the sample transferred quantitatively into the sample bottle for analysis. The impinger was wrapped with aluminum foil to avoid sunrays' interference. In order to determine pollutant variability over daytime periods, air samples were taken at each location over ten defined sixty - minute periods for any sampling day. The ten sampling periods were spaced equally between approximately 6 am and 6 pm to reflect morning, afternoon and evening. Minimum of 30 samples were collected at each site per week for the pollutants monitored. The time of sixty minutes was found to be optimal from the preliminary investigations for the quantitative sampling of these toxic gases within the

environment [Abdul Raheem et al., 2009c]. All samplings reported were carried out in triplicates. As the road traffic is the common source of pollution cutting across all sites classes, the average traffic volume were determined for all sampling zones. Traffic count was manually done, counting the vehicles passing on the road for 10 minutes in every hour from which hourly traffic was calculated [Abam and Unachukwu, 2009]. The daily minimum and maximum temperatures were between 23°C and 36.5°C, throughout the sampling period.

4.1.2 Analysis

A freshly prepared absorbing solution serves as sample reference or blank solution in order to take care of any impurities during preparation. Absorbance of samples for total oxidants was measured at 352 nm with UV / Visible spectrophotometer. The concentration was read out in µg / 10ml from the reference plot of which one of the examples is shown in Figure 3. The concentrations were converted to µgm⁻³ or ppm or ppb using appropriate conversion factor.

4.1.3 Calculation [Vowels and Connell, 1980]

$$\text{Oxidant } (\mu\text{gm}^{-3}) = \frac{\text{total } \mu\text{g O}_3 \text{ per 10ml of absorbing reagent}}{\text{Volume of air sampled in cubic metres}} \tag{15}$$

$$O_x = \frac{M_{O_3}}{V} \tag{16}$$

$$\mu\text{gm}^{-3} = \frac{\text{ppb} \times \text{molar mass}}{24.45} \times 1000 \tag{17}$$

for 1 µgm⁻³ of ozone, the ppb value will be

$$\frac{1 \times 24.45}{48 \times 1000} = 0.51 \text{ppb} \tag{18}$$

QUANTITY	CONTENTS	CODE
2 × 120 MI	Total oxidants reagent #1	7740-J
30MI	Total oxidants reagent #2	7741-G
30MI	Total oxidants reagent #3	7742-G
3	Test Tubes, 5mL, w/ caps	0230
1	Total oxidants in Air Comparator	7739

Table 2. LaMotte total oxidants in air test kit code 7738

4.1.4 La Motte total oxidants sampling procedure

10 mL of reagent #1 was put into impinging tube, followed by 2 drops of reagent #2 added and swirled to mix then 2 drops of reagent #3 added and also swirled to mix. The impinging apparatus was connected to intake of the sampling pump as shown in Figure 5 such that the long tube was immersed in the absorbing solution. The impinging tube was covered with foil to protect it from light while sampling. The flow meter of sampling apparatus was adjusted to collect air at 1.0 Lm⁻¹ rate. The sampling continued until 15 minutes when a measurable pink colour developed. The impinging tube was disconnected from the pumping apparatus and the contents poured into a clean test tube (0230). The test tube was later inserted into the total oxidants in air comparator (7739) and the sample colour was matched with an index value. The index value was recorded and the calibration chat was used to convert the index readings into concentration of the pollutant in the atmosphere in parts per million.

Time(min)	1	2	3	4	5	6	7	8
5	0.14	0.36	0.72	1.08	1.44	2.88	4.32	5.76
10	0.07	0.18	0.36	0.54	0.72	1.44	2.16	2.88
15	0.05	0.12	0.24	0.36	0.48	0.96	1.44	1.72

** Values in ppm

Table 3. Total oxidants in air calibration chart** [LaMotte 6.05] Comparator index number

4.2 Oxides of nitrogen (NO_x)

The absorbing solution used for trapping NO_x was Saltzman solution which is an azo dye forming reagent .

