Determination of volatile organic compounds in ambient air by using thermal desorber, sorbent tubes, canister and GC-MS

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B-Tech: Chemistry

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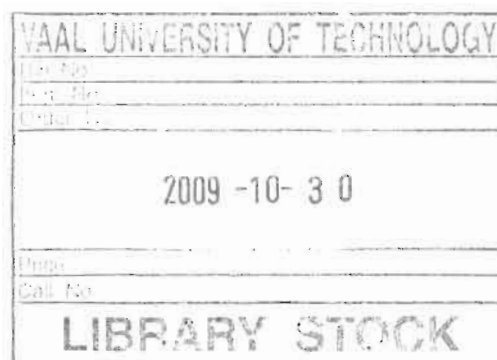
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Declaration

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree Magister Technologiae to the Department of Chemistry, Vaal University of Technology, Vanderbijlpark. It has not been submitted before for any degree or examination to any other university.

Signature:

Date 15 June 2009

Abstract

The dissertation deals with volatile organic compounds that evaporate from the water-oil separate in the refinery, which causes bad odour around the neighbouring communities, the existence of these compounds are being identified and quantified in different seasons for the year.

VOC are emitted whenever wastewater is exposed to the atmosphere. As such, emission points include open drains ditches, manhole sewer outfalls and surface fore bays, separators and treatment ponds. Refinery units such as reactors, fractionators are periodically shutdown and emptied for internal inspection and maintenance. The amount of VOC entering the wastewater is not monitored. The effluent water discharged from the refinery is not checked for the amount of VOC present. The monitoring of the amount of VOC in wastewater stream may lead to a decrease in the emission. From the quantified results at different season, the summer session has the highest VOC emission due to the heat that causes more vapours.

The preparation of a method for determination of VOC's in air presents many difficulties, because of their high volatilities and low concentrations in air. As well, the results of determination are affected by the properties of the sorbent used, mainly its sorption capacity, depending on the properties of the compound under determination. The methods for sampling and analytical procedures for the measurements of volatile organic compounds that are hazardous to air pollution are compendium method TO-14 and sorbent tube method compendium TO-17. Both methods (sorbent tube and canister) differ from each other in their extraction and detection techniques. The well suitable method for the VOC determination is canister method; this method gives more representative sample of the ambient monitoring of 24 hours, where as sorbent tube can do for 2 hours only. The canister method is more advantages due to the sample that will be still remaining for further analyses or re-check.

The integrity of API water-oil separator has been improved to cause less evaporation during high temperature season. As the temperature drops from season to season, the VOC also comes down as its being seen in this study that on the winter results that all the VOC were below 90 µg/kg.

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CHAPTER 1

INTRODUCTION AND PROBLEM STATEMENT

1.1 INTRODUCTION

Environmental pollution caused by refinery emissions may be classified as smoke and particular matter. Hydrocarbons and other gaseous compounds principally oxides of sulphur and nitrogen, including malodorous vapours will affect the health of millions of people. This also affects natural resources such as soil and water. (Stern, AC: 1968, 74-102)

The content of volatile organic compounds in air is considered as a fundamental parameter for assessing the quality of the atmosphere, because some compounds are acting as precursors of photochemical formation, whereas others represent a potential threat to human health. In addition to this, some specific components can contribute to global change, by depleting the stratospheric ozone (such as chlorofluorocarbons) to the radioactive of the earth (such as methane and dimethylsulfide). (Stern, AC: 1968, 74-102)

The detection of volatile organic compounds from atmosphere can go to low level from ppb to ppt. Different sampling and analytical strategies have been developed and applied for identification and quantification of volatile organic compounds in air. With few exceptions sample enrichment is needed in order to meet the sensitivity of the systems. However, different sampling and analytical methods are necessary to cover the full range of volatile organic compounds released or formed in air. If very volatile VOC (component with a vapour pressure higher than 15 kpa) need to be determined, sampling is usually performed on passivated canisters since this system does not provide sample preconcentration. Volatile organic compounds must be concentrated prior to being analyzed by gas chromatograph. (Tipler, A: 1994, 25-43)

For air pollution odour measurement problems occur in four different pairing; (a) effluent source, (b) ambient air, (c) relatively pure compounds, (d) mixture of known or unknown components, in varying concentration.

Odour measurement at the source is the easiest and most accurate for obtaining useful data for odour abatement, whether for pure compounds or mixtures. The concentration of the odour in the stack is usually high, and its presence is assured by its continual outflow. It is undisturbed by wind or atmospheric conditions and a sample may readily be drawn. Ambient odour on the other hand is often weak, even when at the complaint level and may be several thousand dilutions below that in the stack. If the odour is a relatively pure single compound that can be isolated, its threshold and behaviour downwind can be determined by simple analytical and mathematical techniques. (Wallace, L.A: 1996. 1129-1136)

Oil refining technology intricacy of petroleum refining processes and understanding of air pollution control techniques is necessarily depended on the general knowledge of oil industry manufacturing operation. Although a modern refinery is unique in design and contains a composite of many processes employing a multitude of towers, vessels, piping, valves, tubes, exchangers and storage tanks, the operations can be classified into four basic procedures-separation, conversion, treating and blending. (Stern, AC: 1968, 74-102)

Crude oil is initially separated into its various components or fractions (gas, gasoline, kerosene, middle distillates and heavy bottoms), since these initial fractions seldom conform to either the relative demand for each product or to its qualitative requirements. The estimation and evaluation of refinery atmospheric emissions is an immensely complicated project. Individual refineries vary greatly as to the character and quantity of emission. Controlling factors include crude oil capacity, type of crude processed, type and complexity of the processing employed. Air pollution control measures in used and the degree of maintenance and good housekeeping procedures in force. (Pitts, J.N: 1999, 515-527)

1.2 PROBLEM STATEMENT

Oily waters are produced at various stages of refinery processes and these oily waters contribute significantly to atmospheric volatile organic compounds emission that pollutes the air. The oily waters are typically transferred to gravity type water/oil separators for recovery of the oil. Some of the oil floats on the surface of the separator, directly in contact with the atmosphere and a portion of the light hydrocarbons will evaporate. Evaporation is exacerbated at high temperature and with increased turbulence.

The vapour that comes from the oil/water separator causes a bad odour which is a nuisance to humans. It is thus proposed to identify those compounds and quantify them in order to have a valid database of compounds that exist and originate from the refinery.

1.3 PURPOSE OF THE STUDY

The refinery has monitored ambient air over the past four years for BTEX compounds by using the method ISO 17016-1 (reference method EPA TO 17). This method is about the absorption of ambient air onto sorbent tubes. Since 2004 the same sampling method was used with a GC-MS, therefor it was proposed to upgrade the system to fully function on EPA TO-14 method. Currently a number of unknown odours can be detected within the boundaries of refinery which needs to be investigated.

1.4 OBJECTIVES OF THE RESEARCH

The general objectives will be achieved by the following specific objectives:
1.   Sampling method for ambient air (developing analytical methods)
2.   Determination of specific compounds in ambient air by using GC-MS and thermal dersober
3.   Determination of the origin of odours at API
4.   Determination of ambient air quality within the NATREF versus ambient air quality within 2 km

1.5 VALUE OF THE RESEARCH

The study will assist to control and minimise these volatile organic compounds by preventing hydrocarbons from contaminating refinery storm water, drainage fugitive and cooling water systems as far as possible and help achieve good air quality control. These experiments will be carried out at the National Petroleum of South Africa laboratory and continuous meetings will be held to assess progress and to strategize accordingly.

1.6 EXPECTED OUTCOME

Classification of odour measurements in the refinery.

The best method of analysing ambient air between sorbent tubes and canisters.

Improved air quality assurance protocols.

Compliance monitoring and data management system.

CHAPTER 2

LITERAURE SURVEY

2.1 DEFINNING AIR POLLUTION

The presence of air pollution in the atmospheric environment natural and artificial substance that affect human health, and the well-being of any other specific organism. Pragmatically, air pollution also applies to situation where contaminants impact structures and artifacts or esthetic sensibilities, such as visibility or smell. Most artificial impurities are injected into the atmosphere at or near earth surface. The lower atmosphere (troposphere) cleanses itself of some of these pollutants in a few hours or days as the large particles settle to the surface and soluble gases and particles encounter precipitation or are removed through contacts with surface objects. Unfortunately the removal of some pollutants (sulfates, and nitrates) by precipitation and dry deposition results in acid deposition, which may cause serious environmental damage. Also, mixing of the pollutants into the upper atmosphere may dilute the atmosphere including the ozone layer. (Atkinson, R: 2000, 2061-2063)

Human exposure to airborne chemicals vary widely among inhalation microenvironment categories, which include work place, residences, outdoor ambient air, transportation, recreation areas and public places. The are also wide variations in exposure within each category depending on the number and strength of the source of the airborne chemicals, the volume and mixing characteristics of the air within the defined microenvironment, the rate of air exchange between indoor and outdoor air and the rate of loss surface within the microenvironment. (Atkinson, R: 2000, 2061-2063)

2.2 TYPES OF AIR POLLUTION

Air pollution is a general term that covers a broad range of contaminants in the atmosphere. Pollution can occur from natural causes or from human activities. Discussions about the effects of air pollution have focused mainly on human health but attention is being directed to environmental quality and amenity as well. Air pollutants are found as gases or particles, and on a restricted scale they can be trapped inside buildings as indoor air pollutants. Urban air pollution has long been an important concern for civic administrators, but increasingly, air pollution has become an international problem. (Saunders, K.J: 1988, 145-180)

The most characteristic source of air pollution has always been combustion processes. Here most obvious pollutant is smoke. However, the widespread use of fossil fuels have made sulphur and nitrogen oxide pollutants of great concern, with increasing use of petroleum based fuels, a range of organic compounds have become widespread in the atmosphere. (Saunders, K.J: 1988, 145-180)

2.2.1 NATURAL AIR POLLUTION

Whilst man-made pollution and poor air quality is a major environmental concern, there are many natural source of pollution which are often much greater than their man-made counterparts. Natural source of sulphur dioxide include release from volcanoes, biological decay and forest fires. Actual amounts released from natural source in the world are difficult to quantify. In 1983 the United National Environment Programme estimated a figure of between 800 million and 288 million tones of sulphur oxides per year as compared to around 69 million tonnes from human sources world-wide. (Edwards, RD & Jurvelin, J: 2001, 4526-4531)

Natural source of nitrogen oxides include volcanoes, oceans, biological decay and lightning strikes. Estimates range between 20 million and 90 million tones per year of nitrogen oxides released from natural sources as compared to around 24 million tonnes from human sources worldwide. Ozone is a secondary photochemical pollutant formed near ground level as a result of chemical reactions taking place in sunlight. About 10% to 15% of low level ozone, however, is transported from the upper atmosphere (stratosphere), where it is formed by the action of ultraviolet radiation on oxygen (the ozone layer). (Edwards, RD & Jurvelin, J: 2001, 4526-4531)

Natural source of particular matter are less important than man-made source. These include volcanoes and dust storms. However, such sources do account for intense high particular pollution episodes, occurring over relatively short times scale. Volatile organic compounds are naturally produced by plants and trees. Isoprene is a common VOC emitted by vegetation, and some believe it to be a more significant trigger for asthma an allergic reaction than man-made irritants. Plants, grass and trees are also a source of pollen, which can act as triggers in some asthmatic. (Ciccioli, P: 1993, 55-69)

2.2.2 ANTHROPOGENIC AIR POLLUTION

Anthropogenic air pollution comes from many different human activities which occur during our daily lives. Sources include industry, vehicles, agriculture, power generation (coal, oil, or gas power station), mining and waste dumps. It is difficult for the atmosphere to cope with these extra pollutants leading to high concentrations locally and regionally. Air pollution is basically divided into two groups. a) Gases that come mainly from the burning of fossil fuels. b) Gaseous pollutants which affect the atmosphere globally including carbon dioxide, methane and nitrous oxide. These are all greenhouse gases and are responsible for global warning. Although at present throughout much of the atmosphere, gaseous pollutants including nitrogen oxides, sulphur dioxide, carbon monoxide and a wide range of organic compounds are found

only in significant concentrations close to their origin. All these compounds are released during fossil fuel burning although many volatile organic compounds also have significant natural source from plants. (Edwards, RD & Jurvelin, J: 2001, 4526-4531)

2.3 COMMON TYPES OF POLLUTION

The types of air pollution include particulates, noxious fumes, sulphur dioxide and smog. Particulates come from energy production, dust and every day living. Noxious fumes are created in manufacturing, released from building finishes and furnishing, and energy production (Hattermer-Frey, H.A: 1990, 221-232)

2.3.1 SMOG

Smog is chemical mixture of gases that forms a brownish yellow haze primary over urban areas. Components of smog include ground level ozone, nitrogen oxides, volatile organic compounds, sulphur dioxide, acidic aerosols and gases and particular mater. These gases result from a reaction between certain airborne pollutants and strong sunlight. Smog is most prevalent in the summer months, when there is most sunlight and temperatures are high. In large enough quantities, it poses threats to the animals, plants, and human life. The airborne pollutant which makes up 90% of all smog found in urban areas is ground level ozone. (Wallace, L.A:1996. 1129-1136)

The formation of ground level ozone occurs as a result of a chemical reaction between several distinct forms of pollutants and sunlight. Two groups of chemical pollutant are involved: nitrogen oxides and volatile organic compounds. When stagnant air masses linger over urban

areas, the pollutants are held in place for long periods of time. Sunlight interacts with these pollutants transforming them into ground level ozone. The ozone remains in the lower atmosphere until weather system flush out a given area and dissipate them. An 'episode' of ground level ozone can last from several hours to several days. (Wallace, L.A: 1996. 1129-1136)

2.3.2 SULPHUR DIOXIDE

Historically, sulphur dioxide derived from the combustion of fossil fuels has been the main components of air pollution in many parts of the world. The most serious problems have been experienced in large urban areas where coal has been used for domestic heating purposes, or for poorly controlled combustion in industrial installations. In such situations the complex of pollutants has generally been considered collectively, drawing on findings from epidemiological studies done several decades ago in areas formerly heavily polluted. Guidelines developed in this way had been related to averaging times of 24 hours in respect of acute effects and one year in respect of chronic effects. (Wolkoff, P: 1996, 151-157)

Separate attention has been given to sulphur dioxide alone, based largely on findings from controlled human exposure studies. These allow guidelines to be developed in terms of shorter averaging periods, of the order of one hour. These are relevant to exposures to peak concentrations that may arise from source burning coal or heavily oil, whether or not accompanied by substantial concentrations of particulates. Epidemiological studies published in the last decade provide further evidence on the health effects of sulphur dioxide. Thus a section has been introduced in this revision focusing on epidemiological results in locations where the pollution are mainly motor vehicles and various industries. Sulphur dioxide is derived from the combustion of sulphur-containing fossil fuels and is a major air pollutant in many parts of the world. Oxidation of sulphur dioxide, especially at the surface of particles in the presence of metallic catalysts, leads to the formation of sulphurous and sulphuric acids.

Neutralization by ammonia leads to the production of bisulfates and sulfates. Sulphur dioxide is a colourless gas that is readily soluble in water. Sulphuric acid is a strong acid that is formed from the reaction of sulphur trioxide gas with water. (Wolkoff, P: 1996, 151-157)

2.3.3 PARTICULAR MATTER (PM$_{10}$, PM$_{2.5}$)

Airborne particular matter represents a complex mixture of organic and inorganic substance. Mass and composition in urban environments tend to be divided into two principal groups: (a) coarse particle, (b) fine particle. The barrier between these two fractions of particles usually lies between 1µm and 2.5 µm. However, the limit between coarse and fine particle is sometimes fixed by convention at 2.5 µm in aerodynamic diameter (PM$_{2.5}$) for measurement purposes. The smaller particles contain the secondary formed aerosols (gas-to-particle convection), combustion particles and recondensed organic and metal vapours. ((Kennedy, D: 1988, 456-510)

The large particles usually contain earth crust materials and fugitive dust from roads and industries. The fine fraction contains most of the acidity (hydrogen ion) and mutagenic activity of particular matter; although in fog some coarse acid droplets are also present. Whereas most of the mass is usually in the fine mode (particles between 100 nm to 2.5 µm), the largest number of particle is found in the very small sizes, less than 100 nm. As anticipated from the relationship of particle volume with mass, these so-called ultrafine particles often contribute only a few percent to the mass, at the same time contributing to over 90% of the numbers. (Kennedy, D: 1988, 456-510)

Particular air pollution is a mixture of solid, liquid or solid and liquid particles suspended in the air. These suspended particles vary in size, composition and origin. It is convenient to classify particles by their aerodynamic properties because: (a) these properties govern the transport and removal of particles from air; (b) they also govern their deposition within the respiratory system and (c) they are associated with the chemical composition and sources of particles. The

size of suspended particles in the in the atmosphere varies over four orders of magnitude, from a few nanometres. The largest particles, called the coarse fraction (or mode), are mechanically produced by the break-up of larger solids particles. These particles can include wind-blown dust from agricultural processes, uncovered soil, unpaved roads or mining operations. (Kennedy, D: 1988, 456-510)

Traffic produces road dust and air turbulence that can strip up road dust. Near the coast, evaporation of sea spray can produce large particle, Pollen grains, mould spores and plant insect parts are all in this larger range. The amount of energy required to break these particles into smaller sizes increases as the size decreases, which effectively establishes a lower limit for the production of these coarse particles of approximately $1\mu m$. Smaller particles, called the fine fraction or mode are largely formed from gases. The smallest particles, less than $0.1\mu m$ are formed by nucleation that is condensation of low-vapour pressure formed by high temperature vaporizations or by chemical reaction in the atmosphere to form new particles (nuclei). Four major classes of sources with equilibrium pressures low enough to form nuclei mode particles can yield particular matter. (a) Heavy metals (vaporized during combustion), (b) elemental carbon (from short carbon molecules generated by combustion), (c) organic carbons and (d) sulfates. Particle in this nucleation range or mode grow by coagulation, that is, the combination of two or more particle to form a larger particle, or by condensation, that is a condensation of gas or vapour molecules on the surface of existing particles. (Rasmussen, RA & Grosjean, E:1998, 2061-2084

Coagulation is most efficient for large numbers of particles, and condensation is most efficient for large surface areas. Therefore the efficiency of both coagulation and condensation decreases as particle size increases, which effectively produces an upper limit such that particles do not grow by these processes beyond approximately 1 μm. (Rasmussen, RA & Grosjean, E: 1998, 2061-2084

2.4 CRUDE REFINERY PROCESSING UNITY

Petroleum fractions contain various amounts of naturally occurring contaminants, the most important ones being organic sulfur, nitrogen and metal compounds. These contaminants, if not removed contribute to increased levels of air pollution and equipment corrosion, and in some cases would cause difficulties in the further processing of the material. The distillate hydrotreating process is a catalytic hydrogenation method used to upgrade the quality of petroleum distillate fractions such as catalytic and thermally cracked distillates. The vacuum gas oil decomposes the contaminants with a negligible effect on the boiling range of the feed. (UOP training service: 2004, 4-98)

The desired degree of hydrotreating is obtained by processing the feed stock over a fixed bed of hydrotreating catalyst in the presence of large amounts of hydrogen, and at temperatures and pressures that depend on the nature of the feed as well as the amount of contaminant removal required. Naphthans used, as feedstocks to catalytic reforming units must be hydrotreated to such an extent that they are essentially free from all contaminants. (UOP training service: 2004, 4-98)

The activity and the selectivity of the hydrotreating catalyst are influenced, to a slight extent by the type of feed processed. Therefore, the same catalyst, but in varying quantities can be used to hydrotreat everything from a straight-run naphtha to vacuum gas oil including catalytic and thermal cracked distillates. The widespread use of catalytic reforming units has made available large quantities of excess hydrogen, making feasible to hydrotreat many or all distillates produced by the refinery. The are five process applications that must be followed when doing hydrotreating technology.

