

# Ozone Depletion, Chemistry and Impacts

Sem H. Bakker  
Editor

NOVA

# **OZONE DEPLETION, CHEMISTRY AND IMPACTS**

**SEM H. BAKKER**  
**EDITOR**

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**OZONE DEPLETION, CHEMISTRY  
AND IMPACTS**

## PREFACE

Ground-level ozone is an air pollutant with harmful effects on the respiratory systems of animals. Ozone in the upper atmosphere filters potentially damaging ultraviolet light from reaching the Earth's surface. It is present in low concentrations throughout the Earth's atmosphere. It has many industrial and consumer applications. This new book presents the latest research in the field from around the globe.

As explained in Chapter 1, tropospheric ozone is regulated by US EPA (Environmental Protection Agency) as a criterion atmospheric pollutant because of their harmful effects on human's health. VOCs (Volatile Organic Compounds) are monitored in many places as ozone precursor gases such as the PAMS (Photochemical Assessment Monitoring Stations) network by EPA. Online GCs (Gas Chromatograph) and GC/MS are common methods that have been used to analyze speciated VOCs. Usually, these methods can give continuous measurement of speciated VOCs with hourly temporal resolution. Recently, new problems arise in the ozone precursor management and new monitoring techniques can provide the solutions.

Studies have shown that highly reactive VOCs from very local sources, especially fugitive sources, can cause rapid ozone events at very high concentrations at receptor sites, especially in the areas with dense point sources such as refineries and other petrochemical facilities. In order to monitor VOCs at the fence line of major point sources, traditional continuous GCs are not able to capture these short-lived events by the rapid variations in either emission rate or the meteorological conditions. Running the online GC in trigger mode proved to be very effective in capture these events and hence reducing this type of VOC emissions. Analytical instruments with fast response can also help to address this type of issues. For example, PTR-MS (Transfer Reaction Mass Spectrometry), FTIR (Fourier transform infrared spectroscopy, including extractive mode and open path mode), and fast micro GCs can provide speciated VOC concentrations in seconds to minutes, and may be used for special monitoring purpose. Each of these instruments has its own limitations and need more field test before they can be widely used for ambient air quality monitoring.

Nearly half of the VOC emissions from the chemical industries are fugitive. Industrial operators have been using FID based detectors to manually inspect each component for leaks in their facilities as described in the LDAR (Leak Detection and Repair) program. Most of the time, given the huge number of possible leaking components (~millions for a typical mid scale refinery), this turns out to be a highly labor intensive and time consuming process. IR imaging techniques are developed as an efficient tool for the LDAR purposes. The VOC plumes from the leaking components are visualized by the IR cameras. The detection

efficiency can be dramatically improved, and previous unexpected source categories could also be found by using an IR camera. With AI (Artificial Intelligent) tools developed for machine to identify VOCs from IR videos, IR cameras can be operated continuously and in an unattended way to further reduce VOC emissions and improve the industrial process reliabilities.

Comprehensive two dimensional GC techniques have proved to be very powerful in analyzing complex systems such as VOC in ambient air. With a modulator between two independent columns based on different separation mechanisms, two dimensional GCs can better separate background and noises from signal peaks, resulting 2 to 4 fold improvement in sensitivity than traditional one dimensional GC. More importantly, two dimensional GC makes it possible to separate peaks that are previously lumped in one column. For ambient air samples, the number of peaks identified by a two dimensional GC can identify is ten times of a traditional GC. The application of two dimensional GC for ozone precursor monitoring may provide more information to identify the sources and better understanding the ozone formation processes. As a common analytical tool, two dimensional GC is getting mature but methods need to be developed and standardized for their specific applications in ambient air monitoring area such as speciated VOCs.

Ozone has recently received much attention in water treatment technology for its high oxidation and disinfection potential. The use of ozone brings several benefits but has a few disadvantages that limit its application in water treatment, including: i) low solubility and stability in water, ii) low reactivity with some organic compounds and iii) failure to produce a complete transformation of organic compounds into CO<sub>2</sub>, generating degradation by-products that sometimes have higher toxicity than the raw micropollutant. To improve the effectiveness of ozonation process efficiency, advanced oxidation processes (AOPs) have recently been developed (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/UV, O<sub>3</sub>/catalysts). AOPs are based on ozone decomposition into hydroxyl radicals (HO<sup>•</sup>), which are high powerful oxidants. Chapter 2 offers an overview of AOPs, focusing on the role of solid catalysts in enhancing ozone transformation into HO<sup>•</sup> radicals. Catalytic ozonation is a new way to remove organic micropollutants from drinking water and wastewater. The application of several homo- and heterogeneous ozonation catalysts is reviewed, describing their activity and identifying the parameters that influence the effectiveness of catalytic systems. Although catalytic ozonation has largely been limited to laboratory applications, the good results obtained have led to investigations now under way by researchers worldwide. It is therefore timely to provide a summary of achievements to date in the use of solid materials to enhance ozone transformation into HO<sup>•</sup> radicals.