The standard solution and calibration curve were prepared as follows: 2.16g of sodium di - oxo nitrate (III), NaNO₂ was dissolved in 1000 cm³ volumetric flask and the solution labeled A. 1ml of solution A was measured out into 100 ml volumetric flask and the solution made up to the mark. This solution of concentration 0.0216 gL⁻¹ was labeled B. 1ml of B was added to 100 ml volumetric flask and distilled water added to the mark to give 0.000216 gL⁻¹ solution C. 10ml of solution C was added to 100ml volumetric flask and filled to the mark with distilled water to give solution of concentration 0.0000216 gL⁻¹ labeled D. Further dilutions of the last two solutions C and D were used for calibration plot. As the standardization was based on the empirical observation that 0.72 mole of NaNO₂ produces the same colour as 1mole of NO₂ [Hesketh, 1972]. In other words, 1ml of the 0.000216 gL⁻¹ working standard which contains 0.216µg of NaNO₂ should be equivalent to 0.2 µg of NO₂. Series of standard solutions prepared in 10 ml volumetric flasks from solutions C and D above were allowed to stay for 15 minutes for colour development and the spectra run at 550 nm to obtain a set of absorbance value which were recorded against known concentrations. The formation of red azo dye of which the absorbance is picked at 550 nm can be explained according to the equation in Figure 6 However, a plot of absorbance against concentration in µg / 10 ml was made, a straight line graph obtained with regression value of 0.9962 as shown in Figure 7