1) Straight-run naphtha – catalytic reformer fee: the product must meet all the requirements of reformer feed which, in most cases will call for a simple desulfurization to 0.5ppm sulfur. The

nitrogen contents of straight-run naphtha derived from a few crudes are in excess of that acceptable for reformer operation and in such cases denitrification as well as desulfurization are required. (UOP training service: 2004, 4-98)

2) Straight-run kerosine: kerosene usually requires the removal of sulfur down to 0.01 ppm and stripping to meet a specified initial boiling point or flash point. The amount of stripping required depends on the fragments formed during desulfurization, thus on the sulfur of raw stock. Operations of a hydrotreating unit for smoke-point improvement of kerosine stock are relatively severe operation. The degrees of smoke-point improvement that can be obtained depend upon both the aromatic content and paraffin content of the kerosine being treated. (UOP training service: 2004, 4-98)

3) Straight-run diesel and heavier oils: naturally occurring sulfur increases with the boiling range of the fraction recovered from most crude oils but, in many cases the product specification becomes less stringent as the fraction to be processed becomes heavier. The degree hydrotreating required on these heavier stocks generally will depend entirely on the refiner's need to meet the specific requirements related to the final product. (UOP training service: 2004, 4-98)

4) Reactor section: feed can enter the unit either from intermediate storage or from another process unit. In this case of feed from storage, the tank must have been gas blanket to prevent oxygen form dissolved in the naphtha. Even trace quantities of oxygen or olefin in the feed can cause polymerization of olefins in the storage tank when stored for long periods or in the combined feed/reactor effluent exchangers if the feed is not prestripped. (UOP training service: 2004, 4-98)

5) Stripping section: the liquid hydrocarbon in the separator is maintained at a constant level by a level controller. The liquid hydrocarbon exit the separator under pressure through this controller, and flow through a stripper feed/bottom exchanger, where they gain heat before entering near the top of the stripper. A boiler is provided to supply the required heat input for generating vapour. This vapour strips hydrogen sulphide, water, light hydrocarbons and dissolved hydrogen from the feed to the stripper. The stripped feed then flows through an overhead condenser into the overhead receiver. Normally, no net overhead liquid product is produced and all of the liquid in the receiver is pumped back to the stripper as reflux. (UOP training service: 2004, 4-98)

The are six basic types of reactions that occur in the hydrotreating unit, namely

1) Conversion of organic sulfur to hydrogen sulphide

2) Conversion of organic nitrogen compounds to ammonia

3) Conversion of organic oxygen compounds to water

4) Saturation of olefins

5) Conversion of organic halide to hydrogen halide

6) Removal organo-metallic compounds

2.4.1 SULFUR REMOVAL

The reactions that take place on sulfur removal

$CH_3\text{-}CH_2\text{-}CH\text{-}SH + H_2 \rightarrow CH_3\text{-}CH_2\text{-}CH_3 + H_2S$ mercaptan

$CH_3\text{-}CH\text{-}S\text{-}CH\text{-}CH_3 \rightarrow 2CH_3\text{-}CH_3 + H_2S$ sulphide

$CH_3\text{-}CH\text{-}S\text{-}S\text{-}CH\text{-}CH_3 \rightarrow 2\ CH_3\text{-}CH_3 + 2H_2S$ disulphide
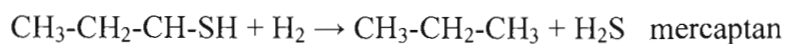
For reforming catalyst, feed naphtha must contain less than 0.5wt-ppm sulfur to optimize the selectivity, and the stability characteristics of the catalyst. In general sulfur removal in the hydrotreating process is relatively easy. For the best operation of a reformer, the hydrotreated naphtha sulfur content should be maintained well bellow the 0.5wt-ppm maximum. However

to operate at too high temperature for maximum sulfur removal it is possible. Recombination of hydrogen sulphide with small amounts of olefins or olefins intermediates can then result, producing mercaptants in the product. If this is occurring, the reactor temperature must be lowered. (UOP training service: 2004, 4-98)

2.4.2 NITROGEN REMOVAL

The reactions that take place

$+ 5H_2 \longrightarrow$ C-C-C-C (and C-C-C-C) + NH_3

$+ 4H_2 \longrightarrow$ $+ NH_3$

$+ 4H_2 \longrightarrow$ C-C-C-C (and) $+NH_3$
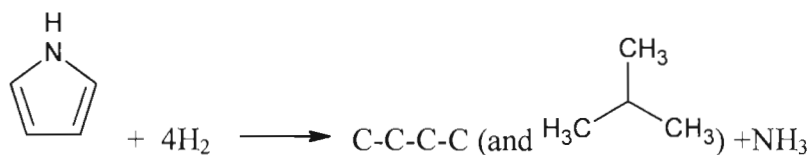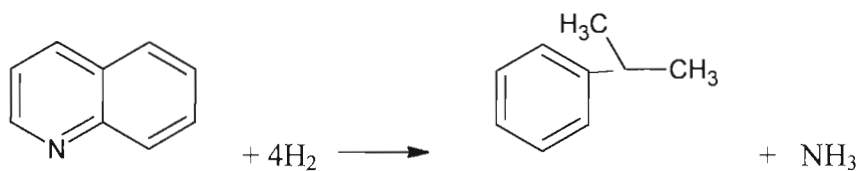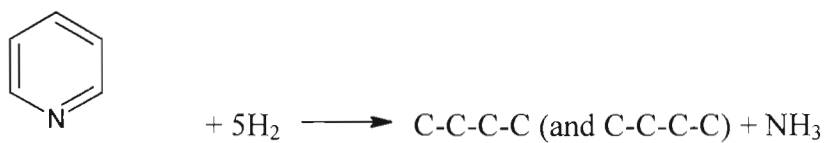
Nitrogen removal is considerably more difficult than sulfur removal. The rate of identification is only about one-fifth the rate of desulfurization. Most straight –run naphtha contain much less nitrogen than sulfur, but attention must be given to ensure that the feed naphtha to a bimetallic reforming catalyst contains a maximum of 0.5 wt-ppm nitrogen and normally much less. Any organic nitrogen that does enter the reformer will react to ammonia and further with the chloride in the recycle gas and form ammonium chloride. The ammonium chloride then deposits in the recycle gas circuit or stabilizer over head system.

This problem can be very annoying and time consuming, but it can be avoided or minimized by maximizing nitrogen removal in the naphtha hydrotreating unit. (UOP training service: 2004, 4-98)

2.4.3 OXYGEN REMOVAL

The reactions that take place

OH
|
$\bigcirc$ + H$_2$ $\longrightarrow$ $\bigcirc$ + H$_2$O
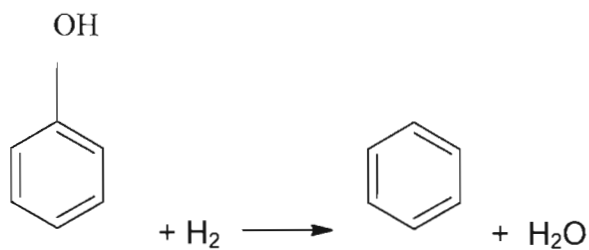
Organically combined oxygen, such as phenols is removed by hydrogenation of the carbon hydroxyl bond forming water and the corresponding aromatic molecule. (UOP training service: 2004, 4-98)

2.4.4 OLEFINS SATURATION

The reactions that take place

C-C=C-C-C-C + H$_2$ $\longrightarrow$ C-C-C-C-C-C
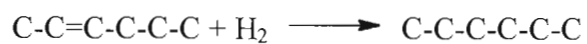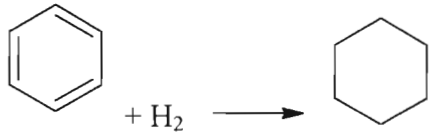
Olefin saturation is almost as rapid as desulfurization. Most straight-run naphtha contains only trace amounts of olefins, but cracked naphtha usually have high olefin concentrations. Processing high concentration olefin in a hydrotreating must be approached with care because of the high exothermic heat of reaction associated with the saturation reaction. (Whatcom,C & Island, S: northwest air pollution authority. 2004,1-77)

2.4.5 HALIDE REMOVAL

The reactions that take place

$HCl + NH_3 \longrightarrow NH_4Cl$
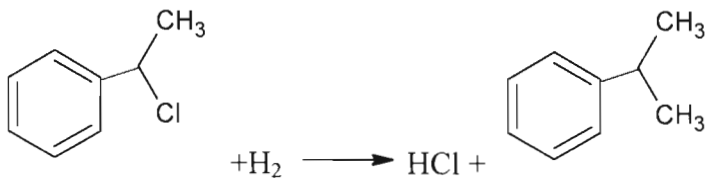
Organic halides can be decomposed in the hydrotreating unit to the corresponding hydrogen halide, which is either absorbed in the reactor effluent water wash or taken overhead in the stripper gas. Decompositions of organic halides is much more difficult than desulfurization. Maximum organic halide removal is thought to be about 90%, but is much less at operating conditions set for sulfur and nitrogen removal only. For this reason periodic analysis of hydrotreating naphtha for chloride content should be made, since this chloride level must be used to set the proper reformer chloride injection rate. (Whatcom,C & Island, S: 2004,1-77)

2.4.6 METAL REMOVAL

Most metallic impurities occur at the part per billion levels in naphtha. Some catalysts are capable of removing these materials at fairly high concentration, up to 5wt-ppm or more intermittent basis at normal operating conditions. Most metallic impurities are permanently deposited on the catalyst when removed from the naphtha. The catalyst loses activities for sulfur removal as higher metal loadings are reached. Some commonly detected components found on the used catalyst are arsenic, iron, calcium, magnesium phosphorus, lead, silicon, copper and sodium. Removal of metal from the feed normally occurs in plug flow with respect to the catalyst bed. Iron is found concentrated at the top of the catalyst beds as iron sulfides. (UOP training service: 2004, 4-98)

Arsenic, even though rarely found in excess of the 1 wt-ppb in straight-run naphtha, is of major importance because it is a potent platinum poison. Arsenic level of 3 wt-percent and higher has been detected on used catalysts that retain their activity for sulfur removal. Contamination of storage facilities by lead gasoline and reprocessing of lead gasoline in crude towers are the common sources of lead on used catalyst. Sodium, calcium and magnesium are apparently due to contact of the feed with salt water or additives. (UOP training service: 2004, 4-98)

The additives are added to protect fractionator overhead system from corrosion or to control foaming accounts for the presence of phosphorus and silicon. Removal of metals is essentially complete above temperatures of 315°C up to a total metal loading of about 2-3wt-% on the catalyst. Above this level, the catalyst begins approaching the equilibrium saturation level rapidly and metal breakthrough is likely to occur. In this regard, mechanical problems inside the reactor such as channelling are especially bad since it result in a substantial overload on a small portion of the catalyst in the reactor. (UOP training service: 2004, 4-98)

2.4.7 CATALYTIC OF REFORMER HYDROCARBON CHEMISTRY

Feed naphtha to a catalytic reforming unit typically contains C_6 through C_{11} paraffins, naphthenes and aromatics. The purpose of the platforming process is to produce aromatics from naphthenes and paraffins, either for the use of motor fuel or as the source of specific aromatics compounds. In the motor fuel applications, the feed naphtha generally contains the whole range of C6 through C11 hydrocarbons essentially maximizing the amount of produced from the crude run. In aromatics applications, the feed naphtha contains a more selected range of hydrocarbons (C6, C6-C7, C6-C8, or C7-C8), which serves as the source of the desired aromatic products. (Mckay, W.A & Pierce, T: 1995, 8873-8892)

For application, the basic naphtha chemistry is identical. In most cases, however aromatics processing emphasizes C_6 and C_7 hydrocarbons reactions. Naphthas from various crude sources vary greatly in their "ease of reforming". This "ease of reforming" is primarily determined by the amount of various hydrocarbons types (paraffins, naphthenes, aromatics) contained in the naphtha. Aromatics hydrocarbons pass through the unit essentially unchanged. Most naphthenes convert rapidly and efficiently to aromatics. This is a basic reaction of platforming. Paraffins are the most difficult compounds to convert. In the most low severity applications, there is a small amount of paraffins conversion to aromatics. In high severity applications, paraffin conversion is low and inefficient and constitutes the real challenge to the process and catalyst. In the catalytic reforming process, there are six reforming reactions that took place. (Mckay, W.A & Pierce, T: a global model of natural VOC emission. *journal of geophysical research, 1995, 8873-8892)*

2.4.7.1 DEHYDROGENATION OF NAPHTHENES

Dehydrogenation of naphthenes is the final step in the formation of an aromatic from naphthenes (either a cyclohexane or a cyclopentane) is the dehydrogenation of a cyclohexane. The reaction of a cyclohexane to the corresponding aromatic is extremely rapid and essentially quantitative. Naphthenes are obviously the most desirable feed components because the

dehydrogenation reaction is easy to promote and produces by-product hydrogen as well as aromatic hydrocarbons. (Fishbein, L: an overview of environmental and toxic aspects of aromatics hydrocarbon. 1984, 189-218)

a) Isomerization of paraffins and naphthenes

The isomerization of an alkylcyclopentane to an alkylcyclohexane must occur as the first step in converting the cyclopentane to an aromatic. This isomerization involves ring rearrangement and probability for rind opening to form paraffin is quite high. Therefore, this reaction of alkylcyclopentanes to cyclohexanes is not quantitative. The reaction is strongly dependent on the processing conditions. Paraffin isomerization occurs readily in commercial catalytic reforming operations. (Fishbein, L: an overview of environmental and toxic aspects of aromatics hydrocarbon. 1984, 189-218)

At typical temperatures, however the thermodynamic equilibrium is only slightly in favour the more desirable (high octane) branched isomers. In the motor fuel applications, this reaction does not make a contribution to octane improvement of the naphtha. Isomerization reactions are promoted by an acidic catalyst function and are not dependent on operating pressure. (Fishbein, L: 1984, 189-218)

b) Dehydrocyclization of paraffin

Dehydrocyclization of paraffin is the most difficult catalytic reforming reaction to promote. It consists of a very difficult molecular arrangement from paraffin to naphthene. In the case of light paraffins, equilibrium considerations limits this reaction. The paraffin cyclization step becomes easier as the molecular weight of the paraffin increases because of increased statistical

probability for the formation of the naphthene. Somewhat counteracting this effect is the increased probability of the heavier paraffin to hydrocrack. Dehydrocyclization is favoured by low pressure and high temperature. Both metal and acid catalyst functions are needed to promote this reaction. ((Fishbein, L: 1984, 189-218)

c) Hydrocracking

Alkylcyclopentane and paraffin feedstock components undergo strained ring isomerization and ring formation reactions and therefore because the catalyst needs to have the acid function. The possibility for acid promoted hydrocracking is strong. Paraffin hydrocracking is relatively rapid and is favoured by high pressure and temperature. (Fishbein, L: 1984, 189-218)

The disappearance of paraffin for the gasoline boiling range via hydrocracking does concentrate aromatics in the product and hence, contributes to octane improvement. The reactions, however consume hydrogen and result in lower reformate yield.

d) Demethylation

Demethylation reactions generally occur only in very severe catalytic reforming operations (high pressure and high temperature). Under certain conditions, they may occur during the initial start up of a unit following catalyst replacement or regenerations. The reaction is metal catalyzed and is favoured by high temperature and pressure. It can be inhibited by attenuation

of the metal catalyst function by addition of sulfur or second metal (as in some bimetallic catalysts). (Fishbein, L: 1984, 189-218)

e) Dealkylation of aromatics

The dealkylation of aromatics is similar to aromatic demethylation, differing only in the size of the fragment removed from the ring. If the alkyl side chain is large enough, this reaction can be visualized as acid catalyzed carbonium ion cracking of the side chain. The dealkylation reaction is also favored by high temperature and pressure. Feeds contain a wide range of paraffin and naphthenes, because the reaction rates vary considerably with the carbon number of the reactant. Reactions occur in series and parallel to each other. (Fishbein, L: 1984, 189-218)

f) Relative reaction rate

The primary reactions for the C_6 and C_7 paraffin proceed at significantly different rates. The rate of dehydrocyclization for hexane is only one third that of hydrocracking so the fraction of normal hexane converted to benzene is relatively low. (Fishbein, L: 1984, 189-218)

Normal heptane hydrocracks at about same rate as normal hexane, so the faster rate of dehydrocyclization (about four times that of hexane) leads to significantly greater fraction conversion to aromatics for normal heptane in comparison to normal hexane. Both paraffins are isomerized very rapidly to the various possible isomers. (Fishbein, L: 1984, 189-218)

Reactions of the naphthenes show marked differences between the alkylcyclopentanes and alkylcyclohexanes. Both cyclohexanes dehydrogenate are very rapidly to produce aromatics. The cyclohexane reacts at a much slower rate and undergo both isomerization to the corresponding cyclohexane and decyclization to paraffin. The ratio of the isomerization rate to

the total rate of reaction (isomerization plus decyclization) is an indication of the expected selectivity to aromatics for the alkylcyclopentanes. This ratio is 0.67 for methylcyclopentane and 0.81 for dimethylcyclopentane. The ease of isomerization increase with carbon number and C_{8+} alkylcyclopentanes have relatively high selectivities to aromatics. Therefore, paraffin shows the lowest reactivity and the poorest selectivity for aromatics formation. Alkylcyclopentanes, while more reactive and selective than paraffins, still provide less than quantitative yields of aromatics. The alkylcyclohexanes are converted very rapidly and quantitatively to aromatics. ((Fishbein, L: 1984, 189-218)

2.4.7.2 FLUID CATALYTIC CRACKING

Feedstocks for the fluid catalytic cracking process are complex mixture of hydrocarbons of various types, from small quantities of gasoline up to large molecules of 60 carbons atoms. The is a relative content of contaminant materials such as organic sulfur, nitrogen compounds, and organometallic compounds.

The relative proportions of all these materials vary with geographic origin of the crude and the particular boiling range of the fluid catalytic cracking feedstock. It is possible, however to rank feedstocks in terms of their "crackabilities", or the ease with which they can be converted in fluid catalytic cracking unit. (UOP training service: 2004, 4-98)

Crackabilities are a function of the relative proportion of paraffinic, naphthenic and aromatic species in the feed. Generally, one can correlate crackability of fluid catalytic cracking feedstocks with the uncracking operation process characterization factor. Sulfur compounds do not affect the crackability. The cracked sulfur compounds are distributed into liquid products, thus creating a need for product cleanup before final use. In addition, sulfur also exits from the fluid catalytic cracking in the form of hydrogen sulphide and sulfur oxides. (UOP training service: 2004, 4-98)

The organo-metallic compounds decompose on the circulating catalyst, with the metals remaining irreversibly deposited on the catalyst. These deposited metals have two rather serious deleterious effects. First; they affect the product distribution, causing more light gases, especially hydrogen to be formed. Second, they have a serious deactivating effect on the catalyst. This latter effects leads to more fresh catalyst makeup to maintain activity. Heavy polynuclear aromatic ring compounds are very refractory and it is generally accepted that these molecules are coke precursors. (UOP training service: 2004, 4-98)

The relative amounts of the above contaminants in the fluid catalytic cracker feed stock generally increase as the end point of the feedstock increases. As end point increase into the "nondistillable" range above $520^{\circ}C$, the increase in these contaminants is dramatic, thus posing a major processing problem.