In Chapter 3, eleven kinds of dyes from the three dye categories of azo, anthraquinone and lush were selected to investigate the decolorization efficiency of dyes by ozone in aqueous solutions. Changes in pH, total organic carbon (TOC), and electronic conductivity (EC) in solutions over reaction time were examined. The major components of dye derivatives during the degradation process were quantified. The results indicated that except for disperse dyes, the decolorization efficiencies of ozone for all soluble dyes exceeded 79% in 20 min. The sequence of the decolorization rate is: reactive > acid > direct > cationic > disperse. In the same type of soluble dyes, the decolorization rates were quicker for dyes with smaller molecular mass. With increasing reaction time, some acidic materials were produced, resulting in a decrease in pH. The final pH for all treatments was less than 4.5. During the reaction process, the decolorization efficiencies increased, while the pH and TOC content

decreased. EC increased with the increasing of decolorization efficiency. Concentrations of the related ions ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{SO}_4^{2-}$ ) and organic derivatives during the reaction process were monitored. The results showed that complicated dye molecules were degraded to simpler organic compounds. Almost all the substituents such as  $-\text{Cl}$  and  $\text{PO}_4^{3-}$  in the dye molecules were transformed into  $\text{Cl}^-$ ,  $\text{H}_2\text{PO}_4^-$ . Almost all  $-\text{SO}_3\text{H}$  is converted to  $\text{SO}_4^{2-}$ . Nitrogen was partially degraded to  $\text{NH}_4^+$  or  $\text{NO}_3^-$  due to the types of groups in dye molecules, and  $\text{NO}_2^-$  was not detected in the degraded solution. Other organics were detected and the organic acids were identified in the solutions. Based on the intermediates produced and the variation of their concentrations, some tentative degradation pathways were proposed.

The irradiation of lignin from pine from steam explosion process in the presence of oxygen, in conditions described for the formation of superoxide ion, for different irradiation time was followed isolating the lignin and determining the average molecular weight. The experiments showed that, until eight hours irradiation,  $M_n$  decreases, while  $M_w$  and  $M_z$  increases. After eight hours irradiation an inverse behaviour was observed, with an increase of  $M_n$  and a decrease of  $M_w$  and  $M_z$ . These results in Chapter 4 are in agreement with an initial polymerization process followed by a photoinduced degradation. Ozonation was carried out in acetonitrile – methanol solution. The reaction showed a zero order kinetics. After 50 min. the average molecular weight of lignin is the half. The reaction mixture was analyzed by using GC-MS. Oxalic acid was determined. The treatment of diluted olive oil mill waste water with Fenton's reagent reduces COD. The reaction followed a zero order kinetics. The reaction needs to use large amounts of reagents to have an appreciable reduction of COD. Treatment of olive oil mill waste water with ozone reduces COD. The reaction followed a first order kinetics. The uv spectrum of olive oil mill waste water after treatment with ozone did not show absorptions. Different degradation methods have been applied to assess the suitability of advanced oxidation process (AOPs) to promote mineralization of imazethapyr, (*RS*)-5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid, a widely used imidazolinone class herbicide, the persistence of which has been demonstrated in surface and ground waters destined to human uses. Independently of the oxidation process assessed, the decomposition of imazethapyr always followed a pseudo-first order kinetic. The direct UV-irradiation of the herbicide as its oxidation with  $\text{O}_3$  and  $\text{H}_2\text{O}_2/\text{UV}$ -oxidation were sufficiently slow to permit the identification of intermediate products, the formation pathway of which has been proposed.  $\text{O}_3/\text{UV}$ ,  $\text{O}_3/\text{UV}+\text{TiO}_2$ ,  $\text{TiO}_2/\text{UV}$ , and  $\text{TiO}_2/\text{UV}+\text{H}_2\text{O}_2$  treatments were characterized by a faster degradation and rapid formation of a lot of little molecules, which were quickly destroyed.