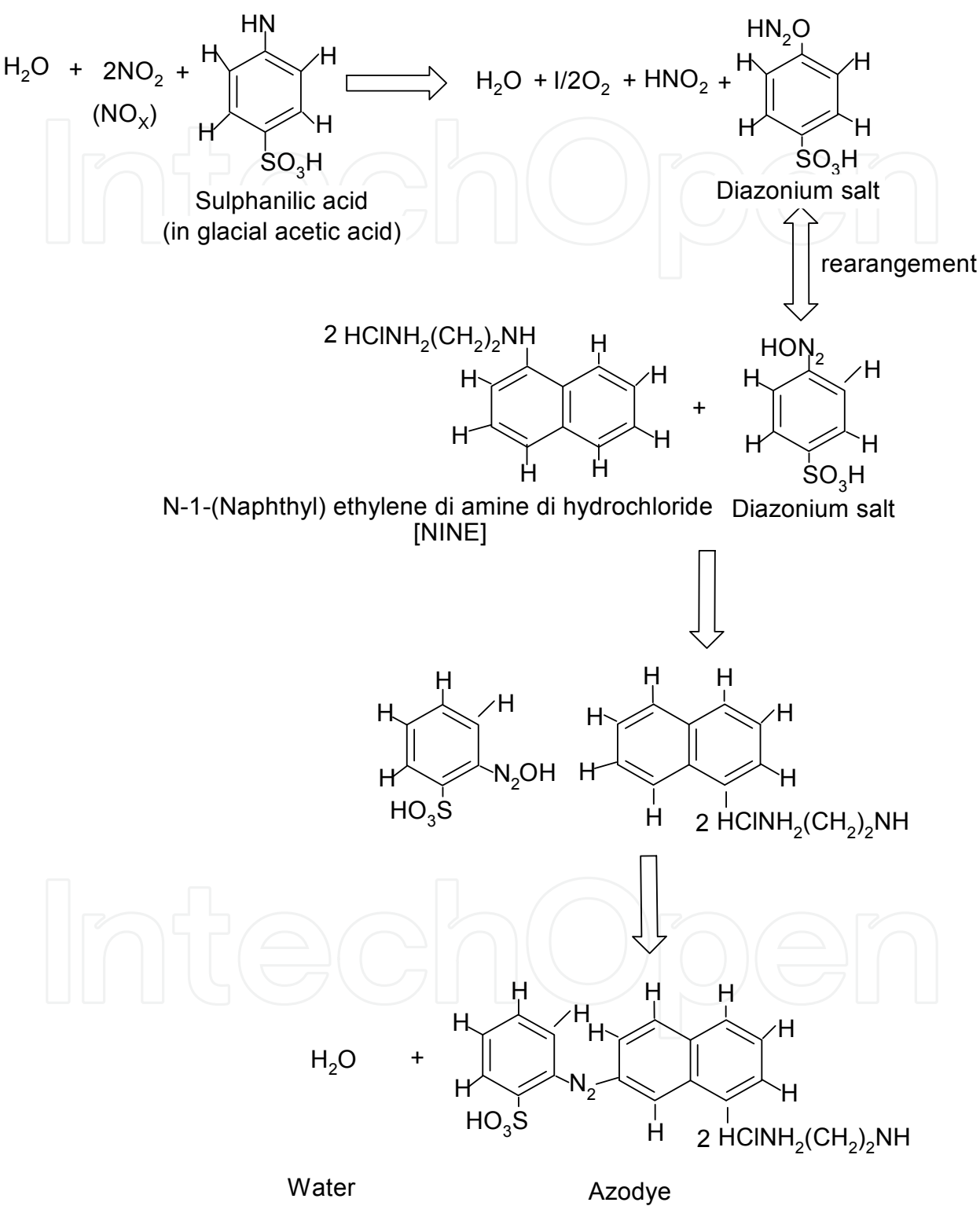


Fig. 6. Equation showing the formation of azo dye

4.2.1 Sampling procedure

The procedure for sampling is as given above

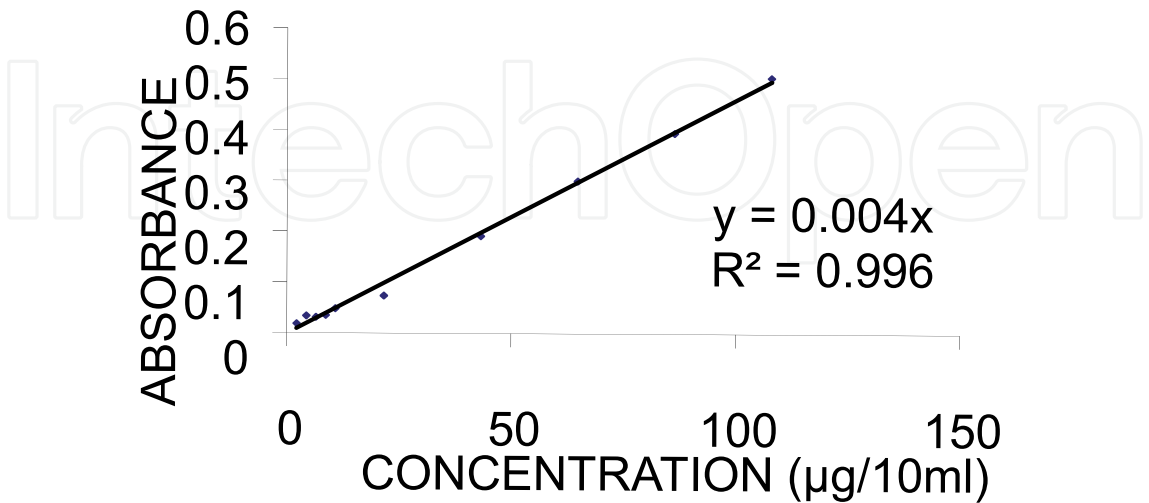


Fig. 7. Oxides of nitrogen (no_x) calibration curve

4.2.2 Analysis

The absorbing solution serves as sample reference or blank solution in order to take care of any impurities during preparation. Absorbance of samples for oxides of nitrogen was measured at 550nm with UV / Visible spectrophotometer. The concentration was read out in µg / 10ml from the reference plot of which an example is shown in figure 7. The concentrations were converted to µgm⁻³ or ppm or ppb of which the conversion factors are explained hereafter.

4.2.3 Calculation [Vowels and Connell, 1980]

$$NO_x(\mu g m^{-3}) = \frac{\text{total } \mu g \text{ NO}_x \text{ per 10ml of absorbing reagent}}{\text{Volume of air sampled in cubic metres}} \tag{19}$$

$$NO_x = \frac{M_{NO_x}}{V} \tag{20}$$

$$\mu g m^{-3} = \frac{ppb \times \text{molar mass} \times 1000}{24.45} \tag{21}$$

for 1 µgm⁻³ of NO_x as NO₂, the ppb value will be

$$\frac{1 \times 24.45}{46 \times 1000} = 0.53ppb \tag{22}$$

QUANTITY	CONTENTS	CODE
2 × 120 mL	Nitrogen (Iv) oxide reagent #1 Absorbing solution	7684-J
30 mL	Nitrogen (Iv) oxide reagent #2	7685-G
10g	Nitrogen (Iv) oxide reagent #3 powder	7688-D
2	Test tubes,10mL, glass, w/caps	0822
1	Spoon, 0.005g, plastic	0696
1	Pipet, droping, plastic	0352
1	Nitroge (IV) oxide in air comparator	7689
1	Tubing	23609
1	Pipet	30410
1	Needle	27336-01