One solution to this problem is to hydrotreat the FCC feedstock. Most of the sulfur and nitrogen leave the hydrotreat in relatively easily disposable forms of H_2S and NH_3. The metals are deposited irreversibly on the hydrotreating catalyst, which is periodically replaced. In addition to removing contaminants, hydrotreating upgrade the FCC feed. Ckrackability and hydrotreated feed do in fact crack with better product selectivity because of their increase hydrogen contents. A mechanism for catalytic cracking reactions is now generally accepted. All cracking catalysts are acidic materials and reactions of hydrocarbons over these materials are well known. (UOP training service: 2004, 4-98)

These reactions are fundamentally different from the thermal cracking. In the thermal cracking bond rupture is random; in catalytic cracking, it is selective. Various theories have been proposed to explain how the cracking process is initiated. One theory proposes that an ion is formed from an olefin which in turn, could be formed by thermal effects upon initial catalyst

oil contact, may be present in the feed. The temperatures involved in catalytic cracking are in the range where thermal cracking can also occur. Alternatively, the ion could be formed by interaction of the hydrocarbon molecule with and acidic site on the catalyst. (UOP training service: 2004, 4-98)

The ions can react in four ways: a) Crack to smaller molecules, b) React with other molecules, c) Isomerize to a different form and d) React with the catalyst to stop the chain. The subject of catalytic coke formation by cracking catalysts, especially its nature and how it is formed is also a complex topic for which many theories have been proposed. The formation of coke on the catalyst, an unavoidable situation in the catalytic cracking, is likely due to dehydrogenation and condensation reactions of polynuclear aromatics or olefins on the catalyst surface.

As coke is produced through these mechanisms, the H/C ratio of the coke increases until it becomes non-volatile and eventually blocks the active acid sites and catalyst pores. The only recourse is to regenerate the catalyst to retain its activity by burning the coke to CO and CO_2. (UOP training service: 2004, 4-98)

2.4.7.3 HYDROCRACKING

Partial conversion mode is used where the refiner desires a fuel oil product. The fractionator bottoms from the unit can be an excellent blending component for fuel oil either for marketing or low sulfur refinery fuel use. In addition, the fractionator bottoms material is an excellent source of desulfurized feedstock for other cracking processes. Kerosines have a high smoke point and low freeze point which make them excellent jet fuels. Diesel oils have a high cetane number. (UOP training service: 2004, 4-98)

Even the residue, produced in the once through operations being saturated make good FCC or ethylene unit feedstock. The flow scheme, catalyst and operation condition can be selected so that the product will be limited to naphtha and lighter hydrocarbons (no distillate fuels) or 60-70% of the product will be distillate fuels and the remainder naphtha and lighter. The Hydrocracking process can be used for Hydrocracking of middle distillates or vacuum gas oils to produce naphthans that can be processed further via catalytic reforming and solvent extraction for production of BTEX aromatics. A series flow processing scheme is often specified for this application in order to obtain high naphtha yields. (UOP training service: 2004, 4-98)

However, naphthas produced in single stage operations can also be upgraded for the production of BTEX aromatics. After recovering of BTEX aromatics by solvent extraction, the light gasoline and C_9-plus naphtha from the catalytic reforming operation are suitable for motor gasoline blending. Raffinate from the extraction operation may also be used for gasoline blending, although it has a low octane rating. (UOP training service: 2004, 4-98)

The hydrocracking process is carried out at elevated temperature and pressure over a fixed catalyst system where the fresh feed is cracked in a hydrogen atmosphere. The exact process conditions vary widely depending on the properties of the charge stock and the product desired. Hydrogen is consumed in all hydrocracking process. Carbon-to-carbon bonds in paraffins are broken and fragments hydrogenated to form two or lower molecular weight paraffins. Polycyclic aromatics are partially saturated and ring opening in one or more places follows, although at least one ring is usually retained. Dual-function catalyst containing both acid activity and hydrogenation-dehydrogenation activity are used. The reaction involved in hydrocracking can be classified as follows: (UOP training service: 2004, 4-98)

a) Contaminant removal by hydrogenation of sulfur, nitrogen, and oxygen compound

b) Hydrogenation of olefins to paraffins and polycyclic aromatics to monocyclic aromatics, both for subsequent hydrocracking

c) Hydrocracking C-C bonds to form lower molecular weight hydrocarbons

Depending on the feedstock and the end product desired, the proportions of the two catalyst functions can be varied. In addition, processing flow scheme and the operating conditions are chosen to enhance product selectivity. According one theory, the hydrocracking reactions are initiated by partial dehydrogenation over the metallic component in the catalyst to form olefins in very low concentration, which are rapidly adsorbed on an acid site and converted to carbonium ions. Skeletal rearrangement may also take place on the acid site. An adsorbed carbonium ion can crack into two fragments, an olefin and a smaller carbonium ion. (UOP training service: 2004, 4-98)

These fragments undergo further cracking but, at some critical molecular weight, they become hydrogenated on the metallic site, are desorbed from the catalyst and constitute final product. Petroleum products released into the environment undergo weathering processes with time. These processes include evaporation, leaching (transfer to the aqueous phase) through solution and entrainment (physical transport along with the aqueous phase), chemical oxidation, and microbial degradation. The rate of weathering is highly dependent on environmental conditions. For example, gasoline, a volatile product will evaporate readily in a surface spill, while gasoline released below 10 feet of clay topped with asphalt will tend to evaporate slowly. (UOP training service: 2004, 4-98)

Evaporation processes are very important in the weathering of volatile petroleum product, and may be the dominant weathering process for gasoline. Automotive gasoline, aviation gasoline contain 20% to 90% highly volatile component. Leaching processes introduce hydrocarbon into water and atmosphere. (UOP training service: 2004, 4-98)

Aromatics and especially BTEX tend to be the most water soluble fraction of petroleum. Petroleum contaminated groundwater tends to enriched in aromatics relative to other petroleum constituents. Relatively insoluble hydrocarbons may be entrained in water through adsorption into kaolinate particle suspended in the water or as an agglomeration of oil droplets. It is not unusual for a plume of water-soluble aromatics to radiate out from the origin of the spill. Storm drains, pipes and utility lines may provide conduits for water and water-soluble hydrocarbons. Generally, entrained hydrocarbons are found in water close to the petroleum source, while dissolved aromatics may be found quite far from the origin of a spill. Oxygenates, such as methyl-butyl ether, is even more water-soluble than aromatics and high mobile in the environment. (UOP training service: 2004, 4-98)

2.5 PHOTOCHEMICAL OXIDANTS

Biodegradation processes can be very complex. The extent of biodegradation is dependent on many factors including the type of micro-organisms present, environmental conditions (temperature, oxygen levels, and moisture), Predominant hydrocarbons types and bioavailability of hydrocarbons contaminants. The primary factor controlling the extent of biodegradation is the molecular composition of the soil contaminant. Multiple ring cycloalkanes are harder to degrade, while PAH display varying degrees of degradation, n-alkanes biodegrade rapidly with branched alkanes and single saturated ring compounds. (Jayanty, KRM, Atmos.Environ: 1989,23-52)

Photochemical oxidant formation primarily occurs in the boundary layer, which is the region of the lower atmosphere or troposphere closest to the ground. The troposphere itself is divided into two parts, the boundary layer and the free or background troposphere. The boundary layer reaches from the ground 1-3 km whilst the free troposphere extends from the boundary layer up to the tropo-pause at between 8 and 13km. The actual heights vary with the time of day, season and the latitude. (Jayanty, KRM, Atmos.Environ: 1989,23-52)

It should be noted that the maximum in the ozone concentration occurs in the stratosphere and forms the so-called ozone layer. Stratosphere ozone is a significant source of the ozone found in the troposphere. It will be useful to give definitions of the terms 'hydrocarbon' and 'volatile organic compounds'. The term hydrocarbon strictly refers to compounds containing only carbon and hydrogen. The more general term, volatile organic compound has therefore been adopted to cover not only hydrocarbons but also compounds of carbon and hydrogen containing other element, such as oxygen nitrogen, chorine and sulphur. (Jayanty, KRM, Atmos.Environ: 1989,23-52)

There are large numbers of volatile organic compounds in use in modern society and most of these are eventually emitted into atmosphere. The emissions vary greatly in the magnitude and in spatial extent. The degree to which each volatile organic compound contributes to ozone formation will differ but in general, four key factors have been identified of which, two are specifically related to emission:

1) The molecular mass of the volatile organic compound as emission inventories are typically quoted as a mass emission.

2) The total amount of the volatile organic compound emitted into the atmosphere

3) The reactivity of the hydrocarbon with OH radicals

4) The chemical structure

Therefore, if the role of individual hydrocarbons in photochemical pollution formation is to be assessed, it is of paramount importance that the emission inventory accounts not only for the total mass of volatile organic compounds emitted into atmosphere but also their specification. A complete and quantitative description of all the major degradation pathways must also be known if the role of each VOC is to be determined. The mechanism by which hydrocarbons are degraded in the atmosphere is complex and involves the following steps. (Jayanty, KRM, Atmos.Environ: 1989,23-52)

2.6 INITIATION REACTION

These reactions can be initiated by ozone itself, the active radicals, OH and NO_3 or solar radiation (photolysis). For saturated compounds, the only initiation reaction of importance is the reaction with OH radicals. For unsaturated compounds, OH and to a lesser extent, O_3 and NO_3 are important in initiating the degradation. Photolytic processes compete with OH radicals in the degradation of carbonyl and aldehydes which absorb solar radiation in the near ultraviolet (280nm $< \lambda <$ 310nm). The reaction with OH radicals involves the addition of or abstraction of H-atoms to form a reactive intermediate which, under tropospheric condition forms a peroxy radical, RO_2

$$RH + OH \rightarrow R + H_2O \qquad \qquad 2.1$$
$$R'H + OH + M \rightarrow R + M \qquad \qquad 2.2$$
$$R + O_2 + M \rightarrow RO_2 + M \qquad \qquad 2.3$$

The OH radicals are generated from a number of sources. Photolysis of ozone in the near ultraviolet produces an excited O atom, O (^{1}D), which react with water to produce OH radicals

$$O_3 + h\nu \rightarrow O (^1D) + O_2 \qquad \qquad 2.4$$
$$O (^1D) + H_2O \rightarrow OH + OH \qquad \qquad 2.5$$
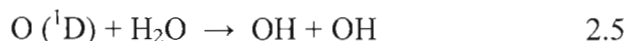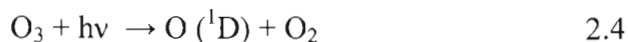
Additional sources of OH radicals in polluted environments arise from photolysis of nitrous acid, HONO or aldehydes, which are emitted directly into the atmosphere from combustion systems.

$$HONO + h\nu \rightarrow OH + NO: RCHO + h\nu \rightarrow R + CHO \qquad \qquad 2.6$$
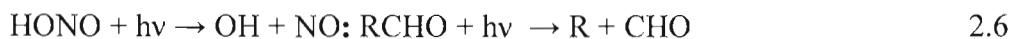
Formyl radicals, CHO react with O_2 to form CO and HO_2. The HO_2 radicals then react with NO to form OH radicals. (Jayanty, KRM, Atmos.Environ: 1989,23-52)

$$CHO + O_2 \rightarrow HO_2 + CO:HO_2 + NO \rightarrow OH \ NO_2 \qquad \qquad 2.7$$

2.7 DEGRADATION REACTION

The fate of the peroxy radicals, RO_2 depends on the chemical structure of the peroxy radicals and ambient concentration of other trace species such as NO, NO_2, and HO_2.

$$RO_2 + NO \rightarrow RO + NO_2 \qquad\qquad 2.8$$

$$RO_2 + NO + M \rightarrow RONO_2 + M \qquad\qquad 2.9$$

$$RO_2 + NO_2 + M \rightarrow RONO_2 + M \qquad\qquad 2.10$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \qquad\qquad 2.11$$
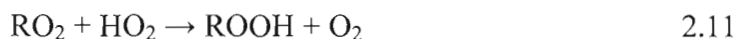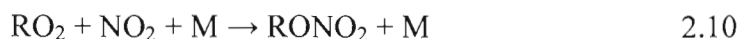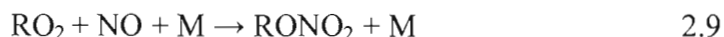
In polluted atmosphere, the dominant loss reaction will be with nitric oxide, whereas in less polluted environments or the free troposphere reaction with HO2 radicals becomes more important. The oxidant of NO to NO2 by peroxy radicals perturbs the photochemical stationary state, which normally exists in the background troposphere. (Jayanty, KRM, Atmos.Environ: 1989,23-52)

2.8 FORMATION OF OTHER PHOTOCHEMICAL

The stable product of the reactions of peroxy radicals (nitrates and hydroperoxides) are photochemical oxidants and contribute to ground level pollution. They also represent temporary reservoir for active radicals, which can be regenerated by thermal decomposition, photolysis or reaction with OH radicals. The alkyl peroxy nitrites are unstable and have limited lifetime. However, the peroxy acyl nitrites are more stable. Hydrogen peroxide formation may often be associated with these pollution episodes and is formed by the self-reaction of HO_2

radicals. However, this is important in less polluted environments ((Brown, R.H & Purnell, C.J: collection and analysis of trace VOC pollutants in ambient atmosphere. 1997, 79-90)

$$HO_2 + HO_2 \rightarrow H_2O + O_2 \qquad\qquad 2.12$$
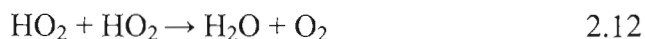
2.9 FURHER DEGRADATION REACTIONS

The fate of the alkoxy radicals, RO formed in the reaction between RO_2 and NO depends on the nature and structure of the particular radical. For the radicals with the structure, RCH_2O can react with O_2 to give HO_2 and carbonyl or thermally decompose.

$$RCH_2O + O_2 \rightarrow RCHO + HO_2 \qquad\qquad 2.13$$

$$RCH_2O \rightarrow R + HCHO \qquad\qquad 2.14$$
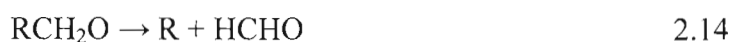
The radical fragment, R will add O_2 to form a peroxy radical and start the process off again. Alkoxy radicals containing long carbon chains (C4 or greater) often undergo isomerisation reactions, in which the alkoxy oxygen can abstract a hydrogen from an alkyl group at the other end of the chain to give a hydroxyalkyl radical.

$$CH_3CH_2CH_2CH_2O \rightarrow CH_2CH_2CH_2CH_2OH \qquad\qquad 2.15$$
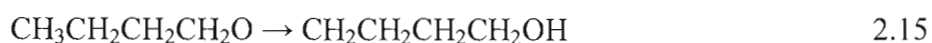
This radical will under atmospheric conditions add O_2 to form a peroxy radical and a similar series of reactions to those indicated above will occur. The fate of the alkoxy radical is important as it can amplify or reduce the ability of a given organic compound to form photochemical ozone and other oxidants. (Brown, R.H & Purnell, C.J: collection and analysis of trace VOC pollutants in ambient atmosphere. 1997, 79-90)

2.10 ENVIROMENTAL OXIDANT

Petroleum derived fuels can be autooxidized in a smaller fashion. Since some refined fraction, such as fuel oil, are often rich in two and three ring condensed aromatic compounds that strongly absorb light, the possibility of sensitized process involving singlet oxygen or electron transfer intermediates is quite likely in these materials. In addition, readily oxidized compounds such as tetrahydronaphthalenes and indans are often abundant. When a fuel oil was exposed to sunlight, a variety of physical and chemical changes took place. The oil darkened in colour and became cloudy due to the formation of insoluble, oxidized, hydrocarbon derived compounds. Include were alkalyted phenols, naphthols, ketones, alcohols and perhaps most interesting, a group of hydroperoxides of the general formula 3. The concentration of these compounds built up over a period of days. Hydroperoxides are interesting environmental pollutants because of their toxicity and mutagenicity and because their water solubilities are much greater than those of their parent hydrocarbons. (Larson, RA & Weber,EJ. Environmental organic chemistry.1994:246-320)

Single oxygen interacts with organic molecules either by collision quenching or chemical reaction. The first type of quenching is exemplified by aliphatic amines, which very effectively deactivate O_2 without undergoing chemical change themselves.

Only a few classes of compounds react readily to form new chemicals substance, usually by ene and diene reaction with O_2. (Larson, RA & Weber,EJ. Environmental organic chemistry.1994:246-320)

Olefins, with the most electron rich (usually tetrasubstituted) varieties reacting fastest. The principal product of these reaction are hydroperoxides, the result of an ene reaction in which the oxygen molecule has formally been added to one of the original double bond which then shifts into an allylic position

$$R_1R_2C^{(0)}{=}CH^{(I)}{-}R_3 \; + \; O_2 \longrightarrow R_1{-}\underset{R_2}{\overset{O{-}^{+(0)}OH}{C^{(0)}}}{-}CH^{(I)}{=}C^{(0)}\underset{R_3}{\overset{H^{(0)}}{}}$$

2.16
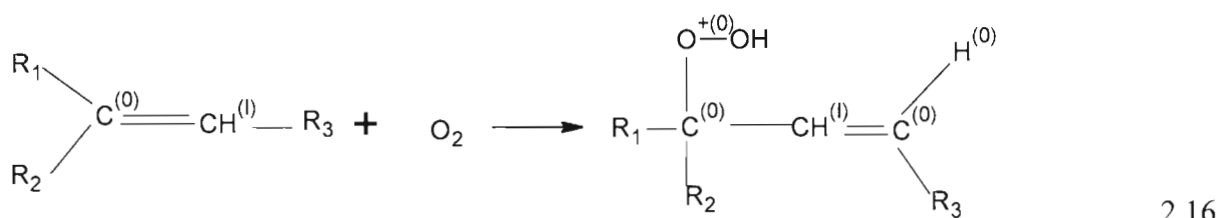
Polycyclic aromatic hydrocarbons, exemplified by anthracene, which forms a cyclic endoperoxide by addition of O_2 in diels-alder (4+2 cycloaddition) fashion. (Larson, RA & Weber,EJ. Environmental organic chemistry.1994:246-320)
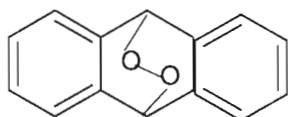
2.17

Cyclic dienes, including heterocyclic dienes such furans and pyrroles as well as carbocyclic dienes. These compounds also usually react initially by the diels-alder route, producing endoperoxides that are usually unstable to further thermal reaction. (add structure) tryptophan, however appears to add O_2 via 2+2 cycloaddition to its indole double bond ring-opening of this intermediate gives the observed product N-formyl kynurenine. Tryptophan, one of the most reactive amino acids toward O_2 may possibly disappear from marine water by a sensitized pathway, although tryptophan does absorb some solar UV and could be destroyed directly. The natural peroxide, ascaridole could be biosynthesized by O_2 reaction form its diene precursor, terpinene. (Larson, RA & Weber,EJ. Environmental organic chemistry.1994:246-320)