As explained in Chapter 5, acute ozone exposure is known to decrease pulmonary function. We have successfully constructed an animal airway hyper-responsiveness (AHR) model by ozone stress, mimicking the airway obstruction, airway inflammatory response, and increased airway responsiveness observed in human AHR disease. The mechanisms leading to the increased AHR are not clear, but epithelial injury is involved. The epithelium is not merely a passive barrier but can generate a range of mediators that may play a role in the inflammatory and remodeling responses. Damage of the bronchial epithelium associated with leukocyte infiltration and increased airway responsiveness are consistent features of asthma. It is reasonably hypothesized that disruption of these functional processes or defects in airway epithelium integrity may be the initial steps leading to airway hyper-responsiveness. Therefore, we damaged the airway epithelium with ozone stress in cultured BEC and animal model, focusing in particular on the roles of airway epithelium in airway inflammation and hyper-responsiveness.

Years of research in our laboratory showed that, after repeated stimulation of bronchial epithelial cells by ozone, a series of events are programmed to occur: defect in function (e.g., anti-oxidation or secretion) or structural integrity (e.g., imbalance in adhesive molecules expression) weaken the protective ability of BEC against exogenous factors or antigens, such that BEC are easily stressed, damaged and even denuded; and thus the sensitivity of the epithelium and sensory nerve ends are enhanced aberrantly. Subsequently the inflammatory mediators are released; antigen-presenting activities are increased, recruiting and activating immune or inflammatory responsive cells with enhanced airway inflammation and hyper-responsiveness. Pulmonary peptidergic innervation remodeling and airway remodeling continued to increase the airway resistance. These events may be involved in the pathogenesis of AHR.

Ozone is known to be formed naturally in the atmosphere, as a colorless gas having a pungent odor and associated with the ability to guard against the sun's harmful ultraviolet radiation. Historically[1], the characteristic odor of ozone was noticed by Van Marum at 1785 in his electrostatic machine during passage of electric sparks. Later at 1801, Cruickshank notice this odor at the anode electrode during water electrolysis. Finally, in 1840 Shonbein named this chemical substance as ozone from the Greek word *ozein*, which means to smell. Siemens 's invention followed the early ozone method production by a corona discharge which is based on passing an electric discharge through dry oxygen or air.

From the side of chemistry, ozone is characterized as a triatomic allotropic form of oxygen ( $O_3$ ) having a molecular weight of 48.

Chapter 6 has focused on the general analysis and evaluation of the industry with the introduction of the ozone generating equipment from the perspective of the evolution of its application and usefulness, as well as its interaction with the environmental and social variables, together with the problems and challenges to be faced contributing in the industry's development. Moreover, ozone application during the last decades brought together great advances in the industry contributing to an effective and sustainable production policy based in a main and capital tool, which is a clean technology with environmental benefits.

Chapter 7 is a review about catalytic ozonation, which is a new way of contaminants removal from wastewater. Despite its current application is mainly limited to laboratory use, the results obtained employing this approach in pollutant degradation showed to be promissory to scale large applications, however further investigation about its efficiency and drawback must be carried out. The aim of this chapter is to give a survey of the application of several homo- and heterogeneous catalysts, with special attention given to the last one. In this context, some metals (for example, Fe, Co, Mn, Zn and Ni) under various forms (salt of reduced metal, solid oxide or deposited metal on support) can be used to enhance the efficiency of ozone towards the removal and/or conversion of different organic compounds in aqueous solution. Moreover, the activity and the parameters that influence the efficiency of these two catalytic systems will be present as a short overview.

In Chapter 8, we consider recently introduced bivariate stochastic volatility models commonly used to analyse financial time series, to study problems related to air pollution data. Such models are used here to estimate the volatility of weekly averaged ozone measurements taking into account two different sets of data provided by the monitoring network of Mexico City. A Bayesian analysis is developed using Markov Chain Monte Carlo (MCMC) methods to simulate samples from the joint posterior distributions and perform the estimates of interest.

The atmospheric sulfur cycle has been the subject of intensive investigation for several decades because of the need to assess the contribution of anthropogenically produced sulfur to such problems as acid rain, visibility reduction, and climate modification. The atmospheric chemistry of sulfur-containing compounds is directly relevant to the formation of sulfur aerosol in marine air. Reduced organic sulfur compounds have been estimated to account for approximately 25% of the total global gaseous sulfur budget. Besides the predominant  $\text{CH}_3\text{SCH}_3$  (dimethyl sulfide, DMS), other reduced sulfur compounds should also be estimated, such as  $\text{C}_2\text{H}_5\text{SCH}_3$  (ethylmethyl sulfide, EMS),  $n\text{-C}_3\text{H}_7\text{SCH}_3$  ( $n$ -propylmethyl sulfide, PMS), and  $\text{C}_2\text{H}_5\text{SC}_2\text{H}_5$  (diethyl sulfide, DES), of which there are only a few kinetics investigations. Based on our previous work of DMS and DES, we have measured the rate constants of the gas-phase reactions of ozone with EMS and PMS at room temperature in our self-made smog chamber. Experiments were conducted under supposedly pseudo-first-order decay conditions, keeping  $[\text{sulfide}]_0 > 50[\text{O}_3]_0$ , but having different combinations of  $[\text{sulfide}]_0$  and  $[\text{O}_3]_0$ . Cyclohexane was added into the reactor to eliminate the effect of OH radicals. The rate constants of the gas-phase reactions of ozone with EMS and PMS were determined to be  $(1.12 \pm 0.18) \times 10^{-19}$  and  $(1.24 \pm 0.15) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. The results in Chapter 9 will enrich the kinetics data of atmospheric chemistry, and provide some useful information for evaluating the loss processes of reduced organic sulfur compounds.