Table 4. LaMotte nitrogen (IV) oxide in air test kit code 7690

4.2.4 Nitrogen (IV) oxide lamotte sampling procedure

10mL of reagent #1 i.e. absorbing reagent was poured into the impinging tube, a gas bubbler impinger (0934). The impinging apparatus was connected to the intake of air sampling pump and the long tube was immersed in the absorbing solution. The special adaptor was attached to the intake of the pump to sample at 0.2Lm⁻¹ while the sampling was done for 20 minutes when a measurable amount of nitrogen (IV) oxide was absorbed. At the end of the sampling period the contents of the impinging tube was poured into test tube (0822). The pipette (0352) was used to add a drop of reagent #2, the test tube capped and mixed after which the 0.05g spoon was used to add 0.05g of reagent #3. The test tube capped and the solution left for 10 minutes for colour development after which the test tube was placed into comparator (7689) and the sample colour matched to index of colour standards. The index number which gave the proper colour matched was recorded and the calibration chart used to convert the index read to concentration of nitrogen (IV) oxide in ppm.

Comparator index number								
Time (min)	1	2	3	4	5	6	7	8
1	0.00	2.8	7.0	14.0	21.0	28.0	42.0	56.0
5	0.00	0.56	1.40	2.80	4.20	5.60	8.40	11.20
10	0.00	0.28	0.70	1.40	2.10	2.80	4.20	5.60
15	0.00	0.19	0.47	0.93	1.40	1.87	2.80	3.74
20	0.00	0.14	0.35	0.70	1.05	1.40	2.10	2.80

Table 5. Nitrogen (IV) oxide in air calibration chart**

4.3 Sulphur (IV) oxide

The absorbing solution used for trapping SO₂ was 0.3M H₂O₂ solution buffered at pH 5 ± 0.2.

The standard solution and calibration curve were prepared as follows:

0.1M H_2SO_4 was used as parent standard solution. All other lower concentrations were prepared from serial dilution of 0.1M H_2SO_4 . 0.1M H_2SO_4 was standardized by titration against Na_2CO_3 using methyl orange as indicator. The conductivity measurement of each of the concentrations of H_2SO_4 (0.001 – 0.01M) obtained from serial dilution were taken, using Hanna Instrument EC 214 conductivity model. A graph of conductivity values in Siemens per centimeter (Scm^{-1}) against concentrations of H_2SO_4 in mol dm^{-3} was plotted. The data gave a straight line which passes through the origin with regression value of 0.9874. The calibration curve so obtained is shown in Figure 8. This was used as a working curve for the determination of SO_2 during the analysis of samples.

4.3.1 Sampling procedure

The procedure for sampling others remained except the flow rate that was increased to 2 Lmin^{-1} for optimization purpose [Abdul Raheem et al., 2009c].