2.18
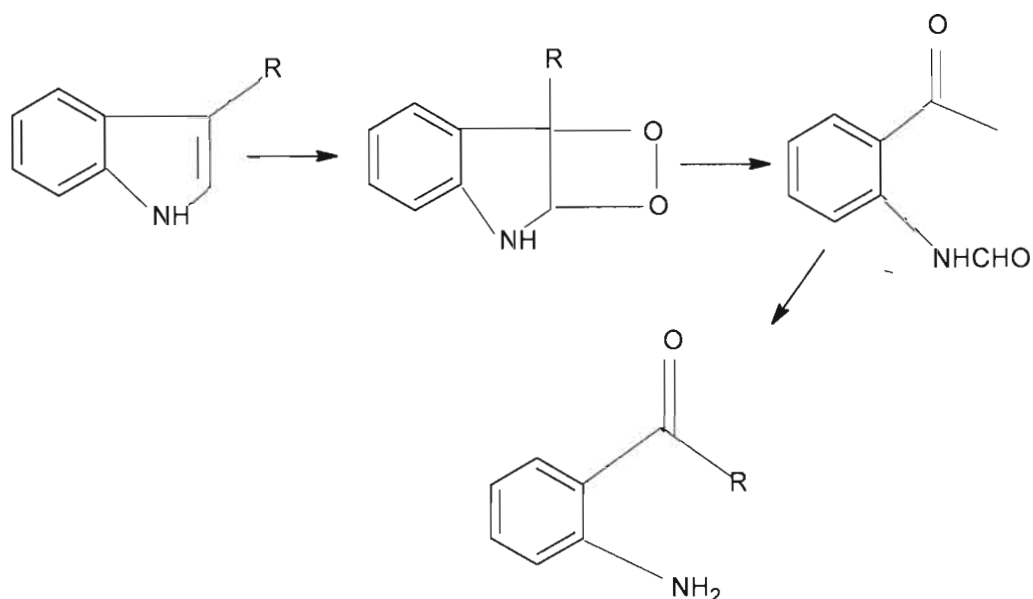
Sulfur compounds undergo rapid reaction with sensitizing dyes that have not been fully characterized mechanistically. Reactions with the triplet state of the sensitizer as well as O_2 reaction are likely. The products include sulfoxides and disulfides. The pesticide disulfoton is photooxidized by sensitized reaction due to aquatic humic materials to the corresponding sulfoxide. (Larson, RA & Weber,EJ. Environmental organic chemistry.1994:246-320)

2.19
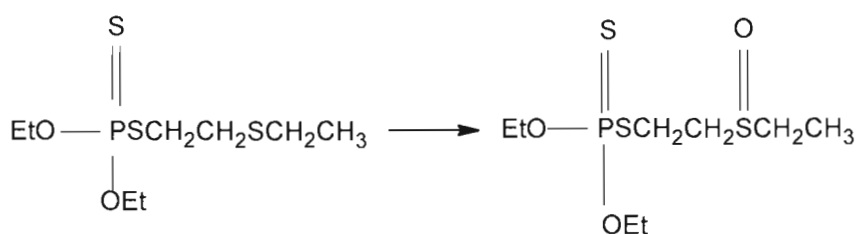
Phenols, especially those with multiple alkyl substitution or those that are otherwise electron-rich, forms cyclohexadienone hydroperoxides with oxygen. Again the mechanism appears to be a preliminary diels-alder addition followed by rearrangement. In cases where the hydroperoxide can eliminate water, quinines
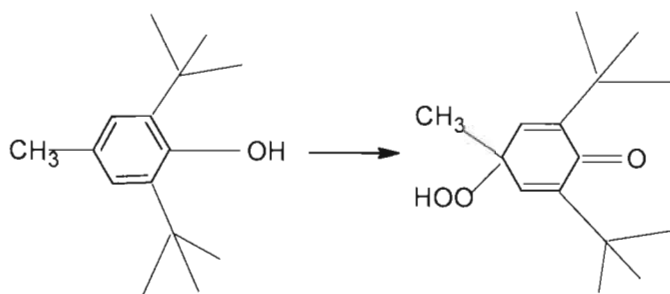
2.20

are the end product. Other extremely electron rich aromatic compound, such as polyalkoxylated benzene and polyalkylated naphthalenes are also reactive toward O_2. The rate constants for the reaction of O_2 with phenols are probably too slow for these compounds to be significantly degraded by sunlight sensitized reaction in most natural waters. However, phenolate anions are much more electron rich than the parent phenols due to the increased electron donating ability of the phenoxide substituent, and at relatively high pH the contribution of their reactions with O_2 may because important. (Larson, RA & Weber,EJ. Environmental organic chemistry.1994:246-320)

Duchstein and Wurm have described an unusual reaction of O_2 with 1.5 dihydroxynaphthalene. The product, juglude is form in high yield in aprotic solvents such as acetonitrile. (add structure) many reactions with sensitizing agents such as methylene blue, riboflavin or rose Bengal have been reported and the product have attributed to O_2 reactions. Stratospheric ozone has been much in the minds of public recently because of concern over the decreased in the UV-absorbing "ozone layer". Ozone is always present, as well, in low concentrations in the troposphere, due to lightning as well as photochemically driven oxidants polluted atmosphere. Ozone is formed in stratosphere by short-wavelength (<240 nm) homolysis of molecular oxygen to two oxygen atoms, followed by the subsequent collision of an oxygen atom with an oxygen molecule to produced O_3. (Larson, RA & Weber,EJ. Environmental organic chemistry.1994:246-320)

The absorption spectrum of ozone (λ_{max} = 255 nm) is such that virtually all the potentially UV wavelength between 200 and 300 nm are screen out before they reach the earth surface. The uptake of UV energy in this region dissociates the ozone molecule into oxygen and an O atom.

Ozone disappears in the atmosphere by reaction with both inorganic and organic species. In cloud droplets, either O_2^- or bisulfites (HSO_3-) are likely to be major reactants with ozone. Ozone reacts at a significant rate with only few organic molecules, particularly olefins, to which it adds rapidly to form ozonides. These intermediate break down to produce a variety of aldehydes and carboxylic acids. Under typical daytime trospheric condition, the fractions of olefinic materials that react with ozone are roughly equal to that which reacts with OH because OH is principally a daytime species, reaction of olefins with ozone become much more significant at night. (Larson, RA & Weber,EJ. Environmental organic chemistry.1994:246-320)

For most organic compounds that enter the troposphere, react with OH govern their disappearance. For example, methane which is by far the most abundant tropospheric hydrocarbon is virtually inert to atmospheric reactions except for its reaction with OH, which initiates a series of free radical reaction that lead to its conversion to oxidized forms:

$$CH_4 + \cdot OH \rightarrow \cdot CH_3 + H_2O \qquad\qquad 2.21$$

$$\cdot CH_3 + O_2 \rightarrow CH_3OO\cdot \qquad\qquad 2.22$$

$$CH_3OO\cdot + RH \rightarrow CH_3OOH \qquad\qquad 2.23$$

$$(or)\ CH_3OO\cdot + NO \rightarrow CH_3O\cdot + NO_2 \qquad\qquad 2.24$$

$$CH_3OOH + h\nu \rightarrow CH_3O. + \cdot OH \qquad\qquad 2.25$$

$$CH_3O\cdot + O_2 \rightarrow CH_2O + HOO\cdot \qquad\qquad 2.26$$

$$CH_2O + HO\cdot \rightarrow \cdot CHO + H_2O \qquad\qquad 2.27$$
$$\cdot CHO + O_2 \rightarrow CO + HOO\cdot \qquad\qquad 2.28$$
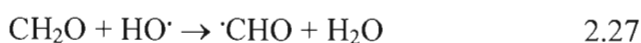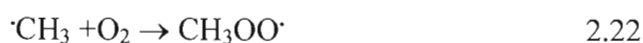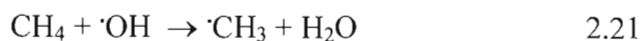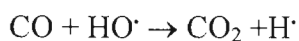
$$CO + HO^\cdot \rightarrow CO_2 + H^\cdot \qquad\qquad 2.29$$

The methylperoxy radical (and probably other peroxy radicals) reacts very rapidly with NO relatively to hydrogen abstraction, so only in very clean environments will the later reaction occur to a significant extent. In polluted atmospheres, nitrogen oxides interfere with several others of the above reactions, leading to the formation of nitrate and peroxy-nitrate esters. Methane is probably the least reactive of all atmospheric hydrocarbons. Its average atmosphere turnover time is probably about four yeas. Longer chain and branched aliphatic compounds offer the possibility of more reactive secondary and tertiary alkyl radicals formation that have many other subsequent possibilities for rearrangement and H-abstraction reactions that are lacking in the case of methane. The fact that higher n-alkanes are not produced at the earth surface in such amounts; combined with their greater rates of reaction with $^\cdot$OH, explain their very small atmospheric concentration. (Larson, RA & Weber,EJ. Environmental organic chemistry.1994:246-320)

Olefins react extremely rapidly with $^\cdot$OH, with most rate constant within an order of magnitude of the diffusion controlled limit. Probably the most reactive hydrocarbon yet tested is the monoterpene myrcene, with two vinyl groups and a trisubstituted double bonds. It reacts with $^\cdot$OH about tree times as fast as isoprene and about thirty times as fast as ethylene. Aromatics compounds usually react somewhat faster than alkanes and somewhat slower than alkenes. (Larson, RA & Weber,EJ. Environmental organic chemistry.1994:246-320)

$$CH_2 = CHCCH_2CH_2CH = C \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{}} \qquad\qquad 2.30$$

with CH_2 double bonded below the third carbon.
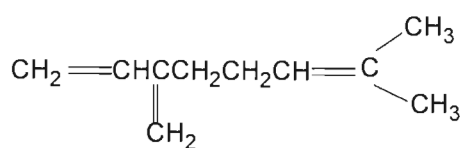
Aldyhydes are oxidized by $^\cdot$OH to acyl radicals, which may also combine with O_2 and NO but also have other modes of decomposition:

$$RCHO + {}^\cdot OH \rightarrow RCO^\cdot + H_2O \qquad\qquad 2.31$$

$$RCO^{\cdot} + O_2 \rightarrow RCO_3^{\cdot} \rightarrow RO^{\cdot} + CO_2 \qquad\qquad 2.32$$

$$RCO_3^{\cdot} + NO \rightarrow RCHO_2^{\cdot} + NO_2 \qquad\qquad 2.33$$
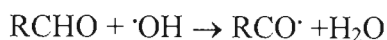
Aldehydes may be partly protected from further oxidation either by reaction with water to form hydrate, a reaction that is highly favoured for formaldehyde but less so for higher aldehydes:

$$RCHO + H_2O \rightarrow RCH(OH)_2 \qquad\qquad 2.34$$
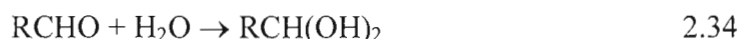
Or by reaction with sulfur oxides or bisulfite to give acidic adducts:

$$RCHO + HSO_3^- \rightarrow RCHOHSO_3 \qquad\qquad 2.35$$

The reaction types of the hydroxyl radical with organic compounds include only two of significant importance: electron abstraction for methane and addition to double bonds. An example of the latter reaction is the addition of HO$^{\cdot}$ to benzene.

2.36
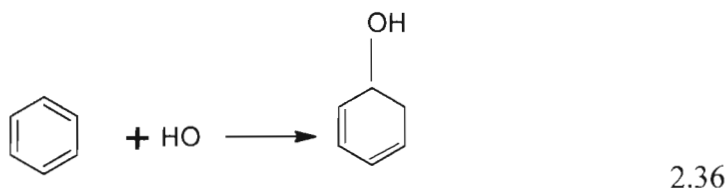
Although $^{\cdot}$OH radicals are very unselective, in practice there is some discrimination among potential sites of attack. For H-abstraction, tertiary hydrogen are often somewhat more reactive than secondary or primary types, but this simplifying assumption does not hold in all cases. Neighbouring substituent on the carbon from which the hydrogen is being abstracted often influence the rate of abstraction significantly. For addition of the radical to an unsymmetrical double bond, the formation of the more stable product radicals would be expected, and in derived from attack of $^{\cdot}$OH on propylene suggest that about two-thirds of the initial adduct is

CH₃CHCH₂OH and the reaming third is CH₃CHOHCH₂·. (Larson, RA & Weber, EJ. Environmental organic chemistry.1994:246-320)

For aromatic compounds, again there is some but much discrimination based on electron density of the ring. The electron rich compound anisole (methyl benzene), for example has a rate, has a rate constant for reaction with HO· only 2.6times larger than that of nitrobenzene, a much more electron poor aromatic compound. Addition to the aromatic ring (to form the intermediate cyclohexadienyl radicals) often predominates by a factor approximately 10 over (add structure21) hydrogen atom abstraction from a side chain or functional group. The addition of HO· to phenol gave a mixture of o- and p- dihydroxybenzene, with o-predominating by nearly 2:1, suggesting an electrophilic substitution without much steric discrimination halophenols. (Larson, RA & Weber,EJ. Environmental organic chemistry.1994:246-320)

Heterogeneous oxidation reactions involving solids surface are important contributors to the interconversion of organic substance both in natural environment and in industrial processes, including wastewater treatment. (Larson, RA & Weber,EJ. Environmental organic chemistry.1994:246-320)

2.11 TROPOSPHERIC LIFETIMES OF VOC AND SULFUR CONTAINING COMPOUNDS

Volatile organic compounds are all non-natural organic components, which are volatile. About 600 of them are categorized and differential. All of them have different effects in the atmosphere and their effects can vary substantially. The most dominant source of VOC's is motor vehicle, from, which VOC's are emitted are emitted as the result of incomplete

combustion of fuel or evaporated due to heat. (Peng, C & Batterman, S: Environmental monitoring 2000, 313-320)

The earth vegetation releases organic compounds, the natural VOC's into the atmosphere. The most abundant are isoprene and mono-terpenes, but the variety of species is large.

All the molecules consist of at least one olefinic double bonds thus making the hydrocarbons extremely reactive. Isoprene is emitted by decidous trees as a byproduct of photosynthesis and photorespiration. Its concentration is temperature and light dependent with increasing temperatures and more light resulting in higher isoprene concentration. Terpenes are emitted by conifers by biophysical process connected to the terpenoid material present in the plant. Compared to the isoprene it is not strongly depending on light but depends on temperature. (Peng, C & Batterman, S: Environmental monitoring 2000, 313-320)

Halocarbons have natural and anthropogenic sources. For the natural source account the oceans, where halocarbons are formed by biological processes and sea pray. Biomass burning and industrial processes are the primary man-made source. Chlorofluorocarbons are very inert in the troposphere and ere transported into a stratosphere, where they are photolytically destructed. The destruction releases Cl atoms, which support catalytically the O_3 destruction in the stratosphere. This destruction mechanism is the only relevant sink for CFC's. Halocarbons containing one or more H are reacting with OH-radicals in the troposphere and thus reach only to a small extent the stratosphere, where they undergo the same mechanism as the CFC's. Some (10-15%) of HCFC's react with sea water accounting another sink. The life time of halocarbons can vary from months to decades. (Peng, C & Batterman, S: Environmental monitoring 2000, 313-320)

Sulfur has a mixing ratio in the earth crust of <500ppm per mass and in the atmosphere a mixing ratio of <1ppm per volume. It can be considered as trace element. Considering this low mixing ratios the role of sulfur-containing in atmospheric chemistry is rather big. Sulfur is

present in five different oxidation stages. (a) H_2S, (b) CH_3SCH_3, (c) SC_2, (d) OCS and (SO_2) the reduced sulfur compounds are rapidly oxidized by hydroxyl radicals and other chemical species. This species occur preferably in the gas phase and due to their reactivity their residence times are rather short (few days). On the other hand sulfur compounds with oxidation stage of +6 are often found in particles or droplets. Their residence times are determined by wet and dry removal. (Peng, C & Batterman, S: Environmental monitoring 2000, 313-320)

Dimethysufide is the dominant sulfur compound from the oceans. It is produced in oceanic water by marine organisms. Phytoplankton produced dimethyl-sulfoniopropionate a precursor to dimethysulfide which is decomposed to dimethysulfide by certain algae species. The concentration of DMS varies strongly in the upper layer of the ocean and is in average of 100ng of sulfur per liter. The concentration is depending on diurnal, seasonal, sea depth and location variations. Due to the high enrichment in the upper layer of the ocean there is a flux from the ocean surface to the atmosphere and the mixing ratio in the marine boundary layer is 80-100 ppt, but falls off to quickly with altitude. Once in the atmosphere DMS reacts with the hydroxyl radical and also with the NO-radical. The fact the OH radicals is formed during a photochemical cycle driven by sunlight effects the DMS concentration. (Rasmussen, RA & Grosjean, E: environmental science and technology, 1998, 2061-2084)

Carbonylsulfide is the most abundant sulfur in the global background atmosphere due to its low reactivity and thus long residence time. In fact it is the only sulfur component which makes all the way through to the Stratosphere, where it is believed to be a main compound of the stratospheric aerosol layer. (Rasmussen, RA & Grosjean, E: environmental science and technology, 1998, 2061-2084)

2.12 DEFINITION OF VOLATILE ORGANIC COMPOUNDS

Volatile organic compounds are organic chemicals that easily vaporize at room temperature. They are called organic because they contain the element carbon in their molecular structures. Volatile organic compound have no colour, smell, or taste. Volatile organic compounds include a very wide range of individual substance, such as hydrocarbons (for example benzene and toluene), halocarbons and oxygenates. Coutant, R.W: theoretical evaluation of stability of VOC and polar VOC chemicals in canister. 1993, june)

Hydrocarbons volatile organic compounds are usually grouped into methane and other non-methane VOC's. Methane is an important component of VOC's, its environmental impact principally related to its contribution to global warning and to the production of ground level or lower atmosphere ozone. Most methane is released to the atmosphere via leakage of natural gas from distribution systems. Benzene, a non-methane hydrocarbon, is colourless, clear liquid. It is fairly stable but highly volatile, readily evaporating at room temperature. Since 80% of man-made emissions come from petrol-fuelled vehicles, levels of benzene are higher in urban areas than rural areas. Benzene concentrations are highest urban roadsides. Oxygenates arise in vehicles exhausts and via atmospheric chemical reactions. Evaporated of solvents, used for paints, course a release of hydrocarbons, oxygenates and halocarbons to the atmosphere. Coutant, R.W: theoretical evaluation of stability of VOC and polar VOC chemicals in canister. 1993, june)

2.13 IMPACT ON AIR QUALITY OZONE BALANCE

Volatile organic compounds are emitted in substantial quantities from both biogenic and anthropogenic sources and have major influence on the chemistry of the lower atmosphere. The gas phase degradation of volatile organic compounds plays a central role in the generation of a variety of secondary pollutants, which may have a harmful impact on human health and on the environment. The complete gas phase oxidation of (VOC) into carbon dioxide and water occurs predominantly (but not exclusively) by sunlight-initiated mechanism, and produces

carbon monoxide and a variety of intermediate oxidised organic products some nitrogen-containing, sulfur-containing which may have detrimental health effects. Furthermore, certain oxidised organic product, particularly those produced from large unsaturated VOC are sufficiently in volatile to promote aerosol formation and growth. (Carroll et al, 1990 world meteorological organisation, 1992, 563-578)

The important contribution of oxygenated organics to secondary aerosols are becoming increasingly recognised, of particular importance however, is the generation of zone as a by product of VOC oxidants in the presence of nitrogen oxides. The establishing of the degradation of each VOC occurs by a unique mechanism (because of difference in reactivity and structure), so that the relative contributions of specific VOC to the formation of ozone and other secondary pollutants varies from one compound to another. (Carroll et al, 1990 world meteorological organisation, 1992, 563-578)

Natural VOC emission are estimated to account for ca. 90% of the global total and can therefore have a major impact on the generation of ozone and secondary organic aerosol on a number of geographical scales. Particularly significant contribution are made by hydrocarbons (especially isoprene and monoterepens, $C_{10}H_{16}$), oxygenated VOC (e.g., methanol and 2-methyl-3-buten-2-ol) from continental vegetation and sulphur and halogenated-containing organic species. The importance of aromatic hydrocarbons in local and regional air pollution is well established (Derwent et al, 1998). Since aromatic hydrocarbons contribute significantly to the formation of photooxidant such as ozone and also to secondary organic aerosol production, particularly in urban air, an understanding of their chemistry is essential for an understanding of the chemistry governing air pollution. Diverse aspect of aromatic hydrocarbon chemistry has been investigated. The studies have included research on the OH-radical initiated photooxidant of benzene, toluene and the xylene isomers. The work has involved (1) studies of the primary oxidation steps and thermochemistry; (2) yields of formation of primary products; (3) kinetic and mechanistic studies of the further oxidation of important products; (4) exploratory work into the chemical composition and hygroscopicity of the secondary organic

aerosol of aromatic photooxidation. (Carroll et al, 1990 world meteorological organisation, 1992, 563-578)