Chapter 10 describes a model based approach to develop an operational public warning system for air pollution monitoring. The proposed methodology is based on hard and soft computing techniques and combines an adaptive nonlinear state space-based prediction mechanism, a gain scheduling strategy and neural network techniques to develop an integrated operational warning system. The overall method was applied to ground-level ozone and  $\text{PM}_{10}$  time-series data measured in Bordeaux, France over four years (1998 to 2001). The aim of model building was to develop predictive models in order to provide forecasts of the maximal daily ground-level ozone and the daily mean  $\text{PM}_{10}$  concentrations. The goals of the forecast are to provide information in order to satisfy needs for public information and to further reduction and prevention of exposure, in cases where pollutant limit values are exceeded over a specified length of time. A key characteristic of such a system is that it is constantly fed with new available data, so its behaviour can be adapted to the short term changes of air pollution. Moreover, the warning system provides additional information regarding the extent of a smog episode. This is an important aspect for planning of counter actions and for assessments of human health hazards and negative environmental effects. Finally, the chapter discusses some inherent shortcomings associated with the commonly used statistical techniques for air pollution modelling, and an alternative solution based on  $l_\infty$  optimization techniques is proposed.

The term Quasi-Biennial Oscillation (QBO) was designated to describe the regular reversals of zonal winds in the equatorial stratosphere occurred with periodicity about 28 months. The phase of QBO cycle, East (E) or West (W) is determined by direction of the zonal winds. Although the wind QBO is mainly a tropical circulation feature, its effects are displayed well beyond the equatorial region. Indeed, the year-to-year fluctuations in the extratropical atmosphere are controlled by QBO, which influence is observed in such parameters as temperature, the total ozone distribution, and others. The most important thing is the well known at present QBO property to modulate the solar activity impact on the stratosphere and troposphere.

Today the dissipation of upward propagating equatorial waves usually examined as a theoretical mechanism for QBO generation. So, it is generally accepted that the proximity of the average QBO period to the double annual one being merely statistical result, whereas the actual period varies from 19 to 36 months. As a result of the high variability and elusive relation to the seasonal cycles, the QBO phase duration seemed to be unpredictable.

A new method for the investigation of the QBO cycle evolution is presented in Chapter 11. The analysis of the height wind profiles makes it possible to reveal new regularities in the equatorial stratosphere wind reversals. The stagnation stage of descending easterlies always starts in solstice, either in December–January or in June–July, and always completes by the equinox being of quantized duration in different QBO-cycles (about 3, 9, or 15 months). So the length of the complete QBO-cycle, if defined as a period between the inceptions of the successive stagnation stages, depends on their durations and may be equal to 24, 30, or 36 months. Consequently, the full QBO cycle length can be predicted as soon as end of the stagnation stage is found while observing the zonal wind transformation.

In turn the duration of the stagnation stage depends on the intensity of solar UV flux. The short stalling period (3–4 months) is observed under condition of the high level or steady increase of the UV irradiance during the first equinox in course of the partial QBO cycle. If the UV flux is low or decreases during the proper equinox, the easterly winds do not descend from the upper layer to the lower stratosphere, and the stalling period length at about 20–40 hPa increases to 9–10 or 15–16 months. The intensity of the spring ozone depletion within Antarctic polar vortex is thought to be also dependent on the phase of the equatorial QBO cycle. It is shown the relation of the season regularities of the equatorial QBO-circulation to the interannual fluctuations and the intensity of total ozone (TOZ) destruction over Antarctica during “ozone hole” phenomenon.