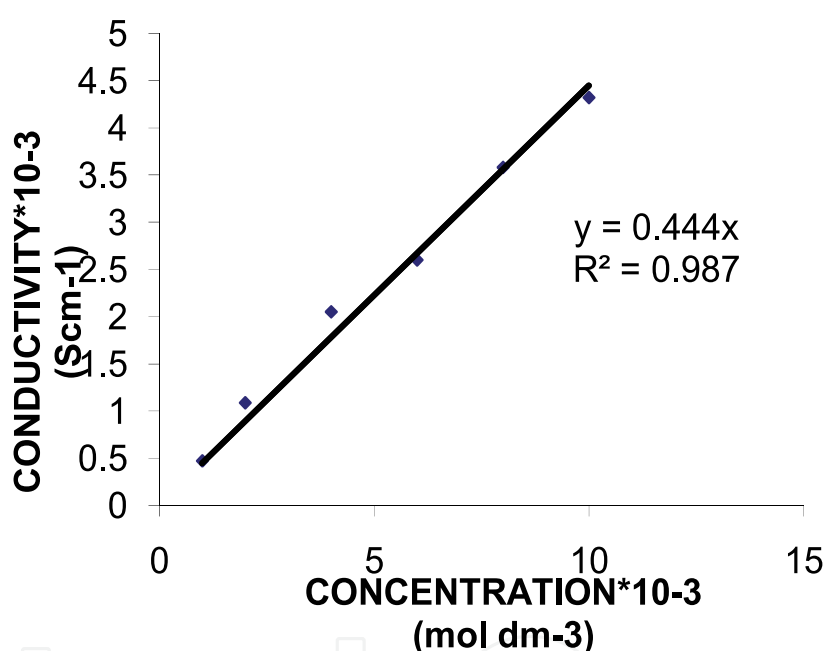


Fig. 8. Sulphur (iv) oxide calibration curve

4.3.2 Analysis

Conductivity measurements were undertaken using the Hanna Instrument Model E 214 conductivity meter. From the sample and reference solutions 20 cm^3 volume was measured respectively into a liquid sample holder test tube of Hanna model conductivity meter. The concentrations in mol dm^{-3} of H_2SO_4 formed from SO_2 of the samples were read out from the reference plot (Fig.8), the concentrations obtained in mol dm^{-3} were converted to parts per million or parts per billion or microgram per cubic meter (ppm or ppb or μgm^{-3}) as shown below using appropriate conversion factor. Equation of reaction for formation of H_2SO_4 from SO_2 is shown below:



4.3.3 Calculation [Stanley, 1975; Vowels and Connell, 1980]

$$ppm = \frac{moldm^{-3} \times mmSO_2 \times samplingvol.}{flowrate \times samplingduration} \tag{24}$$

$\mu gm^{-3} = \frac{ppm \times molar\ mass}{24.45} \times 1000$ (25)

for 1 moldm⁻³ of SO₂ , ppm value will be

$$\begin{aligned} &= \frac{1 \times 64 \times 30}{2 \times 60 \times 1000} \\ &= 1.6 \times 10^{-2} ppm \end{aligned} \tag{26}$$

in μgm⁻³ , the value becomes:

$$\frac{1.6 \times 10^{-2} \times 64 \times 1000}{24.45} = 41.88 \mu gm^{-3} \tag{27}$$

QUANTITY	CONTENTS	CODE
2 × 250 mL	Sulphur (IV) oxide absorbing solution	7804-K
15g	Sulphur (IV) oxide reagent #1	7693-E
30mL	Sodim hydroxide, 1.0 N	4004PS-G
60mL	Sulphur (IV) oxide passive bubbler indicator	7805-H
2	Pipets, 1.0mL, plastic	0354
2	Test tubes, 5 mL, plastic, w/caps	0230
2	Test tubes, Hester, w/caps	0204
1	Spoon, 0.25g	0695
1	Dispenser caps	0693
1	Sulphur (IV) oxide passive bubbler comparator	7746

Table 6. LaMotte sulphur (IV) oxide in air test kit code 7714

4.3.4 Sulphur (IV) oxide lamotte sampling procedure

10mL of Sulphur (IV) oxide absorbing solution was added to impinging tube and connected to the impinging apparatus as shown in Figure 5. The long tube was immersed into the absorbing solution. Sampling was done at 1.0 Lpm for 60 minutes or 90 minutes. The impinging apparatus was covered with foil to protect it from light. At the end of the sampling time the small test tube (0230) was filled to the line with the sample and 0.25g

spoon was used to add a level measured of Sulphur (IV) oxide reagent #1. The test tube containing the mixture was capped and vigorously shaken to dissolve the powder. A 1 mL pipette was used to add 1mL sodium hydroxide, 1.0N, to the same small test tube, capped and inverted several times to mix. The other 1mL pipette was also used to add 2mL (2 measures) of Sulphur (IV) oxide passive bubbler indicator (7805) to a large test tube (0204). The contents of the small test tube were poured into the large test tube containing the indicator. Immediately the tube capped and inverted six times, holding the cap firmly in place with the index finger. After waiting for 15 minutes, the test tube was placed into the Sulphur (IV) oxide passive bubbler comparator (7746). The sample colour matched with the standard colour and the index number read and recorded from the comparator. The index number was converted to concentration in ppm using the calibration chart provided.

Comparator index number								
Time (min)	1	2	3	4	5	6	7	8
10	0.00	0.19	0.29	0.38	0.48	0.57	0.67	0.76
30	0.00	0.06	0.10	0.13	0.16	0.19	0.22	0.25
60	0.00	0.03	0.05	0.06	0.08	0.10	0.11	0.13
90	0.00	0.02	0.03	0.04	0.05	0.06	0.07	0.08

** Values in pp
Table 7. Sulphur (IV) oxide in air calibration chart**

5. Quality assurance

The impinger was well rinsed with distilled water and properly wrapped with foil paper before each use. The tubing’s and corks in the sampling train were checked before and during sampling, in case they had become slackened, however silicone grease was used to increase the pressure by making them air tight.