A large proportion of kinetics, product and mechanistic information originating from work on the photooxidation of aromatic hydrocarbons have been included in a recent review on aromatic atmospheric chemistry (Calvert et al., 2002) and also into the Master Chemical Mechanism (MCM). The understanding of the primary oxidation steps of the photooxidation of aromatic compounds, and of the chemistry of major oxidation product, there remain uncertainties. Branching ratio for the various reaction pathways leading to ring-opening and fragmentation, which are much needed for mechanistic modelling still, remain very poorly characterised. However, the various projects have laid an excellent and authoritative experimental and theoretical basis on which future research can build. (Carroll et al, 1990 world meteorological organisation, 1992, 563-578)

Similarly, the identification of the major precursor to secondary organic aerosol formation from the oxidation of aromatic hydrocarbons still remains elusive. Although alkenes are typically found at lower concentrations in the atmosphere than those of saturated hydrocarbons, they are important because of their higher reactivity. The atmospheric reactions of alkenes are mainly initiated by addition to the double bond. In the case of reaction with OH, this addition leads to formation of a hydroxyl-substituted peroxy radical. The empirical relationship or quantum mechanical calculation, not only the rate coefficients for these subsequent fate. Reactions with NO_3 radicals (and possibly Cl atoms) also appear to be of atmospheric importance for alkenes. The reactions of alkenes with ozone are often fast enough to be of atmospheric relevance, particularly in the case of highly branched alkenes. Ozonolysis reactions are of special interest because they provide a source of OH radicals. (Carroll et al, 1990 world meteorological organisation, 1992, 563-578)

Oxygenated organic compounds are being used increasingly as industrial solvents and fuel additives or alternatives. The increase release of this type of species into the atmosphere is likely to affect ozone levels in the troposphere and lead to the formation of other secondary

pollutants, which may affect air quality. Oxygenated organic compounds are also formed in the atmosphere as intermediate products in the degradation of compounds such as alkanes and alkenes. The atmospheric oxidation of oxygenated VOC in the gas phase is initiated mainly by their reactions with OH and NO_3 radicals as well as O_3. Photolysis may play a significant role in the degradation of some compounds. In order to assess the environmental impact of large scale and emissions of these chemicals, a complete understanding of the timescale and mechanism of their oxidation is required. (Carroll et al, 1990 world meteorological organisation, 1992, 563-578)

Halogenated compounds in great variety are released to the atmosphere from natural and anthropic sources. The degradation of these compounds is of particular interest because the final or intermediate product may possess adverse properties (such as mutagenicity or phytotoxicity) and thus might have an impact on the environment even at very low concentration. The atmospheric oxidation of fluorinated alcohols, and of choral, and the reactivity of these compounds towards attack by OH or Cl has been rationalised in terms of the substitution. (Carroll et al, 1990 world meteorological organisation, 1992, 563-578)

2.14 DEGRADATION OF ANTHROPOGENCI VOLATILE ORGANIC COMPOUNDS

Addition to the ring is the major reaction pathways in the OH-radicals initiated oxidation of aromatic hydrocarbons. To facilitate an understanding of the results on the chemistry of the aromatic hydrocarbons for possible reaction pathways following addition of OH to the ring.
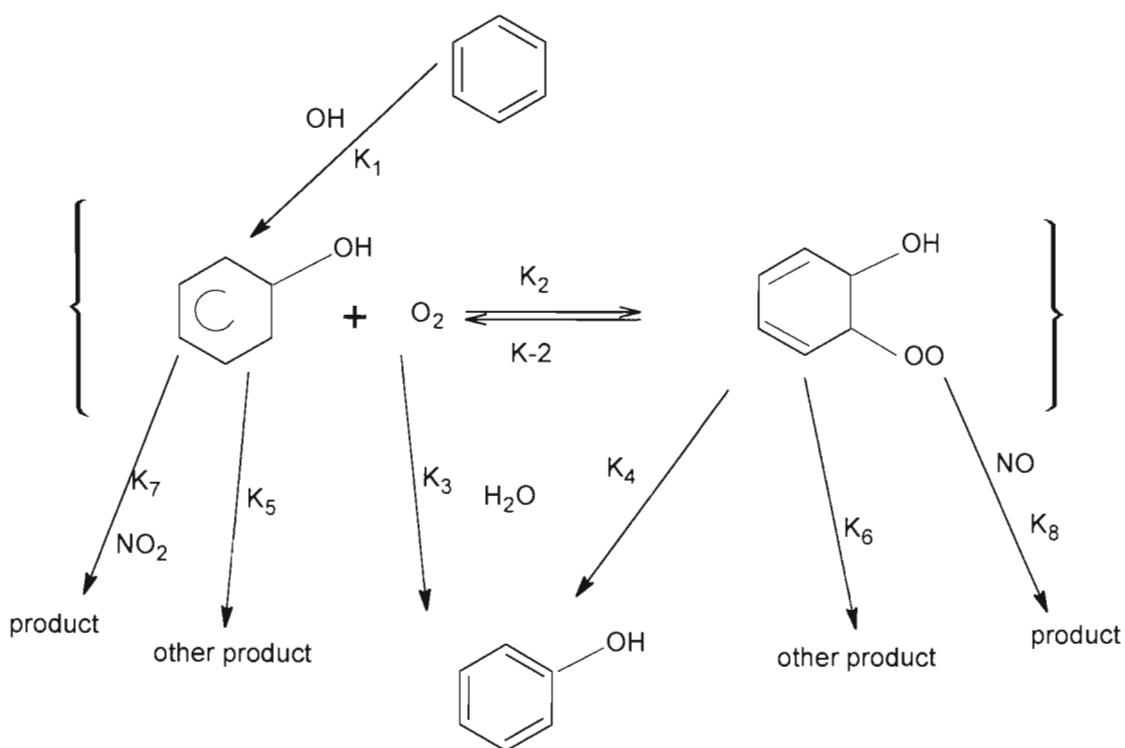
Addition of an OH radical to the aromatic forms a HO-aromatic adduct (k_1; ADDO$_2$). This is followed by reaction of the HO-aromatic adduct with O2 (k_2, K_{-2}; ADDO$_2$).

Cross sections for several HO-aromatic adducts have been obtained at 308nm and calibrated UV spectra of the HO-benzene adduct (HO-C$_6$H$_6$) (Johnson et al., 2002) and the OH-toluene adduct (HO-C$_6$H$_5$CH$_3$) have been obtained from 265 to 340 nm. Between the different groups involved in these measurements the cross section values are in good agreement for the HO-benzene adduct at 308nm. However, although similar methods were employed, there is a discrepancy for the OH-toluene adducts which remains unexplained. (Soldat, JK: air pollution control association, 1960, 265-270)

It has been demonstrated for the first time, using UV-laser long-path absorption technique and conventional UV absorption spectrometry that the kinetics of the reaction of several different OH-aromatics adducts with O$_2$ are consistent with the reversible formation of stable peroxy radical (RO$_2$) intermediates. (Soldat, JK: air pollution control association, 1960, 265-270)

HO-aromatic + O$_2$ ⇌ HO-aromatic-O$_2$ (RO$_2$) ⟶ other product
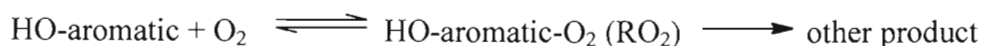
Measurement of the equilibrium constant for these reactions have been performed, in some cases at various wavelength an as a functional of temperature. However, the data base is still quite limited and there is a discrepancy of a factor of approximately three between the measured equilibrium constant $K_2 = k_2/k_2$ for the measurements on benzene and toluene between the different groups involved in the work which needs to be resolved. (Soldat, JK: air pollution control association, 1960, 265-270)

2.15 SAMPLING TECHNIQUES FOR VOC

The gas chromatographic system that must be capable of temperature programming. The column oven can be cooled to subambient temperature (e.g. -50 $^{\circ}$C) at the start of the gas chromatographic run to effect a resolution of the very volatile organic compounds. In other designs, the rate of release of compounds from focussing trap in a two stage system obviates the need for retrapping of compounds on the column the system include or be interfaced to a concentrator and have all required accessories including analytical columns and gases. (Harper, M: evaluation of solid sorbent sampling methods by breakthrough volume. 1995, 792-800)

Chromatographic columns must be 100 % methyl silicone or 5% phenyl, 95% methyl silicone fused silica capillary columns of 0.25 to 0.53 mm I.D. of varying lengths are recommended for separation of many of the possible subsets of target compounds involving nonpolar compounds. However, considering the diversity of the target list, the choice is left to the operator subject to the performance standards given. Mass spectrometer is a linear quadrupole which is capable of scanning from 35 to 550 amu every one second or less, utilizing 70 volts electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 50 ng or less of p-bromofluorobenzene is analysed (Harper, M: evaluation of solid sorbent sampling methods by breakthrough volume. 1995, 792-800)

The linear quadrupole consist of a parallel set of four rod electrodes mounted in a square configuration. The field within the analyser is created by coupling opposite pairs of rods together and applying radiofrequency and direct current potentials between the pairs of rods.

Ions created in the ion source from the reaction of column eluates with electrons from the electron source are move through the parallel array of rods under the influence of the generated field. Ions which are successfully transmitted through the quadrupole are said to possess stable trajectories and are subsequently recorded with the detection system. When direct current potential is zero, a wide band of m/z values is transmitted through the quadrupole. The radio frequency (only) mode is referred to as the total ion mode. In this mode, the quadrupole acts as a strong focusing lens analogous to a high pass filter. The amplitude of the radio frequency determines the low cut-off. A mass spectrum is generated by scanning the direct current and radio frequency voltages using a fixed DC/RF ratio and a constant drive frequency or by scanning the frequency and holding the DC and RF constant. (Harper, M: evaluation of solid sorbent sampling methods by breakthrough volume. 1995, 792-800)

Thermal desorption is a technique that extracts volatiles from a non-volatile matrix by heating the matrix/sample in a stream of inert gas. The extracted volatiles are subsequently refocused onto a cold trap from which they are transferred in a narrow band to a gas chromatographic column for analysis. The sample is contained in a small capped tube. A leak test is automatically performed to ensure that the tube has been sealed correctly and to ensure that the rest of the system is leak tight. The tube is then purge with carrier gas at ambient temperature to remove oxygen and moisture. The sample is subsequently heated with a flow of inert gas to extract the volatiles. The volatiles are concentrated on a low thermal mass, electrically cooled cold trap prior to transfer to the gas chromatographic column through a heated transfer line.

Heating the cold trap rapidly ensures that the analytes are transferred to the gas chromatograph quickly. This sample transfer method is fully compatible with high resolution capillary chromatography. (Harper, M: evaluation of solid sorbent sampling methods by breakthrough volume. 1995, 792-800)

greater. This method applies under most condition in sampling of ambient air into canister. However, the composition of gas mixture in a canister, under unique or unusual condition will change so that the sample is known not to be a true representation of the ambient air from which is taken. Low humidity condition in the sample may lead to losses of certain VOC's on the canister walls, losses that would not happen if the humidity were higher. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water soluble compounds. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence absolute storage stability cannot be assigned to a specific gas. (Riggin, R.M:April 1999)

The monitoring procedure involves puling a volume of air through a sorbent packing to collect VOC's followed by a thermal desorption capillary GC-MS procedure. Conventional detectors are considered alternatives for analysis subject to the performance criteria listed below.

1) selection of a sorbent or sorbent mix tailored for a target compound
2) screening the sampling location for VOC's by taking single tube samples to allow estimates of the nature and amount of samples gases
3) initial sample sequences with two tubes at nominally 1 and 4 liter total sample volumes
4) analysis of the sample and comparison to performance criteria
5) acceptance or rejection of the data
6) if rejection, then review of the experimental arrangement including repeat analysis with backup tubes

This method is an alternative to the canister based sampling and analysis methods that are presented in Compendium methods TO-14 and to the previous sorbent based methods that were formalized as Compendium TO-1. All these methods are of the type that includes sampling at one location, storage and transport of the sample, and analysis at another, typically more favourable site. The collection of VOC's in ambient air sample by passage through solid sorbent packing is generally recognised to have a number of advantages for monitoring.

• The small size and light weight of the sorbent packing and attendant equipment

- The placement of the sorbent packing as the first element (with the possible exception of a filter or chemical scrubber for ozone) in the sampling train so as to reduce the possibility of contamination from upstream elements

- The commercial availability of thermal desorption systems to release the sample from the sorbent into the analytical system

- The availability of a large selection of sorbent to match the target set of compounds including polar VOC's

- The possibility of water management using a combination of hydrophobic sorbent (to cause water breakthrough while sampling) dry gas purge of water from the sorbent after sampling and splitting of the sample during analysis. Sorbent based monitoring can be combined with canister based monitoring methods, on site auto GC system, open path instrumentation, and other specialized point monitoring instrument to address most monitoring needs for volatile organic gases. More than one of these approaches can be used simultaneously as a means to check and insure the quality of the data being produced. (Riggin, R.M: April 1999)

2.16.2 AIR SAMPLING WITH CANISTER

Ambient air sampling involves collecting a representative sample of ambient air for analysis. If the environment is not changing, or if only a qualitative sample is needed a simple "grab" sample can be obtain. An evacuated sample canister can be open and sample rapidly collected at a non-controlled rate, usually over several seconds, until the container attains equilibrium with atmospheric pressure. Generally this qualitative approach is used when unknown analytes must be identified, when the air contains high concentrations at certain (short) time, or when an odour is noticed and sample must be obtained quickly. Paired grab samples (before/after or smell/no smell) often are employed to qualitatively diagnose a perceived problem.

To obtain a more representative sample requires time-integrated sampling. A flow restrictor is used to spread the sample collection flow over a specific time period, to ensure an "average" composited or time weighted average sample. A time weighted average sample will accurately reflect the mean conditions of the ambient air in the environment and is preferred when, for a regulatory or health reason. Typically exposure concentration is required for a situation that may have high variability, as in an occupational setting.

Figure 3.1: Canister used for sampling

In passive sampling an air sample is pulled through a flow controller into an evacuated canister over a chosen period of time, raging from 5 minutes to 24 hours. The sampling period and flow rate determine the canister volume required. In non-passive (active) sampling, a pump is used to push the sample through a mass flow controller and into the canister. Additional sample can be collected, relative to the amount that can be collected by passive sampling, by pressurizing the canister with sample. Commonly the sample is pressurized to 15 psig, effectively doubling the volume. Sampling can be time integrated (e.g. an 8 hour sample) or a dip tube design can be used to establish a flow through the system and flush the sample container with sample. (Coutant, R.W: theoretical evaluation of stability of VOC and polar VOC chemicals in canister. 1993)

To ensure a valid sample when using a passive sampling technique, it is important that the flow rate is not change greatly during the time interval specified for the integrated sample. The proper sampling equipment helps accomplish this objective. A typical passive sampling train should include the components, all constructed of stainless steel: a sampling inlet, a sintered metal particle filter, a critical orifice, a flow controlling device, a vacuum gauge, and canister.

The sampling inlet-the entrance to the sampling train – typical stainless steel tubing, either ¼ or 1/8 ID Compendium TO-14 recommends sampling height of 2 meter above the ground. In highly trafficked area, this would minimize the problem of dust particle entering the sampling train. This height is not mandatory however, and it is practice to use an inlet that is 1/3 meter high. Particle filter is installed in the sampling train prior to the flow-controlling device, the particle filter prevents airborne from entering the sample flow path. (Coutant, R.W: theoretical evaluation of stability of VOC and polar VOC chemicals in canister. 1993)

Particles could partially obstruct the flow path and alter the flow rate during sampling. In extreme cases, particles could plug the flow path and stop the sample flow. The smallest orifice commonly used in a passive sampling train is 0.00012 "(approximately 30 micrometers). Without a particle filter, dust particles could occlude this opening as they accumulate in the orifice fitting. Particle also can affect the leak integrity of the valve, and

possibly can damage the valve. (Coutant, R.W: theoretical evaluation of stability of VOC and polar VOC chemicals in canister. 1993)

The critical orifice restricts the flow to a specific flow range. In conjunction with the flow controller, this allows the canister to fill at a specified rate over a specified time period. The most common critical orifice design is a series of interchangeable stainless steel 1/4 compression unions. Each fitted with a precisely bored sapphire orifice. Each orifice provides a specific flow range. Stability over a wide range of temperature makes sapphire the construction material of choice. Typically during field sampling, the sampling train is subjected to temperature fluctuations that would cause metals to contract or expand, affecting the diameter of the aperture and thereby affecting flow. Sapphire will not expand or construct across any ambient temperature extremes incurred during sampling. A critical orifice can be used as the sole flow restricting device, but it cannot ensure uniform flow. The source pressure of the flow changes during sampling, and the flow rate through the orifice also would change, producing an invalid time integrated sample. It is important that a highly consistent flow rate be maintained during passive sampling. This is accomplished by the flow controller that incorporates the critical orifice. (Coutant, R.W: theoretical evaluation of stability of VOC and polar VOC chemicals in canister. 1993)

The flow controller maintains a constant sample flow over the integrated time period, despite changes in the vacuum in the canister or in the environmental temperature. The critical orifice acts as a flow restrictor, upstream of a constant back pressure. This constant back pressure is established by the balance between the mechanical spring rate of the diaphragm and the pressure differential across the diaphragm. The latter is established by the pressure difference between the atmospheric pressure and the vacuum in the canister and the flow through the critical orifice. The net result is a constant flow. The critical orifice determines the flow range the adjustable piston is used to set a specific, fixed rate within the flow range. An adjustment to the position of the piston changes the back pressure, which changes the pressure differential across the critical orifice. If the piston is lowered away from the diaphragm, the flow rate will decrease. This flow controller will accurately maintain a constant flow despite changes in vacuum over a range of 30 Hg to 7 Hg. Flow is constant until the vacuum range of the device is exceeded, making the flow controller unable to maintain the constant pressure differential.