Rising concerns about the quality of drinking water have led both public and private bodies to invest considerable human and economic resources in the development of novel water treatment processes to more effectively remove organic micropollutants, highly toxic for human health (pesticides, herbicides, microtoxins) and sometimes responsible for altering organoleptic properties of the water. Processes based on the simultaneous use of ozone and activated carbon have proven to be very effective for removing contaminants from drinking waters. The results obtained by using naphthalenesulphonic acids as model pollutants have shown that O<sub>3</sub>/activated carbon systems have a great efficiency in drinking water treatment because i) it is possible to remove micropollutants due to the high adsorption capacity of activated carbon, and/or ii) they oxidise polar micropollutants, characterised by a low reactivity with ozone, due to the enhancement of ozone transformation into OH· radicals catalysed by activated carbon. Moreover the presence of activated carbon during water ozonation processes reduces the concentration of dissolved organic carbon (TOC) increasing the benefits of the process. Two processes are involved in TOC decrease: i) adsorption of oxidation by-products on activated carbon and ii) mineralization of organic matter by hydroxyl radicals generated in the interaction between ozone and activated carbon. New carbon materials have been developed in our lab in order to potentiate ozone transformation into OH· radicals (activated coke, nitrogen enriched activated carbons and metal doped carbon aerogels) obtaining interesting results especially with metal doped carbon aerogels. The mechanism and the influence of operational parameters in the efficacy of O<sub>3</sub>/activated carbon system have also been studied in Chapter 12.

# CONTENTS

<b>Preface</b>		<b>vii</b>
<b>Chapter 1</b>	Ozone Precursor Monitoring—New Problems and Solutions <i>Liming Zhou</i>	<b>1</b>
<b>Chapter 2</b>	Ozone Decomposition by Catalysts and Its Application in Water Treatment: An Overview <i>J. Rivera-Utrilla, M. Sánchez-Polo and J.D. Méndez-Díaz</i>	<b>17</b>
<b>Chapter 3</b>	Decolorization Efficiency of Ozone and Ozone Derivatives for Several Kinds of Dye in Aqueous Solution <i>Hanjin Luo</i>	<b>53</b>
<b>Chapter 4</b>	Ozone in the Degradation of Phenols and Xenobiotics <i>Maurizio D'Auria, Lucia Emanuele and Rocco Racioppi</i>	<b>97</b>
<b>Chapter 5</b>	Airway Inflammation and Hyper-Responsiveness Induced by Ozone Exposure <i>M.D. Yang Xiang and Xiaoqun Qin</i>	<b>117</b>
<b>Chapter 6</b>	Ozone History and Ecosystems: A Goliath from Impacts to Advance Industrial Benefits and Interests, to Environmental and Therapeutical Strategies <i>Eugenia Bezirtzoglou and Athanasios Alexopoulos</i>	<b>135</b>
<b>Chapter 7</b>	Catalytic Ozonization: A New Approach to the Treatment of Wastewater <i>Luciana Serra Soeira and Renato S. Freire</i>	<b>147</b>
<b>Chapter 8</b>	Bivariate Stochastic Volatility Models Applied to Mexico City Ozone Pollution Data <i>Jorge A. Achcar, Henrique C. Zozolotto and Eliane R. Rodrigues</i>	<b>163</b>
<b>Chapter 9</b>	Rate Constants of the Gas-Phase Reaction of Ozone with Organosulfides at Room Temperature <i>Maofa Ge, Lin Du and Kun Wang</i>	<b>187</b>

<b>Chapter 10</b>	A Model-Based Warning System for Air Pollution Monitoring (Application to Ground-Level Ozone and PM10 Time Series Measured in Bordeaux, France) <i>Ali Zolghadri</i>	<b>195</b>
<b>Chapter 11</b>	The Quasi-biennial Oscillations in the Equatorial Stratosphere: Seasonal Regularities, Dependence on the Solar UV Flux, and Relation to Ozone Depletion in Antarctica <i>I. Gabis and O. Troshichev</i>	<b>239</b>
<b>Chapter 12</b>	Ozone/Activated Carbon: A New Advanced Oxidation Process to Remove Water <i>J. Rivera-Utrilla and M. Sánchez-Polo</i>	<b>269</b>
<b>Index</b>		<b>315</b>

*Chapter 1*

## **OZONE PRECURSOR MONITORING—NEW PROBLEMS AND SOLUTIONS**

*Liming Zhou*

Providence Engineering and Environmental LLC, Baton Rouge, LA

### **Abstract**

Tropospheric ozone is regulated by US EPA (Environmental Protection Agency) as a criterion atmospheric pollutant because of their harmful effects on human's health. VOCs (Volatile Organic Compounds) are monitored in many places as ozone precursor gases such as the PAMS (Photochemical Assessment Monitoring Stations) network by EPA. Online GCs (Gas Chromatograph) and GC/MS are common methods that have been used to analyze speciated VOCs. Usually, these methods can give continuous measurement of speciated VOCs with hourly temporal resolution. Recently, new problems arise in the ozone precursor management and new monitoring techniques can provide the solutions.