The absorbing reagents were always prepared freshly ahead of sampling for the solution to stabilize. They were stored in amber coloured bottles and refrigerated because of light interference. They were always allowed to thaw and assume the 25°C temperature before use. Lengthy contact with air by the absorbing reagent was avoided during both preparation and use to prevent absorption of the oxides. The absorbance of the reagent blank was deducted from that of the samples where the machine could not be adjusted to zero to avoid matrix error, especially with the conductivity meter.

For the nitrogen oxides determination, a gas bubbler impinger (fritted gas bubbler) was used instead of a general purpose impinger as absorption tube. The general purpose impinger has been reported to give low absorption efficiency with oxides of nitrogen [ICMA, 1972; Onianwa et al., 2001; Saltzman, 1954]. However the results were corrected and correlated with the fritted bubbler as well as standardized absorbing solution imported from LaMotte and Company, USA.

Greatest accuracy has been reported to be achieved by standardizing the sampling train with accurately known gas sample in a precision flow dilution system like a permeation tube [Dara, 2004]. Due to lack of the apparatus necessary for the standardization of the train,

the actual collection efficiency is not known. However with the use of LaMotte sampling pump with inbuilt flow meter and standardized reagents, we recorded high collection efficiency at sites with increase concentrations of samples.

6. Results

This is already discussed extensively in Abdul Raheem, 2007 and Abdul Raheem et al., 2009^{a,b,c}. Typical tables are shown to show the typical measurements concentration results and the meteorological data

Start of sampling	End of sampling	OX (ppb)	NOx (ppb)	SO ₂ (ppb)	RELHUM (%)	WND ms ⁻¹	DWND (°C)	AIRTEMP (°C)	Sun ExpWm ⁻²
6.30am	7.30am	29.08 ±11.73	1.47	7.83	78.17	27.60	144.60	22.70	-1.55
7.45am	8.45am	29.72 ±10.5	3.44	6.54	71.67	36.30	156.40	23.20	0.51
9.00am	10.0am	29.71 ±5.57	0.43	4.17	57.30	44.60	156.50	27.90	8.63
10.15am	11.15am	33.11 ±5.51	1.67	4.42	53.30	42.00	160.50	29.80	12.61
11.30am	12.30pm	46.69 ±7.49	1.73	6.27	42.00	42.30	153.20	31.50	15.36
12.45pm	1.45pm	69.94 ±15.45	1.04	7.36	38.67	43.40	154.00	32.80	16.09
2.00pm	3.00pm	35.55 ±11.21	2.46	8.84	35.50	41.60	160.00	34.30	13.39
3.15pm	4.15pm	21.44 ±6.31	2.46	7.62	37.17	39.40	167.90	33.80	10.16
4.30pm	5.30pm	17.62 ±3.13	2.69	9.52	39.00	39.30	178.00	33.00	5.66
5.45pm	6.45pm	11.56 ±2.19	2.91	9.11	42.67	37.60	176.70	31.30	0.86

Table 8. Dry season environmental data for Ilorin

Start of sampling	End of sampling	OX (ppb)	NOx (ppb)	SO ₂ (ppb)	RELHUM (%)	WND ms ⁻¹	DWND (°C)	AIRTEMP (°C)	Sun Exp Wm ⁻²
6.30am	7.30am	14.26	12.40	10.72	90.58	3.07	107.02	25.99	-1.65
7.45am	8.45am	22.92	5.89	7.20	87.58	4.67	156.38	26.38	2.80
9.00am	10.0am	28.95	5.39	11.15	73.75	7.09	189.02	29.05	8.90
10.15am	10.0am	46.86	5.66	14.82	67.92	7.35	182.63	30.25	11.00
11.30am	12.30pm	43.21	6.41	10.51	63.50	8.76	170.67	31.30	12.06
12.45pm	1.45pm	85.31	5.68	12.74	60.33	10.11	159.55	32.00	17.30
2.00pm	3.00pm	73.77	6.45	16.62	60.08	10.36	155.00	31.98	15.10
3.15pm	4.15pm	26.06	6.84	15.47	62.67	10.94	163.79	31.37	13.20
4.30pm	5.30pm	12.23	5.72	16.48	67.00	10.21	165.22	30.38	10.70
5.45pm	6.45pm	8.58	6.90	19.21	72.75	8.99	166.64	29.20	3.30