For example, the flow rate is constant from 29.9 Hg to approximately 7 Hg, at which point the flow rate decreases because the flow rate is unable to maintain the proper pressure differential. A vacuum gauge enables sampling personnel to visually monitor changes in the vacuum in the canister during sampling. If the flow rate changes unexpectedly (e.g. due to a leak or an incorrect setting), the vacuum gauge will indicate a disproportionately high or low vacuum in the canister, and corrective action can be taken (i.e., flow adjusted) in time to ensure a valid sample. This type of vacuum gauge is attached to the sampling train, for use in the field. The vacuum gauge should be of high quality to ensure that it does not introduce contaminants into the sample. (Coutant, R.W: theoretical evaluation of stability of VOC and polar VOC chemicals in canister. 1993)

2.16.3 SAMPLING WITH ADSORBENT TUBES

Low flow active sampling techniques collecting vapours and gases using thermally desorbable adsorbents are now feasible and desirable in many applications as they permit long integration times, the potential for miniaturized sampling configurations and other advantages. At very low air flow rates (<1 ml/min) diffusive uptake on adsorbents in conventional sorbent tubes may equal or exceed the active (pumped) uptake rate, and even at low flow rates, diffusive uptake may significantly bias measurement. Thus, corrections to account for the diffusive flux or means to limit the diffusive uptake are needed in low flow applications. (Harper, M: evaluation of solid sorbent sampling methods by breakthrough volume. 1995, 792-800)

Applications of active adsorbent sampling have used flow rates between 5 and 200 ml/min. A minimum flow rate allows collection of sufficient mass to allow analysis, and it may avoid problems of low sampling efficiency. However, flow rates well below 60 ml/min can be extremely useful and are motivated by several factors. First, as the performance of analytical procedures improves, analyte mass sample volume requirements will drop. Traditional chemical desorption technique require µg quantities, existing thermal desorption technique require ng quantities, and it is not unrealistic to expert that pg masses may be sufficient in few years with more sensitive detector. Smaller masses enable proportional decreases in sampling

flow rates. Second, most application of active sampling have used short sampling period, 1 to 8 hours being most common. Longer periods are often advantageous as they obtain more representative results if concentrations vary in time, for example, 24 hours samples are widely used to sample ambient air toxics. Week long samples often used in residences and other indoor air quality applications to estimate long term exposure. (Harper, M: evaluation of solid sorbent sampling methods by breakthrough volume. 1995, 792-800)

Extended sampling periods require low flow rates to stay within the 'safe sampling volume', thus avoiding breakthrough problems. Third, while passive sampling may be a more tempting alternative than flow active sampling for sampling times on the order of days or weeks, significant loss of sampled material may occur due to reverse diffusion. While probably restricted to only very volatile VOC's, for example, vinyl chloride or pentane, active. (Harper, M: evaluation of solid sorbent sampling methods by breakthrough volume. 1995, 792-800)

CHAPTER 3

EXPERIMENTAL METHODS

3.1 INTRODUCTION

Monitoring of volatile organic compounds in ambient air has received substantial attention over the past several years because certain VOC are known to be hazardous to human health. The majority of the methods that have been developed for ambient VOC monitoring have been either canister (EPA TO 15) or sorbent tube (ISO 17116-1). There are respective advantages and limitations of these two methods. Two analytical methods for determination of volatile organic compounds in ambient air are compared. The methods differ from each other in the sampling techniques, sorbent material used and canister. The results and conclusion of the methods used shows a significant influence of the way in which the analysis is carried out, on the final result of the analysis. The canister method collects air samples directly with evacuated stainless steel canister and the method is very costly and it may be difficult to recover quantitatively some polar and low volatility VOC. The sorbent tube method is capable of enrichment with high sensitivity, ease of use and cost-effectiveness.

Sampling methods for ambient air on wastewater separator for ambient air quality which is situated on the northern side of the refinery was sampled by using these methods. The sampling was done seasonal as shown on (table 2 and 3) sampling data sheets. Both methods complianent thermal desorption technology and offering high sensitivity measurement of air toxic, single analytical platform for both canister and sorbent tubes had being extensively validated for monitoring air toxics. Canister and sorbent tubes offer complementary air monitoring technology, canister offer ideal sampling technology for monitoring trace levels of very volatile and volatile organic compounds in ambient air, particular if grab sampling is an option, canister are not normally used for personal exposure assessment and highly boiling compounds. Sorbent tubes are best for suited to work place, indoor and ambient monitoring of analyte from propane through semi volatiles.

3.2 SORBENT TUBE PREPARATION

Stainless steel thermal desorption tubes with inner diameter of 4 mm and length of 10.6 cm were cleaned in ultrasonic shaker with methanol for 2 h and dried in oven at 100 °C for 1 h. Clean tubes were then packed with 100 mg of Carbopack B separated by a glass wool plug and plugged at both ends with same material. Subsequently, tubes were conditioned after packing and prior to use. The conditioning oven had a heating capacity of up to 1000 °C and condition parameters were optimized after several trials at 200 °C, 250 °C 300 °C and 350 °C conditioning temperature; at 6 and 12 h. Optimum conditions were found to be at 300 °C for 12 h packing. If conditioned tube were store for long period of time without any use, re-conditioning was done for 2 h at the same temperature. Conditioned tubes were capped tightly with brass caps having PTFE seals and kept in pre-clean container to prevent possible contamination. Tubes were kept in the freezer at 4 °C for storage.

3.3 CANISTER PREPARATION

All canisters were connected to the cleaning system, and then pressure was released within any of the canisters. The system was then put under pressure, to evacuate the canister for 1 hour at 50 kPa then reduced to 23-25 kPa which was sufficient for general cleaning. The canisters were allowed under vacuum for approximately 1 h; then pressurized the canister with humidified nitrogen. Pressurization dilutes the impurities and the moist air hydrolyses them. Canisters were then pressurized to 30 kPa followed by heating to 155 °C, to help removed less labile impurities. Heated canisters were then filled with humidified air for at least 1 h. Re-evacuation of canisters was done to remove and the desorbed impurities, Canisters were then allowed to reach equilibrium for an hour. They were then certified by filling the canister with humidified air and passing the air from the canister through an adsorbent trap and analysed the targeted VOC by GC-MS. The analytical system was not allowed to detect greater than 0.02 µg/kg, other wise the whole process would have to be repeated to ensure the cleanness of the canisters.

3.4 SAMPLES COLLECTION

Carbopack B is a strong sorbent and has surface area of 100 m^2g^{-1}. Samples were collected at the Carbopack B at the end of the tube in order to allow the heavier hydrocarbons first. Air samples were collected using SKC vacuum pumps. Sample pumps were operated at 80 ml/min for 1 h and recording was done on datasheets.

Current meteorological conditions, nearby potential pollution source and problems encountered during sampling were recorded in the field datasheets in addition to the sampling information (tube number, start time and flow rate). This information was used during quality control of the analytical data to trace back if there would be problems. Samples were then immediately brought to the laboratory in coolers after collection and stored at 4 °C.

The atmospheric air was sampled by introduction of air into a specially prepared stainless steel canister. A certified mass flow meter was attached to the inlet line of the manifold, just in front of the filter. The canister was evacuated to 0.05 mm Hg. When the canister was opened to the atmosphere containing VOC to be sampled, the differential caused the sample to flow into the canister with a mass flow controller and critical orifice. With a critical orifice flow restrictor there was a decrease in flow rate as the pressure approaches atmospheric. However, with a mass flow controller, the subatmospheric sampling was maintained at constant flow rate from full vacuum to within about 7 kPa. After 2 minute 3.5 ml/min flow rate was adjusted for 24 hour sampling. Subsequently, air sample was collected, the canister valve was closed and identification tag was also attached to the canister.

3.5 INSTRUMENTAL SET UP

Prior to the analyses of any samples, blanks, or calibration standard, it was necessary to establish that a given GC-MS meets tuning and standard mass spectral abundance criteria prior

to initiating for any data collection. The GC-MS system was set up according to the manufacture specifications. The mass calibration and resolution of the GC-MS system were then verified by the analysis of the instrument performance check standard, bromoflourobenzene (BFB). The instrument performance check solution was analysed once per 24-hour frequency operation. The 24-hour frequency for GC-MS instrument performance check and standard calibration begins with injection of the BFB which the laboratory documented as compliance tune. The analysis of the instrument performance check standard was performed by trapping 50 μg/kg of BFB under the optimized pre-concentration parameters.

The BFB was introduced from a cylinder into the GC-MS via a sample loop valve injection system. The mass spectrum of BFB must be acquired in the following manner. The three scans (the peak apex scan and the scans immediately preceding and following the apex) were acquired and averaged. Background subtraction was conducted using a single scan prior to the elution of BFB.A system consisted of a thermal desorption unit and an electronic control unit. The thermal desorption unit was placed directly into the GC-MS injection port, where it was utilized for the direct desorption of the samples into the GC-MS injection port and column. Due to its "short path" of sample flow, this system overcomes shortcomings of pervious desorption systems by eliminating transfer lines, which are easily contaminated by samples, and by providing for the optimum delivery and therefore maximum sensitivity of samples to the GC-MS injector. Analytes of interest were thermally desorbed from sorbent tubes and canisters respectively and directly entered into GC-MS inlet. Desorbed analytes were cryogenically cooled and trapped at the very front of the analytical column. An automatic thermal desorption cryofocusing injector system (PerkinElmer TD500) was connected by a transfer line maintained at 180 °C to Agilent 6890 GC system equipped with 7310 N mass selective detector. The multi-sorbent tubes were thermally desorbed at 200 °C for 5 min.

The direction of the gas flow was always reversed during thermal desorption so that higher boiling compounds were back flush easily from the sampling end of the tube. The desorbed analytes were re-trapped at -30°C by cold trap filled with 2cm deactivated glass beads (mesh 60/80). The thermocouple was attached to the trap tubing to provide temperature feed back. After sample concentration, the trap was flash-heated to 300°C at 40°C/s for 5min, and the

trapped analytes were introduced into a moisture control system to remove water vapour before being injected into GC-MS system. The trap was then cleaned by baking at 350°C for 20min after each   desorption. The analytical column was HP5-MS fused silica capillary column of 60 m x 0.32mm ID with 0.5µm film thickness. The inlet pressure of the ultra pure helium carrier gas was set at 20 kPa. Oven temperature were program as follows: start at 35°C hold for 5min; ramp at 3°C/min to 100°C and hold for 5min; finally ramp at 5 to 160°C/min and hold for 5min. the total analysis time was 35min. The transfer line between GC and MS was kept at 280 °C. The mass selective detector with electron ionization was operated in scan mode at a rate of 6.1scans/s from 40 to 260amu.
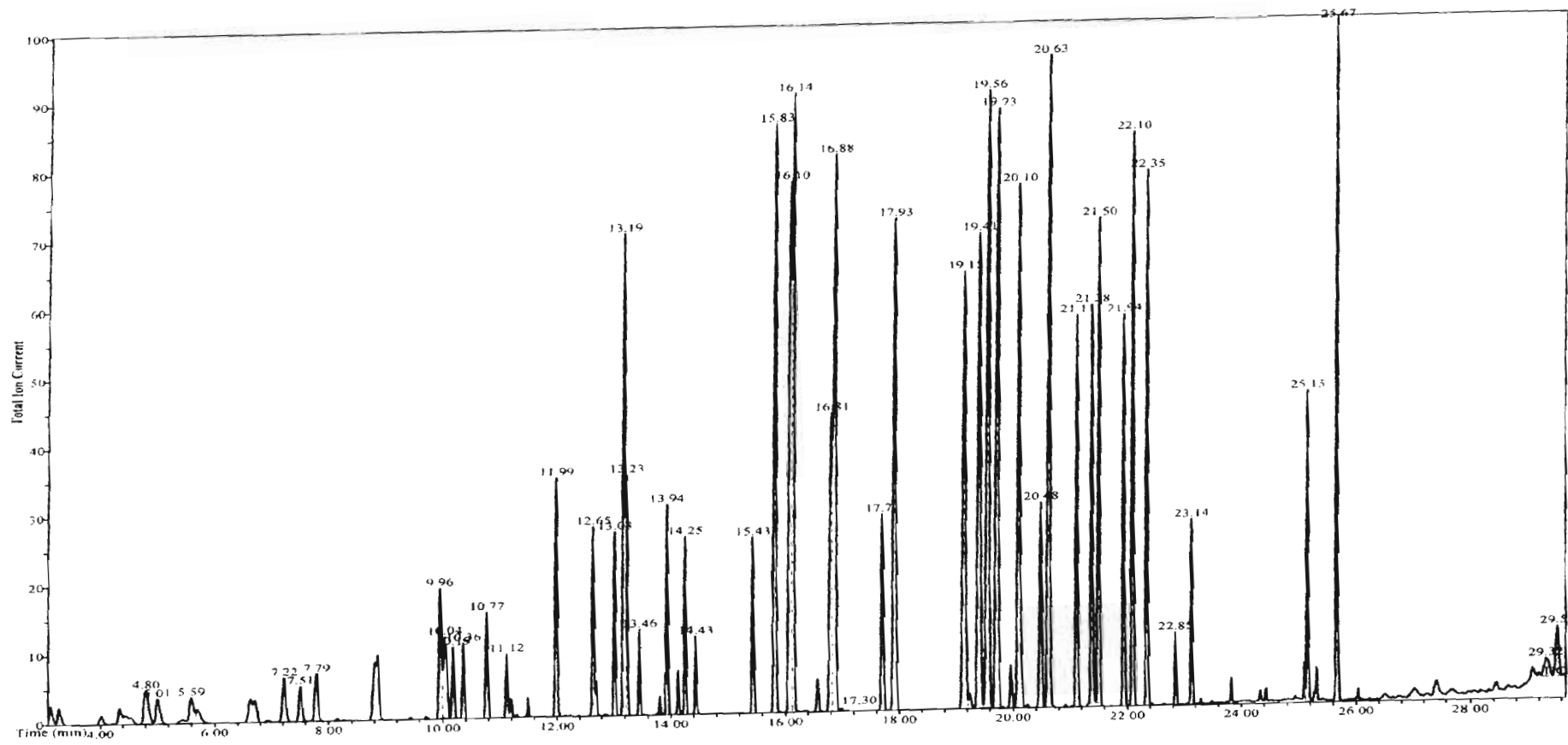
Figure 3. 2: Calibration standard mixture of compounds for 1 mg/kg

Table 3. 1 Calibration standard of TO-14A mix with 41 components

Component	Retention time	Areas X10E+8	Concentration (μg/kg)	Time	Volume	A/CV X 10E+6
Propylene	4.80	3.23	1.02	2	50	6.33
Propane	5.01	1.95	1.06	2	50	3.68
Isobutane	5.59	2.85	1.05	2	50	5.43
1-Butene	7.22	3.30	1.06	2	50	6.22
n-Butane	7.51	2.35	1.06	2	50	4.43
Trans-butane	7.79	2.57	1.04	2	50	4.85
1-Pentene	9.96	3.64	1.04	2	50	7.00
Pentane	10.04	2.84	1.04	2	50	5.46
Trans-2-Pentene	10.36	4.21	1.05	2	50	8.02
2,2-Dimethylbutane	10.77	3.22	1.06	2	50	6.08
Cyclopentane	11.12	4.36	1.05	2	50	8.30
2,3-methylbutane	11.99	5.24	1.05	2	50	2.54
3-Methylpentane	12.65	5.36	1.03	2	50	1.04
Hexene	13.08	4.28	1.06	2	50	8.08
Hexane	13.19	4.80	1.06	2	50	1.02
Methylcyclopentane	13.23	1.42	1.01	2	50	2.81
Benzene	13.46	2.45	1.06	2	50	3.21
Cyclohexane	13.94	4.77	1.06	2	50	9.00
2-Methylhexane	14.25	1.84	1.06	2	50	3.47
2,3-Dimethylpentane	14.43	1.56	1.08	2	50	2.89
3-Methylhexane	15.43	5.36	1.08	2	50	9.93
2,2,4-Trimethylpentane	15.83	5.33	1.06	2	50	1.01
Heptane	16.10	4.51	1.06	2	50	2.02
Methylcyclohexane	16.14	4.05	1.06	2	50	7.64
2,3,4-Trimethylpentane	16.81	4.13	1.05	2	50	7.87
2-Methylheptane	16.88	3.65	1.05	2	50	6.95
Toluene	17.71	4.47	1.05	2	50	1.09
3-Methylheptane	17.93	7.31	1.05	2	50	1.39
Octane	19.15	4.37	1.04	2	50	4.60
Ethylbenzene	19.41	4.26	1.05	2	50	1.03
p-Xylene	19.56	5.41	1.05	2	50	1.03
m-Xylene	19.73	3.69	1.04	2	50	7.09
Styrene	2.10	5.36	1.04	2	50	6.85
o-Xylene	2.48	3.29	1.04	2	50	6.33
Nonane	20.63	1.16	1.04	2	50	6.95
Isopropylbenzene	21.11	3.35	1.04	2	50	2.89
Propylbenzene	21.38	2.37	1.06	2	50	1.04
m-Ethyltoluene	21.50	3.33	1.06	2	50	3.47
p-Ethyltolune	21.94	2.28	1.01	2	50	6.95
1,3,5-Trimethylbenzene	22.10	3.40	1.04	2	50	6.95
Decane	22.35	2.78	1.03	2	50	2.89

Table 3. 2: Canisters sampling data sheet for sampling at API and 2km away from API

Sampling date	Canister	Sample point	Volume/L	Time
February 2006	1	API	6	24 hr
March 2006	2	API	6	24 hr
April 2006	3	API	6	24 hr
June 2006	4	API	6	24 hr
July 2006	5	API	6	24 hr
August 2006	6	API	6	24 hr
September 2006	1	API	6	24 hr
October 2006	2	API	6	24 hr
November 2006	3	API	6	24 hr
December 2006	4	API	6	24 hr
January 2007	5	API	6	24 hr
February 2007	6	API	6	24 hr
March 2007	1	API	6	24 hr
April 2007	2	API	6	24 hr
May 2007	3	API	6	24 hr
February 2006	4	API 2km away	6	24 hr
March 2006	5	API 2km away	6	24 hr
April 2006	6	API 2km away	6	24 hr
June 2006	1	API 2km away	6	24 hr
July 2006	2	API 2km away	6	24 hr
August 2006	3	API 2km away	6	24 hr
September 2006	4	API 2km away	6	24 hr
October 2006	5	API 2km away	6	24 hr
November 2006	6	API 2km away	6	24 hr
December 2006	1	API 2km away	6	24 hr
January 2007	2	API 2km away	6	24 hr
February 2007	3	API 2km away	6	24 hr
March 2007	5	API 2km away	6	24 hr

Table 3. 3: Sorbent tube data sheet for sampling at API

Date	Tube No	Sample point	Ambient Temp °C	Wind Direction	Wind Speed km/h	Flow rate	Sample Time	Total sample volume
12-05-2006	17532	API site	15	184	12	80 ml/min	09H00-10H00	4800 ml
19-05-2006	15478	API site	20	270	9	80 ml/min	11H00-12H00	4800 ml
12-06-2006	15478	API site	19	360	11	80 ml/min	14H00-15H00	4800 ml
14-08-200-6	15236	API site	21	120	15	80 ml/min	10H00-11H00	4800 ml
13-09-2006	12589	API site	25	175	8	80 ml/min	15H00-16H00	4800 ml
27-09-2006	11478	API site	26	169	11	80 ml/min	09H00-10H00	4800 ml
17-10-2006	11458	API site	32	254	9	80 ml/min	14H00-15H00	4800 ml
13-11-2006	11236	API site	31	289	13	80 ml/min	10H00-11H00	4800 ml
16-01-2007	458711	API site	28	175	14	80 ml/min	09H00-10H00	4800 ml
30-01-2007	11457	API site	34	169	9	80 ml/min	14H00-15H00	4800 ml
14-02-2007	36587	API site	27	320	8	80 ml/min	11H00-12H00	4800 ml
22-02-2007	14578	API site	26	326	15	80 ml/min	14H00-15H00	4800 ml

CHAPTER 4

RESULTS AND DISCUSION

4.1 INTRODUCTION

Two analytical methods for the determination of VOC's vapour in ambient air are discussed. The two methods differ from each other in the sampling technique, type of sorbent method of extraction. The methods uses various technique for sample analysing showed a significant influence of the way in which analysis are carried out. The preparation of equipment that will be used as per method required. Standard calibration mixture of forty one compounds was used to identify the nature of the compounds that do exist at the API. These compounds are shown on the addendum figure 1 and there retention time which will be the indication of these compounds when the samples are tested. The detection of these compounds depends from the weather condition (temperature, wind speed and humidity). Sampling and analysis of these sample was done from February 2006 up to March 2007. These was done to cover all the seasons in order to determine which season has a highest concentration of VOC. Table 4 contains seasonally average concentration and it shows that the VOC will be high on the summer season especially for pentane, 2,2-methylbutane, hexene, hexane, methylcyclopentane, heptane and octane.(see figure 4). During the summer season the temperature are reaching $\pm$ 30 $^{\circ}$C these causes more vapours to evaporate. As the season goes by the concentration of these VOC drops especially in winter