Studies have shown that highly reactive VOCs from very local sources, especially fugitive sources, can cause rapid ozone events at very high concentrations at receptor sites, especially in the areas with dense point sources such as refineries and other petrochemical facilities. In order to monitor VOCs at the fence line of major point sources, traditional continuous GCs are not able to capture these short-lived events by the rapid variations in either emission rate or the meteorological conditions. Running the online GC in trigger mode proved to be very effective in capture these events and hence reducing this type of VOC emissions. Analytical instruments with fast response can also help to address this type of issues. For example, PTR-MS (Transfer Reaction Mass Spectrometry), FTIR (Fourier transform infrared spectroscopy, including extractive mode and open path mode), and fast micro GCs can provide speciated VOC concentrations in seconds to minutes, and may be used for special monitoring purpose. Each of these instruments has its own limitations and need more field test before they can be widely used for ambient air quality monitoring.

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using an IR camera. With AI (Artificial Intelligent) tools developed for machine to identify VOCs from IR videos, IR cameras can be operated continuously and in an unattended way to further reduce VOC emissions and improve the industrial process reliabilities.

Comprehensive two dimensional GC techniques have proved to be very powerful in analyzing complex systems such as VOC in ambient air. With a modulator between two independent columns based on different separation mechanisms, two dimensional GCs can better separate background and noises from signal peaks, resulting 2 to 4 fold improvement in sensitivity than traditional one dimensional GC. More importantly, two dimensional GC makes it possible to separate peaks that are previously lumped in one column. For ambient air samples, the number of peaks identified by a two dimensional GC can identify is ten times of a traditional GC. The application of two dimensional GC for ozone precursor monitoring may provide more information to identify the sources and better understanding the ozone formation processes. As a common analytical tool, two dimensional GC is getting mature but methods need to be developed and standardized for their specific applications in ambient air monitoring area such as speciated VOCs.

## 1. Introduction

Ground level ozone or tropospheric ozone is regulated by US EPA (Environmental Protection Agency) as one of the criterion pollutant gases because of their harmful health effects. Tropospheric ozone is formed through photochemical reactions by the precursor gases including Volatile Organic Compounds (VOCs) and  $\text{NO}_x$ [1]. Most  $\text{NO}_x$  are produced by combustion at high temperatures where oxygen and nitrogen in the air directly react.  $\text{NO}_x$  itself is also regulated by US EPA as a criterion pollutant through ambient monitoring and CEMS (Continuous Emission Monitoring System).

VOCs come from various sources, including both natural and anthropogenic sources. The VOC emissions experience a number of physical process as well as chemical reactions. When meeting  $\text{NO}_x$  during the transport, photochemical reactions may happen at correct conditions and secondary ozone is produced. Since ozone formation is directly associated with VOC emission, VOCs are monitored to provide information for ozone management purposes.

Usually, there are three sampling methods to gather VOC samples from the ambient air for successive analysis, dynamic enrichment, denudation enrichment, and passive enrichment[2]. The dynamic method uses a pump to draw air samples directly into either a container or the analytical instrument. The denudation method uses the dynamic sampling method and a tube where the analytes diffuse to the coated wall. In passive methods, analytes diffuse into the container or the tube without extra devices to provide driving force. Because of its slow sampling rate, passive methods are used for long term sampling and monitoring. In this article, only a dynamic or a denudation method is used for any mentioned VOC monitoring activities.

## 2. Conventional Gas Chromatography Techniques

Gas Chromatography (GC) Techniques are the major methods in VOC monitoring [3,4]. Based on sampling methods, this type of techniques can be classified into online GC and canister sampling followed by a GC analysis in an analytical laboratory. When running in an online mode, pre-concentrators based on thermal absorption and desorption are usually used to enrich the analyte. Modern pre-concentrating techniques can improve the sensitivity up to

1000 times. These methods are standardized by EPA as described in EPA methods TO14 and TO15.

Two types of detectors are commonly used in combination with GC, FID (Flame Ionized Detector) and MSD (Mass Spectrum Detector). FID detectors rely on the retention time on the column to identify VOC species and high resolution column is needed for a sufficient separation of VOC species.