Table 9. Dry season environmental data for Lagos

This is showing typical results of statistical modeled analysis of Ilorin and Lagos during dry season MLR with backward selection in stepwise mode (without intercept) results in the following equation:

$$OX_{ILO} = 6.092 \times SO_2 + 0.657 \times RHUM - 2.653 \times ATEMP + 4.385 \times SUNEXP$$

(28)

Where $R = 0.981$, $F(4, 6) = 38.389$, $p < 0.000$
This shows that only four of the variables are found to be significant for retention in the model.
MLR using backward selection in stepwise mode (without intercept) results in the following equation:

$$OX_{Lag} = 1.679 \times ATEMP + 5.622 \times SUNEXP - 8.079 \times WND$$

(29)

where, $R = 0.961$, $F(3, 7) = 27.874$, $p < 0.000$
MLR shows that only three of the variables are significant for retention in the model.

A table Comparing the ozone measured concentration with calculated results from MLR model equations

	ILORIN		LAGOS	
	RAIN	DRY	RAIN	DRY
MEASURED	21.86 ± 2.47	32.44 ± 5.13	9.87 ± 0.99	36.22 ± 5.76
MODELED	16.12 ± 1.86	44.32 ± 4.25	9.89 ± 0.82	36.29 ± 3.87

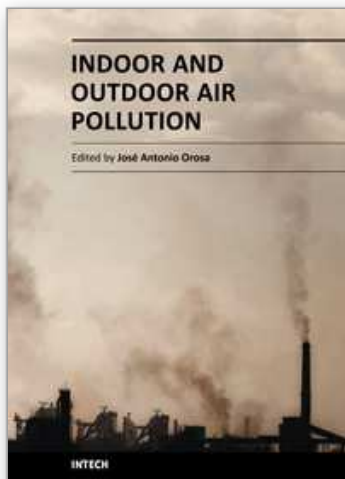
Table 10. MLR equation modeled results for ozone compared with monitored results for the two cities of interest during rainy and dry seasons (ppb)

7. General conclusion

The direction and spatial extent of transport and the relative contribution of transported ozone and precursors to individual downwind areas are highly variable. A number of factors influence site to site differences in ozone concentrations, including sources of precursor’s emissions and meteorological conditions.
Data analysis also reveals that NO_x and SO₂ as well as volatile organic compounds contribute to ozone formation and this is in accordance with other researchers [Winer *et al*, 1974; Canada – US, 1999; chou *et al*, 2006]. The relative effectiveness of reductions of these three precursors can vary with location and atmospheric condition. Overall the concentrations of ozone could be said to be influenced globally by background concentrations, locally generated concentrations and transported concentrations.
On the whole the chemometric multivariate analysis results confirmed our experimental results and unfold the fact that meteorological influence plays a major role in the atmospheric chemistry of ozone.
Finally, these results and analysis suggested that ozone acting in concert with other pollutants need to be recognized as important health and ecosystem related air quality concern in Nigeria. Based on increasing evidence on regional transport of ozone all over the world, there is need for recognition that ground – level ozone would be an appropriate issue to be considered by the Nigerian government. In particular, a proactive measure has to be formulated towards reducing NO_x and SO₂ and by consequence O₃ in Nigeria.

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Indoor and Outdoor Air Pollution

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Air pollutants are continuously released from numerous sources into the atmosphere. Several studies have been carried out on the quantification of pollutants and their consequences on public health. Identification of the source characteristics of air pollution is an important step in the development of regional air quality control strategies. Air quality is a measure of the degree of ambient atmospheric pollution. Deterioration and damage to both public health and environment due to poor air quality have been recognized at a legislative and international level. In consequence, indoor and outdoor air quality must also be considered. This book tries to reveal different points of view of the wide concept of air quality in two different sections. In this context, there will be an initial introductory chapter on the main concepts of air quality, following which there will be real case studies on outdoor and indoor air quality with an aim to provide a guideline for future standards and research works.

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