Table3. 4: Session average concentrations for API Canister sample

DF: Dilution Factor; ND: Not Detected

Component	Retention Time (min)	Average Concentration (spring) µg/kg	Average Concentration (summer) µg/kg	Average Concentration (autumn) µg/kg	Average Concentration (winter) µg/kg
Propylene	4.80	124	101	45	13
Propane	5.01	27	18	8	4
Isobutane	5.59	9	7	2	1
1-Butene	7.22	88	68	20	6
n-Butane	7.51	3	1	0	0
Trans-butane	7.79	8	3	0	0
1-Pentene	9.96	45	38	12	5
Pentane	10.04	546	436	210	96
Trans-2-Pentene	10.36	110	82	20	9
2.2-Dimethylbutane	10.77	ND	ND	ND	ND
Cyclopentane	11.12	89	68	28	11
2.3-methylbutane	11.99	175	130	44	15
3-Methylpentane	12.65	ND	ND	ND	ND
Hexene	13.08	352	251	110	48
Hexane	13.19	652	485	198	88
Methylcyclopentane	13.23	328	288	157	55
Benzene	13.46	125	74	22	2
Cyclohexane	13.94	81	67	28	7
2-Methylhexane	14.25	135	113	54	19
2.3-Dimethylpentane	14.43	ND	ND	ND	ND
3-Methylhexane	15.43	ND	ND	ND	ND
2.2.4-Trimethylpentane	15.83	ND	ND	ND	ND
Heptane	16.10	489	440	198	89
Methylcyclohexane	16.14	185	175	85	14
2.3.4-Trimethylpentane	16.81	ND	ND	ND	ND
2-Methylheptane	16.88	ND	ND	ND	ND
Toluene	17.71	149	132	60	25
3-Methylheptane	17.93	74	39	14	2
Octane	19.15	138	124	56	23
Ethylbenzene	19.41	99	81	51	11
p-Xylene	19.56	ND	ND	ND	ND
m-Xylene	19.73	74	43	19	5
Styrene	2.10	38	20	5	ND
o-Xylene	2.48	26	15	2	ND
Nonane	20.63	15	7	1	ND
Isopropylbenzene	21.11	39	28	8	ND
Propylbenzene	21.38	27	22	9	ND
m-Ethyltoluene	21.50	39	18	2	ND
p-Ethyltolune	21.94	31	13	1	ND
1.3.5-Trimethylbenzene	22.10	11	5	3	ND
Decane	22.35	42	26	4	ND

VOC summer season

VOC summer season

Figure 3. 3: Summer season

Volatile organic compounds were measured in all four season (summer, autumn, winter and spring) thirty three compounds where detected during summer. The highest concentration detected was for hexane (652 µg/kg) then pentane (546 µg/kg) and heptane (489 µg/kg). From the thirty three compounds that were detected seventy of these compounds were above 50 ppb, these high concentrations are contributed to the fact of high temperature during this season. The refinery uses more water during this season to cool the reactors and more of these compounds are carried out during the drainage of water to oily separator. More vapours are emitted to the atmosphere and most of these compounds are from the cracking of bigger molecules
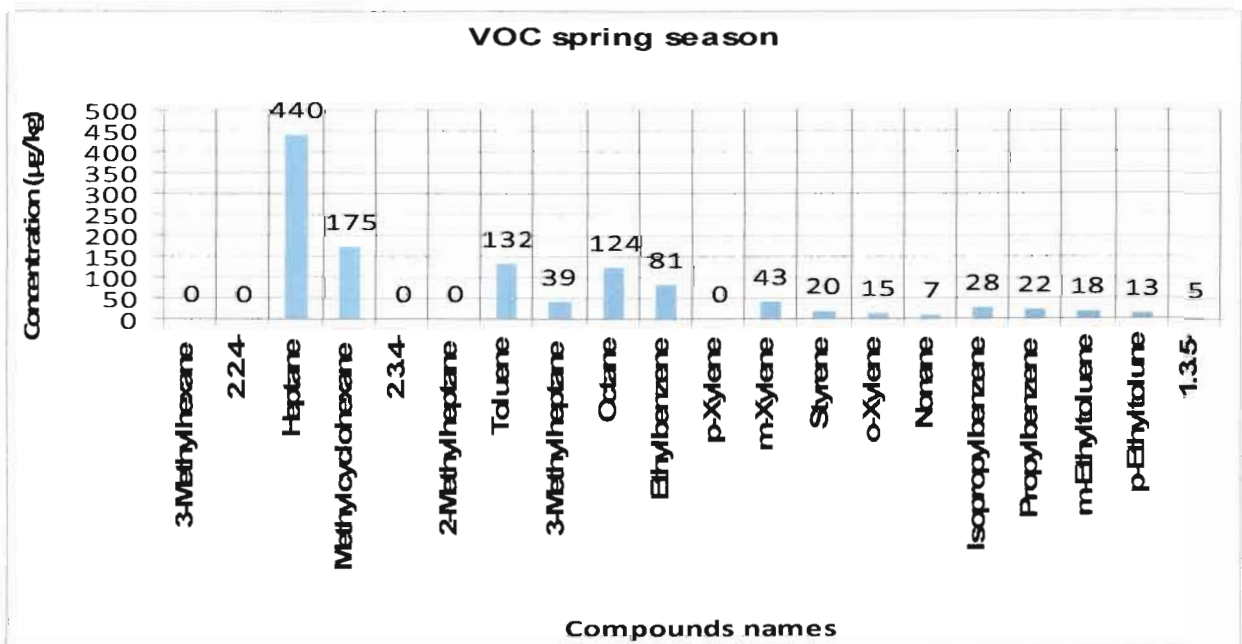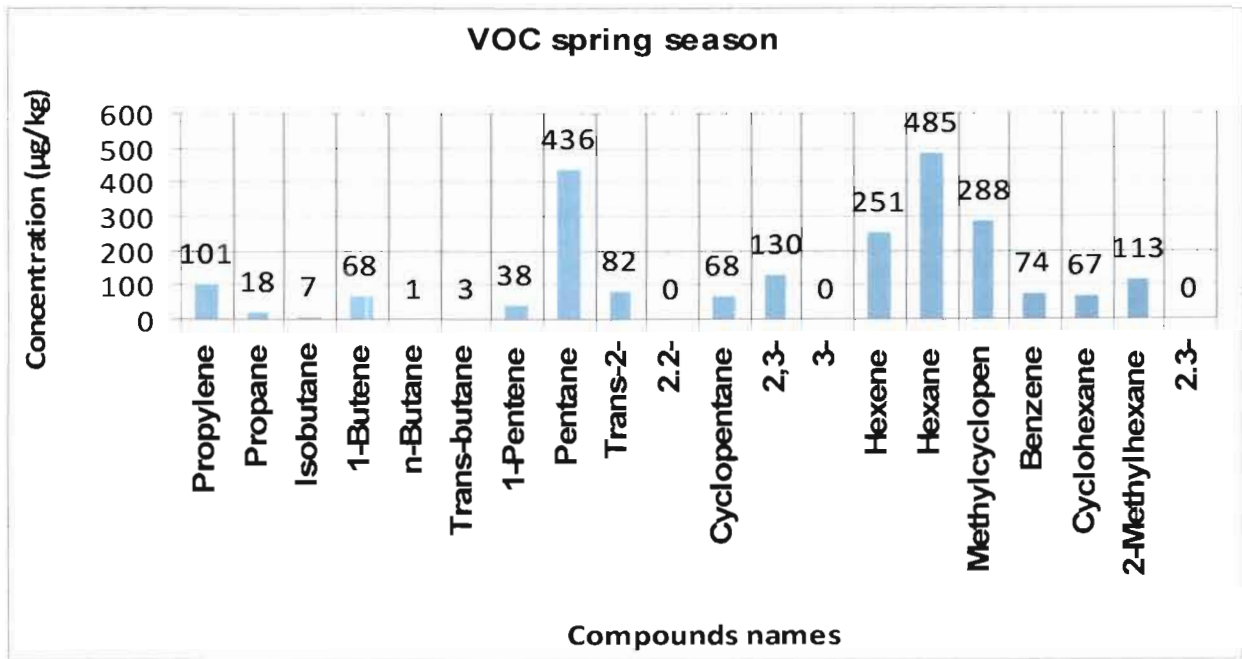
Figure 3. 4: Spring season

During the spring season the VOC concentration will slowly rise from low concentration to the high concentration as the ambient temperature raises month by month by the end of the season the VOC concentration for pentane, hexane and heptane are above 400 µg/kg, while hexene and methylcyclopentane are at 250 µg/kg and above.

VOC winter season
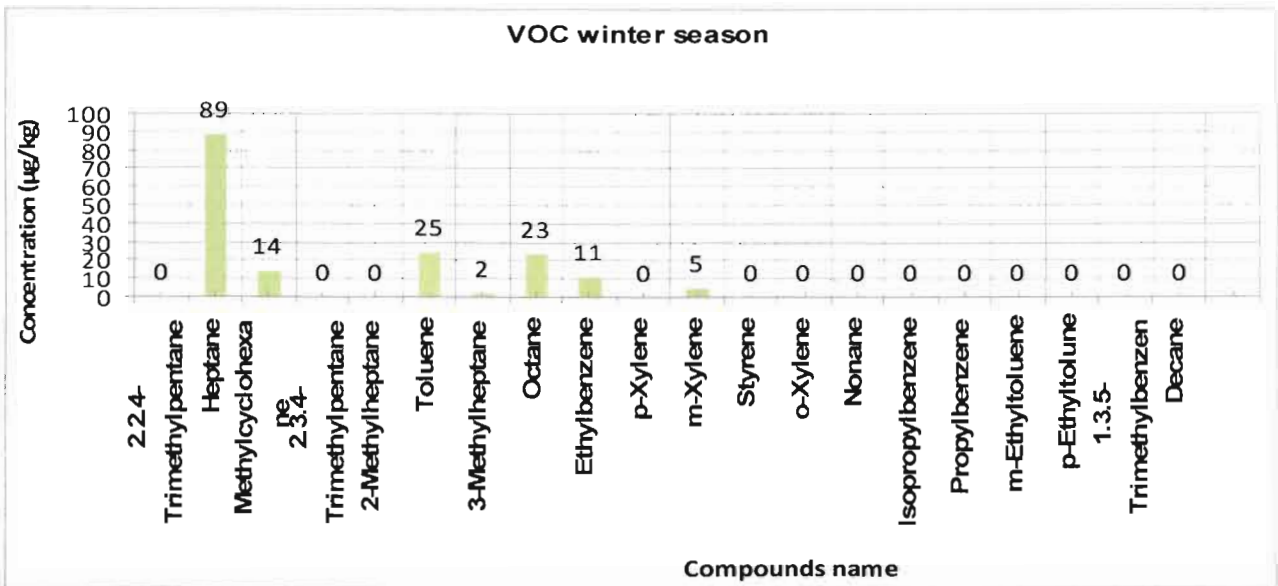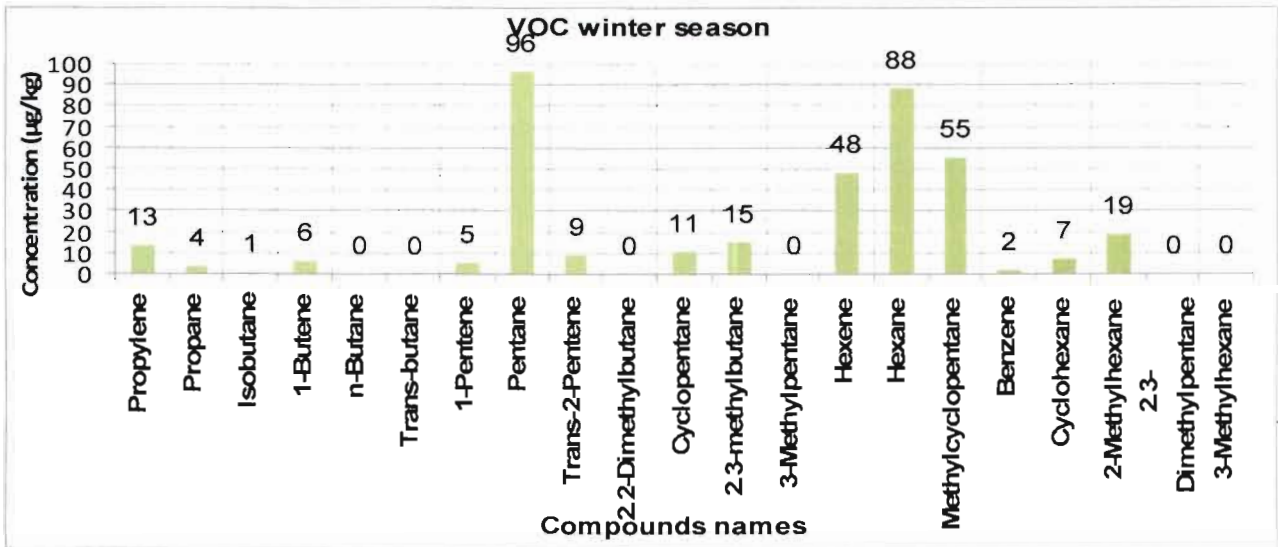
VOC winter season

Figure 3. 5: Winter season

During winter season the VOC concentrations are low below100 µg/kg. The concentration of pentane, hexane and heptane as shown on figure 4 are low in winter compare to the summer. Only twenty two compounds were detected on these season compare to summer, the ambient temperature is mostly below 18°C this makes less vapours to evapoarate.

VOC autumn season
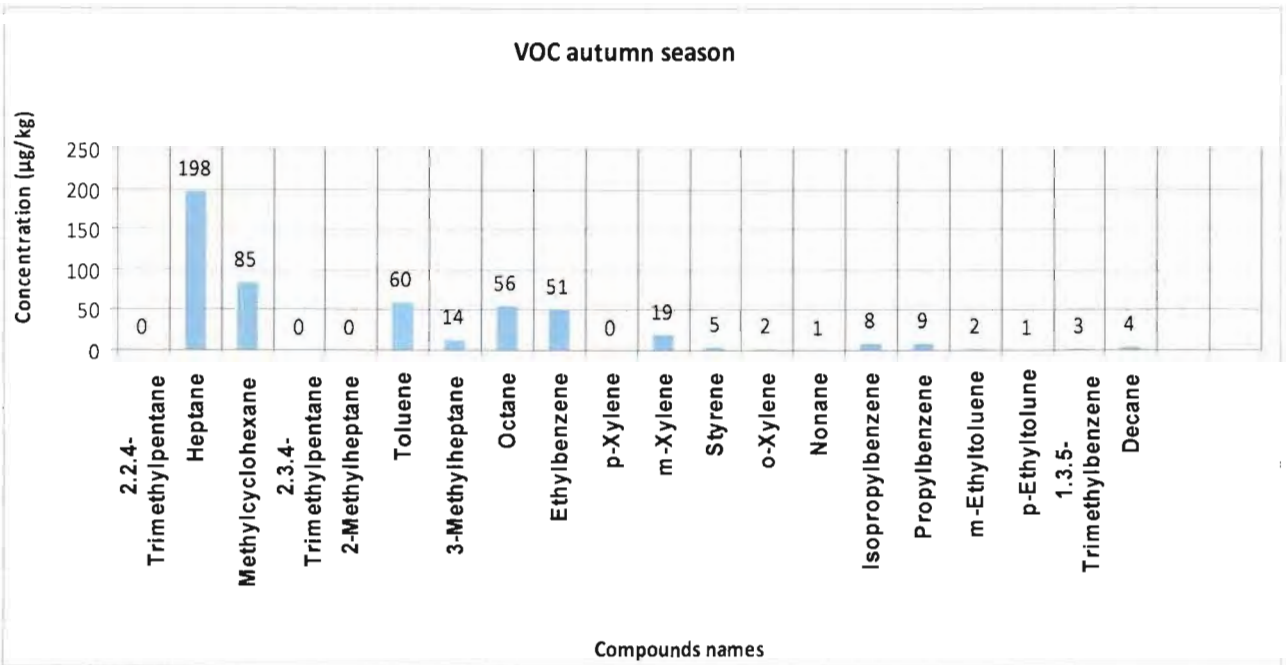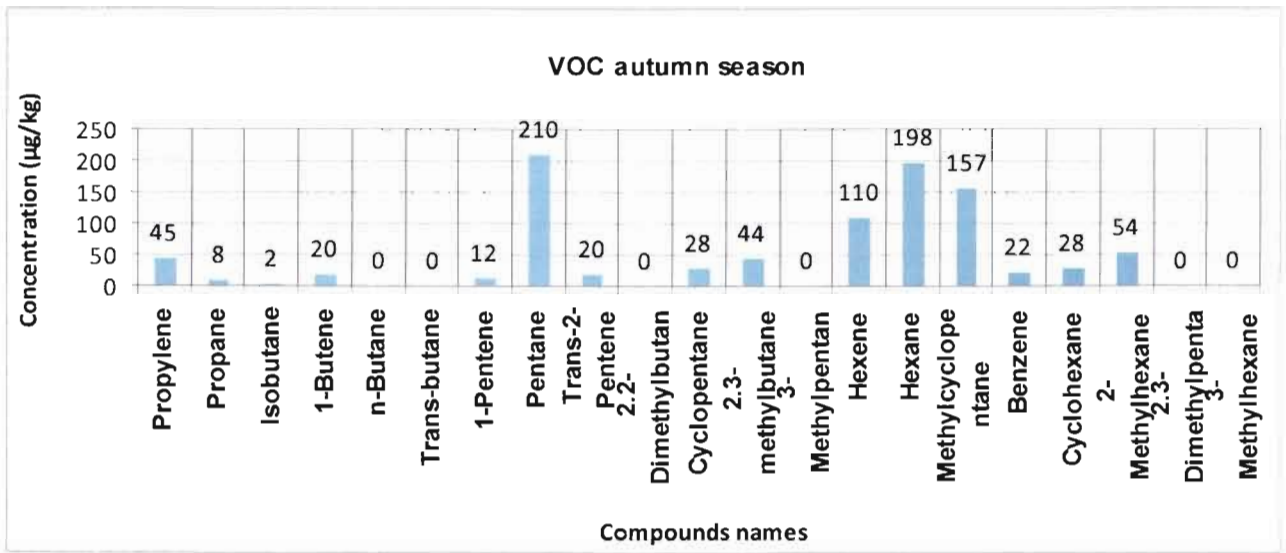
VOC autumn season

Figure3. 6: Autumn season

At this season the, the concentration of VOC will drop from high to low, the high concentration at the beginning of the season will be from the summer. The drop to a lower concentrations will slowly pass by as the winter season approaches, these will be observed as the ambient temparature drops. Most of the compound are detected through the season

4.2 CONCLUSION

The API system is exposed to the atmosphere. The rectangular basins used in the API system are open and for this reason are exposed to the atmosphere. This makes it easy for constant emission of VOC into the atmosphere. The amount of VOC entering the waste water is not monitored. The effluent water discharged from the refinery is not checked for the amount of VOC present. The monitoring of the amount of VOC in waste water stream may lead to a decrease in the emission. From the quantified results at different season, the summer session has the highest VOC emission due to the heat that causes more vapours. When the units (operations plants) are not stable as they should, this will results to more flaring and drainage of hydrocarbons which are streamline to the API where the oil separation will take place. As the temperature drops from season to season, the VOC also comes down as its being seen on the winter graph (figure 3) results that all the VOC were below 90 μg/kg.

The preparation of a method for determination of VOC's in air presents many difficulties, because of their high volatilities and low concentrations in air. As well, the results of determination are affected by the properties of the sorbent used, mainly its sorption capacity, depending on the properties of the compound under determination. Both methods (sorbent tube and canister) differ from each other in their extraction and detection techniques. The well suitable method for the VOC determination is canister method; this method gives more representative sample of the ambient monitoring of 24 hours, where as sorbent tube can do for 2 hours only. The canister method is more advantages due to the sample that will be still reaming for further analyses or re-check.