Figure 1 illustrates a GC-FID system for online VOC sampling and analyses. Two columns separate VOC species on boiling point. The BP column is used for heavy components and the PLOT column is for light components. Samples first go through the BP column. Light components elute first on the BP column and are switched to PLOT column for better separation and then go to an FID detector. Heavy components are directly sent to another FID since they may poison the PLOT column. Typically, this configuration needs 40 to 50 min to complete the GC analytical cycle and can identify over 50 VOC species. When running at a continuous manner, a careful coordination with the pre-concentrator, with usually a 40 min sampling period, can provide hourly speciated VOC concentrations. This system is used in EPA's PAMS (Photochemical Assessment Monitoring Stations) network (<http://www.epa.gov/oar/oaqps/pams/>). The VOC species monitored in PAMS include alkanes, alkenes and some mono-ring aromatic hydrocarbons.

GC-FID may suffer from co-elution issues, that different may have similar retention time. Using an MSD as detector may partially resolve this issue. Certain mass charge ratios are used to identify a component in addition to retention time (EPA Method TO14). Because of its relatively simple operation and reliability, GC-FID is more often used in ambient air monitoring stations in an unattended way.

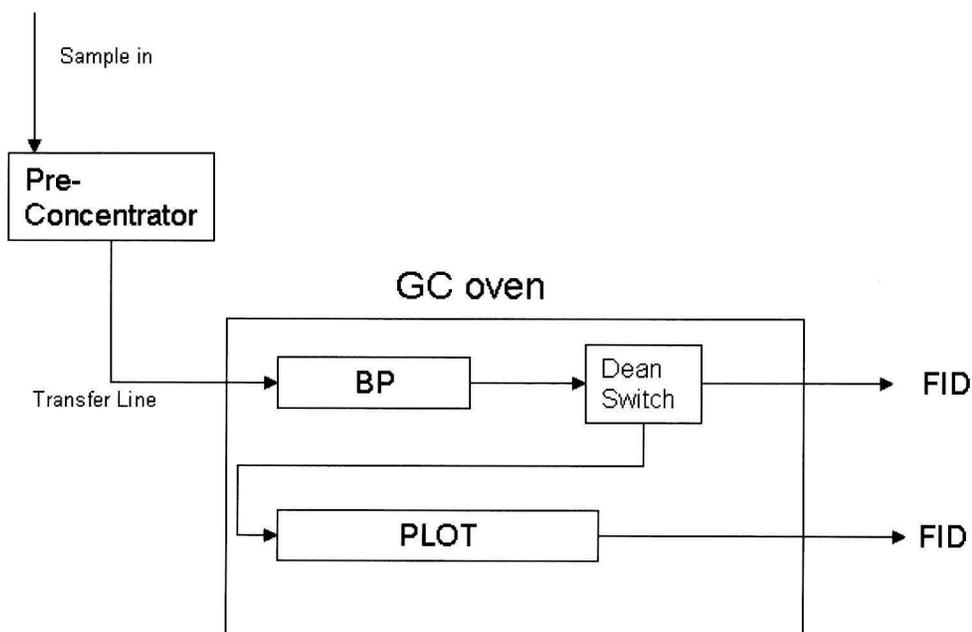


Figure 1. Dean switch dual column TD-GC system for ozone precursor measurement.

Other detectors used include PID (PhotoIonization Detector) and ELCD (Electrolytic Conductivity Detector). PID is used to detect aromatic and olefinic hydrocarbons in the presence of alkanes and other saturated hydrocarbons. ELCD is used for a selective detection of halogen-containing compounds (Allen AE on Chlorine compound on ozone).

### 3. Fast Response Monitoring Techniques

The contributions from very local sources changes rapidly with the micro meteorological conditions or the emission itself does not last enough long time, especially in an area with a dense distribution of industrial facilities. Recent research has shown that half of the VOC emission is fugitive and concentrated in a very short period rather than evenly distributed across a year [5]. The time scale of these changes is usually at sub hour level [6]. Thus, the one hour resolution provided by the online GC in the previous section becomes insufficient for identifying these very local sources.

Although current total non-methane VOC analyzer provides a time resolution of 10 min, it cannot provide speciated information. This type of analyzer is usually used in combination with canister samplers to collect sample of elevated total hydrocarbon events for a successive lab analysis with GC or GC-MS.

#### 3.1. Online GC in a Trigger Mode

In order to provide a prompt response for rapid and short life VOC plumes, a TNMOC analyzer has been used with an online GC for fence-line VOC monitoring[6].