The existence of the VOC's from source up to 2 km away were found not detectable, these may caused by wind speed and the dilutions from the air.

4.3 RECOMMENDATIONS

4.3.1 REDUCTION METHODS FOR WASTE WATER SEPARATOR SYSTEM

Use floating covers on oily water separators can be obtained by covering the unit. This covering of the unit will minimise the one emission and the process minimising the amount of VOC emitted. There are two types of covering V12 fixed and floating covers. Fixed roof covers can be steel plates, concrete slabs, rigid plastics on coated fabrics, floating covers can be small plastic spheres on aluminium honey comb slab.

4.3.2 INSTALLATION OF THERMAL OXIDISON TO DESTROY VOC

In this device, the VOC are transferred to a second phase where they are destroyed. It requires supplementary fuel to support combustion if the calorific value of the waste stream is low and therefore it cannot release enough heat to maintain auto-thermal firing condition. This technology presents technological limitation, safety concerns, energy impacts and economic impact.

4.3.3 INSTALLATION OF THE BIOTREAT AS A CONTROL DEVICE FOR VOC

This VOC device control acts as a bio-filter in an absorbing and bio-oxidising VOC in air. It recycles secondary effluent containing concentrated bio-mass. It attain low liquid phase in the last step. It also increases the oxygen transfer rate and bank capacity by augmentation of spent aeration of gases.
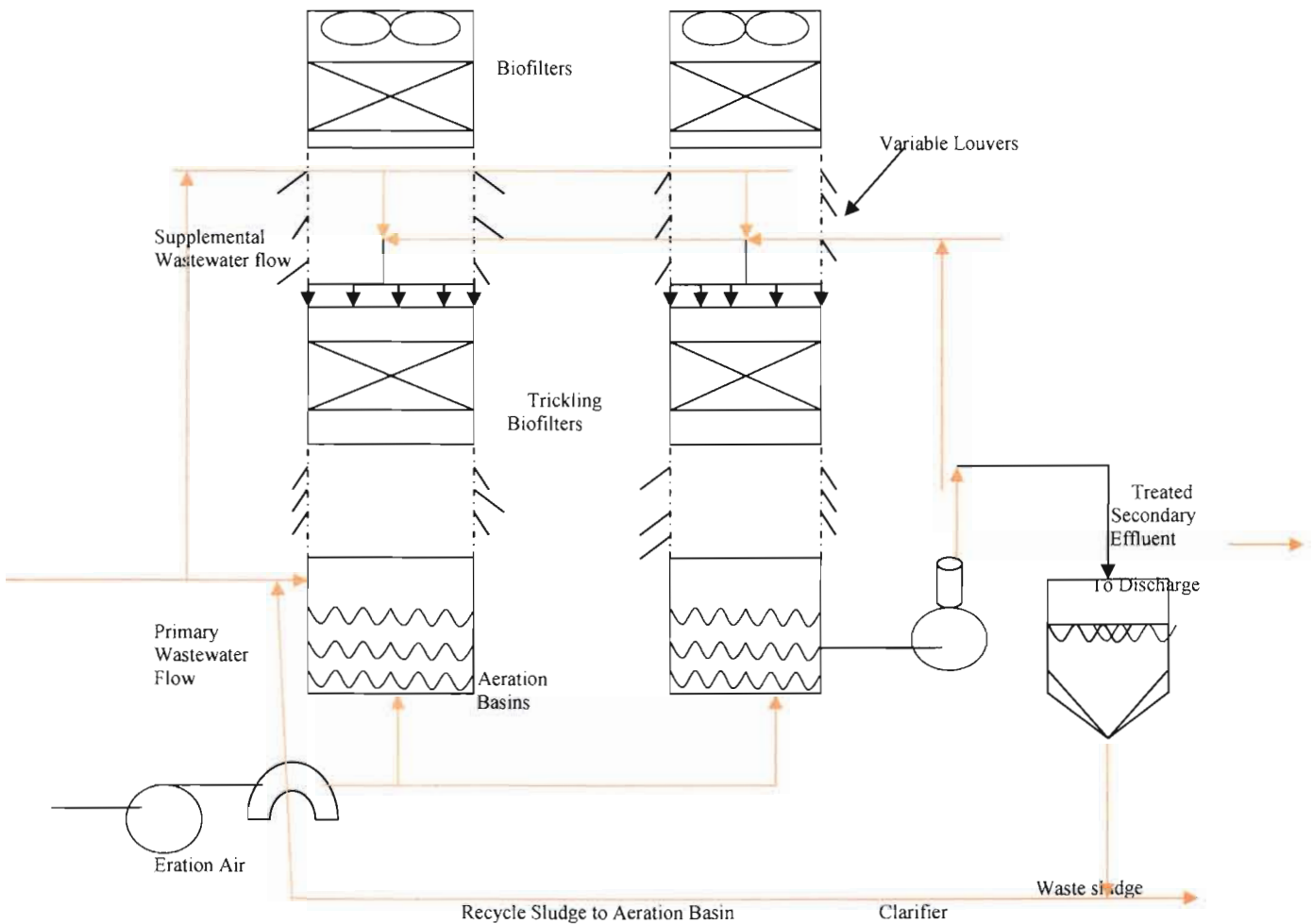
Figure3. 7: The Biofilter

4.3.4 CLASSIFICATION OF VOC

4.3.4.1 Identify the VOC source

In the process of identifying the VOC source, a flow diagram for the waste water collection should be developed. This should trace the path of each source of VOC contaminated waste water entering the system.

4.3.4.2 Quantify each source of VOC emission

A material balance for the manufacturing process must be done. This material balance must detail flow rate and composition of each waste water stream entering the treatment train

4.3.4.3 Determine treatment goals for each source

This serves to assure compliance with permit requirements, new regulation, and corporate and site environmental goals.

4.3.4.4 Choose the treatment methods that appear to be most applicable

Individual wastewater streams must be reviewed to determine which should be treated using separate treatment processes.

4.3.4.5 Size treatment systems for each method

A design for each alternative treatment train being considered should be develop. This should include any ancillary equipment and facility modifications needed.

4.3.4.6 Evaluate life-cycle costs for each method

These are based on the projected life of the facility, include the initial cost of the facility, the frequency and cost of replacement components, staffing and other fixed and variable costs.

4.3.4.7 Choose the best method for the application

This should include consideration of: costs, the advantage and disadvantages of leading contenders the impact of the current and future regulatory climates as well as potential need to expand the plant in the future.

4.4 ADDENDUM

Table3. 5: VOC from the source
API Sorbent Tube

DF: Dilution Factor; ND: Not Detected

Component	Retention Time (min)	Areas X10E+8	Concentration (µg/kg)	Time (min)	Volume	DF
Propylene	4.80	3.33	101	60	4800	2
Propane	5.01	4.94	18	60	4800	2
Isobutane	5.59	2.64	7	60	4800	2
!-Butene	7.22	3.33	68	60	4800	2
n-Butane	7.51	9.48	1	60	4800	2
Trans-butane	7.79	4.06	3	60	4800	2
1-Pentene	9.96	1.42	38	60	4800	2
Pentane	10.04	3.10	436	60	4800	2
Trans-2-Pentene	10.36	3.88	82	60	4800	2
2.2-Dimethylbutane	10.77	ND	ND	60	4800	2
Cyclopentane	11.12	1.06	68	60	4800	2
2.3-methylbutane	11.99	7.34	130	60	4800	2
3-Methylpentane	12.65	ND	ND	60	4800	2
Hexene	13.08	4.87	251	60	4800	2
Hexane	13.19	6.81	485	60	4800	2
Methylcyclopentane	13.23	4.05	288	60	4800	2
Benzene	13.46	1.67	74	60	4800	2
Cyclohexane	13.94	9.64	67	60	4800	2
2-Methylhexane	14.25	1.50	113	60	4800	2
2.3-Dimethylpentane	14.43	ND	ND	60	4800	2
3-Methylhexane	15.43	ND	ND	60	4800	2
2.2.4-Trimethylpentane	15.83	ND	ND	60	4800	2
Heptane	16.10	1.46	440	60	4800	2
Methylcyclohexane	16.14	1.69	175	60	4800	2
2.3.4-Trimethylpentane	16.81	ND	ND	60	4800	2
2-Methylheptane	16.88	ND	ND	60	4800	2
Toluene	17.71	2.74	132	60	4800	2
3-Methylheptane	17.93	5.47	39	60	4800	2
Octane	19.15	1.99	124	60	4800	2
Ethylbenzene	19.41	1.35	81	60	4800	2
p-Xylene	19.56	ND	ND	60	4800	2
m-Xylene	19.73	1.34	43	60	4800	2
Styrene	2.10	3.90	20	60	4800	2
o-Xylene	2.48	4.03	15	60	4800	2
Nonane	20.63	1.16	7	60	4800	2
Isopropylbenzene	21.11	3.35	28	60	4800	2
Propylbenzene	21.38	2.37	22	60	4800	2
m-Ethyltoluene	21.50	3.33	18	60	4800	2
p-Ethyltolune	21.94	2.28	13	60	4800	2
1.3.5-Trimethylbenzene	22.10	3.40	5	60	4800	2
Decane	22.35	2.78	26	60	4800	2

Table3. 6: VOC from the source
API Canister sample

DF: Dilution Factor; ND: Not Detected

Component	Retention Time (min)	Areas X 10E+7	Concentration (μg/kg)	Time (min)	Volume	DF
Propylene	4.80	9.27	112	20	1200	2
Propane	5.01	1.54	22	20	1200	2
Isobutane	5.59	5.58	6	20	1200	2
1-Butene	7.22	1.24	58	20	1200	2
n-Butane	7.51	3.67	3	20	1200	2
Trans-butane	7.79	2.20	6	20	1200	2
1-Pentene	9.96	3.86	41	20	1200	2
Pentane	10.04	7.07	398	20	1200	2
Trans-2-Pentene	10.36	8.40	72	20	1200	2
2.2-Dimethylbutane	10.77	ND	ND	20	1200	2
Cyclopentane	11.12	4.54	81	20	1200	2
2.3-methylbutane	11.99	1.61	114	20	1200	2
3-Methylpentane	12.65	ND	ND	20	1200	2
Hexene	13.08	1.32	271	20	1200	2
Hexane	13.19	1.53	481	20	1200	2
Methylcyclopentane	13.23	3.94	307	20	1200	2
Benzene	13.46	3.46	61	20	1200	2
Cyclohexane	13.94	2.08	58	20	1200	2
2-Methylhexane	14.25	4.11	124	20	1200	2
2.3-Dimethylpentane	14.43	ND	ND	20	1200	2
3-Methylhexane	15.43	ND	ND	20	1200	2
2.2.4-Trimethylpentane	15.83	ND	ND	20	1200	2
Heptane	16.10	3.36	448	20	1200	2
Methylcyclohexane	16.14	4.37	181	20	1200	2
2.3.4-Trimethylpentane	16.81	ND	ND	20	1200	2
2-Methylheptane	16.88	ND	ND	20	1200	2
Toluene	17.71	7.96	154	20	1200	2
3-Methylheptane	17.93	1.54	42	20	1200	2
Octane	19.15	5.55	138	20	1200	2
Ethylbenzene	19.41	3.07	74	20	1200	2
p-Xylene	19.56	ND	ND	20	1200	2
m-Xylene	19.73	2.30	29	20	1200	2
Styrene	2.10	8.18	17	20	1200	2
o-Xylene	2.48	2.76	4	20	1200	2
Nonane	20.63	1.34	32	20	1200	2
Isopropylbenzene	21.11	5.62	19	20	1200	2
Propylbenzene	21.38	8.48	31	20	1200	2
m-Ethyltoluene	21.50	4.16	9	20	1200	2
p-Ethyltolune	21.94	7.75	17	20	1200	2
1.3.5-Trimethylbenzene	22.10	8.95	4	20	1200	2
Decane	22.35	3.76	14	20	1200	2

Table3. 7: VOC from 0.5 km away
API Canister sample

DF: Dilution Factor; ND: Not Detected

Component	Retention Time (min)	Areas *10E+7	Concentration ($\mu g/kg$)	Time (min)	Volume	DF
Propylene	4.80	1.08	13	20	1200	2
Propane	5.01	ND	ND	20	1200	2
Isobutane	5.59	ND	ND	20	1200	2
1-Butene	7.22	ND	ND	20	1200	2
n-Butane	7.51	ND	ND	20	1200	2
Trans-butane	7.79	ND	ND	20	1200	2
1-Pentene	9.96	ND	ND	20	1200	2
Pentane	10.04	4.26	24	20	1200	2
Trans-2-Pentene	10.36	ND	ND	20	1200	2
2.2-Dimethylbutane	10.77	ND	ND	20	1200	2
Cyclopentane	11.12	ND	ND	20	1200	2
2.3-methylbutane	11.99	4.37	31	20	1200	2
3-Methylpentane	12.65	ND	ND	20	1200	2
Hexene	13.08	1.41	29	20	1200	2
Hexane	13.19	1.27	40	20	1200	2
Methylcyclopentane	13.23	3.51	10	20	1200	2
Benzene	13.46	5.68	1	20	1200	2
Cyclohexane	13.94	ND	ND	20	1200	2
2-Methylhexane	14.25	ND	ND	20	1200	2
2.3-Dimethylpentane	14.43	ND	ND	20	1200	2
3-Methylhexane	15.43	ND	ND	20	1200	2
2.2.4-Trimethylpentane	15.83	ND	ND	20	1200	2
Heptane	16.10	3.15	42	20	1200	2
Methylcyclohexane	16.14	7.24	3	20	1200	2
2.3.4-Trimethylpentane	16.81	ND	ND	20	1200	2
2-Methylheptane	16.88	ND	ND	20	1200	2
Toluene	17.71	1.55	3	20	1200	2
3-Methylheptane	17.93	ND	ND	20	1200	2
Octane	19.15	ND	ND	20	1200	2
Ethylbenzene	19.41	ND	ND	20	1200	2
p-Xylene	19.56	ND	ND	20	1200	2
m-Xylene	19.73	ND	ND	20	1200	2
Styrene	2.10	ND	ND	20	1200	2
o-Xylene	2.48	ND	ND	20	1200	2
Nonane	20.63	ND	ND	20	1200	2
Isopropylbenzene	21.11	ND	ND	20	1200	2
Propylbenzene	21.38	ND	ND	20	1200	2
m-Ethyltoluene	21.50	ND	ND	20	1200	2
p-Ethyltolune	21.94	ND	ND	20	1200	2
1.3.5-Trimethylbenzene	22.10	ND	ND	20	1200	2
Decane	22.35	ND	ND	20	1200	2

Table3. 8: Session average concentrations

API Canister sample DF: Dilution Factor; ND: Not Detected

Component	Retention Time (min)	Average Concentration (spring) µg/kg	Average Concentration (summer) µg/kg	Average Concentration (autumn) µg/kg	Average Concentration (winter) µg/kg
Propylene	4.80	124	101	45	13
Propane	5.01	27	18	8	4
Isobutane	5.59	9	7	2	1
1-Butene	7.22	88	68	20	6
n-Butane	7.51	3	1	0	0
Trans-butane	7.79	8	3	0	0
1-Pentene	9.96	45	38	12	5
Pentane	10.04	546	436	210	96
Trans-2-Pentene	10.36	110	82	20	9
2.2-Dimethylbutane	10.77	ND	ND	ND	ND
Cyclopentane	11.12	89	68	28	11
2.3-methylbutane	11.99	175	130	44	15
3-Methylpentane	12.65	ND	ND	ND	ND
Hexene	13.08	352	251	110	48
Hexane	13.19	652	485	198	88
Methylcyclopentane	13.23	328	288	157	55
Benzene	13.46	125	74	22	2
Cyclohexane	13.94	81	67	28	7
2-Methylhexane	14.25	135	113	54	19
2.3-Dimethylpentane	14.43	ND	ND	ND	ND
3-Methylhexane	15.43	ND	ND	ND	ND
2.2.4-Trimethylpentane	15.83	ND	ND	ND	ND
Heptane	16.10	489	440	198	89
Methylcyclohexane	16.14	185	175	85	14
2.3.4-Trimethylpentane	16.81	ND	ND	ND	ND
2-Methylheptane	16.88	ND	ND	ND	ND
Toluene	17.71	149	132	60	25
3-Methylheptane	17.93	74	39	14	2
Octane	19.15	138	124	56	23
Ethylbenzene	19.41	99	81	51	11
p-Xylene	19.56	ND	ND	ND	ND
m-Xylene	19.73	74	43	19	5
Styrene	2.10	38	20	5	ND
o-Xylene	2.48	26	15	2	ND
Nonane	20.63	15	7	1	ND
Isopropylbenzene	21.11	39	28	8	ND
Propylbenzene	21.38	27	22	9	ND
m-Ethyltoluene	21.50	39	18	2	ND
p-Ethyltolune	21.94	31	13	1	ND
1.3.5-Trimethylbenzene	22.10	11	5	3	ND
Decane	22.35	42	26	4	ND

Table3. 9:API Sorbent Tube 2 km away
DF: Dilution Factor; ND: Not Detected

Component	Retention Time (min)	Areas	Concentration (µg/kg)	Time (min)	Volume	DF
Propylene	4.80	ND	ND	60	4800	2
Propane	5.01	ND	ND	60	4800	2
Isobutane	5.59	ND	ND	60	4800	2
1-Butene	7.22	ND	ND	60	4800	2
n-Butane	7.51	ND	ND	60	4800	2
Trans-butane	7.79	ND	ND	60	4800	2
1-Pentene	9.96	ND	ND	60	4800	2
Pentane	10.04	ND	ND	60	4800	2
Trans-2-Pentene	10.36	ND	ND	60	4800	2
2.2-Dimethylbutane	10.77	ND	ND	60	4800	2
Cyclopentane	11.12	ND	ND	60	4800	2
2.3-methylbutane	11.99	ND	ND	60	4800	2
3-Methylpentane	12.65	ND	ND	60	4800	2
Hexene	13.08	ND	ND	60	4800	2
Hexane	13.19	ND	ND	60	4800	2
Methylcyclopentane	13.23	ND	ND	60	4800	2
Benzene	13.46	ND	ND	60	4800	2
Cyclohexane	13.94	ND	ND	60	4800	2
2-Methylhexane	14.25	ND	ND	60	4800	2
2.3-Dimethylpentane	14.43	ND	ND	60	4800	2
3-Methylhexane	15.43	ND	ND	60	4800	2
2.2.4-Trimethylpentane	15.83	ND	ND	60	4800	2
Heptane	16.10	ND	ND	60	4800	2
Methylcyclohexane	16.14	ND	ND	60	4800	2
2.3.4-Trimethylpentane	16.81	ND	ND	60	4800	2
2-Methylheptane	16.88	ND	ND	60	4800	2
Toluene	17.71	ND	ND	60	4800	2
3-Methylheptane	17.93	ND	ND	60	4800	2
Octane	19.15	ND	ND	60	4800	2
Ethylbenzene	19.41	ND	ND	60	4800	2
p-Xylene	19.56	ND	ND	60	4800	2
m-Xylene	19.73	ND	ND	60	4800	2
Styrene	2.10	ND	ND	60	4800	2
o-Xylene	2.48	ND	ND	60	4800	2
Nonane	20.63	ND	ND	60	4800	2
Isopropylbenzene	21.11	ND	ND	60	4800	2
Propylbenzene	21.38	ND	ND	60	4800	2
m-Ethyltoluene	21.50	ND	ND	60	4800	2
p-Ethyltolune	21.94	ND	ND	60	4800	2
1.3.5-Trimethylbenzene	22.10	ND	ND	60	4800	2
Decane	22.35	ND	ND	60	4800	2

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