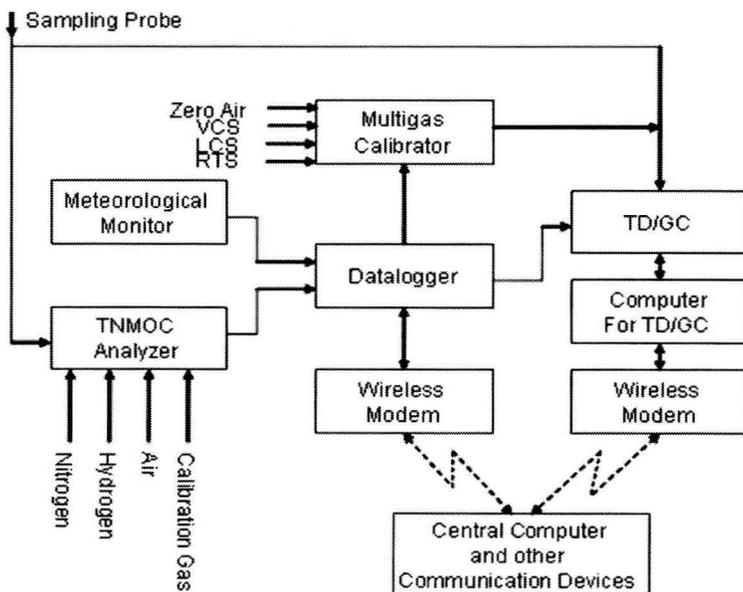


Figure 2. Schematic of a triggered GC system.

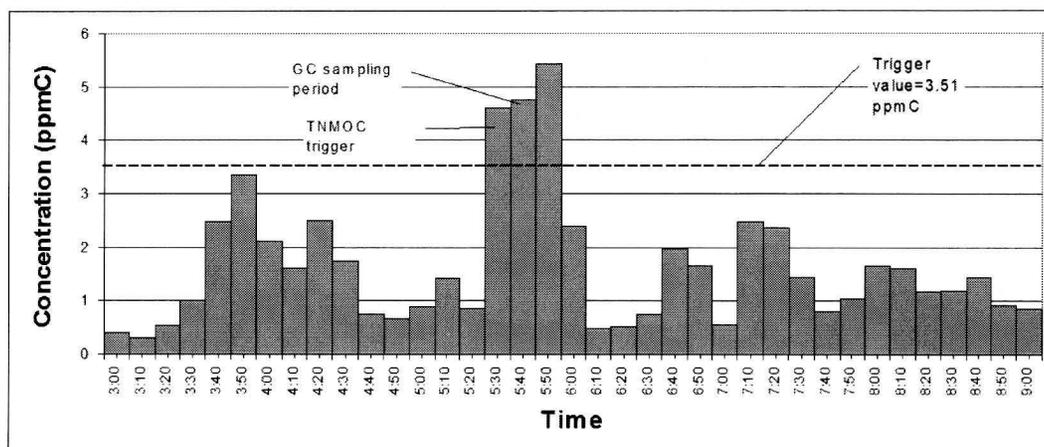


Figure 3. TNMOC events and a GC trigger sample.

A schematic of such a system is presented in Figure 2. A datalogger is used to record total non-methane organic carbon (TNMOC) concentration and meteorological data. When the TNMOC exceeds a certain threshold, the datalogger triggered the online GC to start sampling and analysis. A shorter sampling period is used to better capture the VOC plumes from nearby sources. In Figure 3, an example of TNMOC concentration and GC sample are illustrated, where TNMOC events lasts for twenty minutes. If a continuous GC is used, the sample capture may not be as good as the triggered GC and the speciated VOC concentration may not be less representative. Also, since the sample is performed in a dynamic way, the calibrations are also performed dynamically controlled by the datalogger in accordance with the trigger samples. With this measure, the triggered GC system has good performance comparable to continuous online GCs.

This method proves effective in providing prompt analysis results for both environmental and industrial operators to locate and fix VOC sources. This practice has proved to be very successful in reducing expected VOC release and has contributed to reducing local ozone levels [7]

### 3.2. PTR (Transfer Reaction Mass Spectrometry) –MS

Online VOC measurement with an MS using direct sampling method is popular for vehicle based mobile monitoring stations[8]. For these common mass spectrometers, thermal electrons are used as the ionization source [9]. The electrons bombard the target molecules to generate ions. When used for analysis of organic molecules, instead of forming a single ionized species, most molecules break down into smaller fragment ions. When several compounds enter the MS detector simultaneously, the final mass spectrum may be too complex to interpret or to quantify. Although species can be separated by using a GC in front, the slow GC cycles prevent fast response. An inter-comparison of PTR-MS and GC-PTR-MS was performed and the validation of using a GC in front verified that the PTR-MS gives accurate measurement [10] for the ambient air samples collected during the study.

PTR-MS uses a “soft ionization” method to ionize the organic molecules, where the VOC molecules are reacted in a drift tube with charged ions, with hydroxonium ions ( $H_3O^+$ )