

Removal of toxic vapors by oxidation Development of laboratory test procedures for in-duct air cleaning systems

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SUMMARY

Exposure to volatile organic compounds (VOC) in workplaces can cause acute effects such as irritation of the skin, the eyes, the mouth, and the nose. Some products may also cause chronic effects including asthma and cancer. Preventing these adverse effects on the health of workers through the adoption and implementation of measures to eliminate or to at least reduce the risk is important. Among the approaches developed so far to reduce the exposure to indoor air pollutants (e.g. VOCs), ventilation is the most conventional and applied technique. During ventilation, the outdoor air is brought into the indoor environment and mixed with the indoor air to lower the concentration of VOCs. In an approach to optimize energy costs for heating and cooling, part of contaminated return air is sucked into the ventilation system and is recirculated in the premises. Ventilation systems are then provided with a system of air purification to remove contaminants in the recirculated air. For removing gaseous contaminants, the use of traditional adsorption-based air cleaning systems such as activated carbon requires quality maintenance and regular media changes. New oxidation-based purification technologies, such as photocatalytic oxidation and non-thermal plasma, are now available for general ventilation systems. Such technologies can be more energy efficient and may require less maintenance because these systems work continuously in ideal conditions without the accumulation of pollutants affecting their performance. However, there is no standardized protocol to evaluate the effectiveness of these new technologies.

This project aimed at the development of a laboratory evaluation protocol for air purification systems that are directly applied in ventilation systems, using an oxidation process as the main removal mechanism of pollutants in gaseous or vapor form. Dynamic single pass tests were conducted in a test rig which consisted of four identical test ducts with individual flow control. This setup allowed for the simultaneous evaluation of four different air purification systems under identical conditions. Three oxidation-based air cleaning technologies were considered: photocatalytic oxidation (PCO), non-thermal plasma (NTP), and ozonation (O_3). The first step was to test the installation to ensure to obtain reproducible results. The second step was to analyze the three technologies simultaneously under various conditions to understand their capacity and to develop a protocol for testing the systems' air purification capability. The protocol developed in this study was then examined using a full-scale setup complying with the ANSI/ASHRAE Standard 145.2-2016.

Once the test method was examined through repeatability tests, 18 different configurations of oxidation-based air cleaning units were tested in the 4-duct test rig. These include 12 different commercial PCO units, one in-house pilot PCO, 3 plasma and 2 ozonation units (i.e., 430 ppb and 1300 ppb of ozone). Sixteen of them were tested for the removal of 0.1 ppm methyl ethyl ketone (MEK) and their single pass removal efficiency varied from 0 to 37%. Ozonation and PCO using ozone generating vacuum UV lamps generally showed higher efficiency than PCO with non-ozone generating UVC lamps or plasma units. Formaldehyde, acetaldehyde, and acetone were the oxidation by-products detected in MEK testing. PCO-based systems tended to generate more by-products. Based on this test outcome, four units using different technologies were selected: PCO-A for pure PCO technology, PCO-A1 for a combination of PCO and ozonation technologies, O3-A for ozonation, and NTP-A (or NTP-C) for plasma.

The selected four units were then tested for toluene removal at different air velocities. Increasing air velocity reduces the residence time required for oxidation reactions between air contaminants and oxidizing agents generated by the air cleaning systems. Therefore, increasing air velocity showed a decrease in removal efficiency. However, no clear trends were observed in by-product generation rates. It was also found that the performance of PCO-A1 and O3-A technologies was more sensitive to air velocity changes.

The selected units were tested for 6 different VOCs: n-hexane, n-octane, toluene, o-xylene, styrene, and iso-butanol. The test results showed that the removal efficiency and by-product generation patterns of an air-cleaning unit differed substantially depending on the challenge VOC. Styrene and iso-butanol removal efficiency were higher in all devices because they have higher rate constants for the reaction with hydroxyl radical, which is the main oxidizing agent in the considered air cleaning technologies. In comparison to the other VOCs, the removal efficiency of styrene and iso-butanol was more sensitive to the employed air cleaning unit. Therefore, in order to pinpoint which air cleaning system is more effective in removing VOCs, styrene, and iso-butanol could be more ideal as challenge air pollutants. On the other hand, styrene showed a clear interference in ozone monitoring, so it was ruled out.

The effects of challenge gas concentrations in the range of 0.05 to 2 ppm and relative humidity levels between 20 and 60% were also studied for iso-butanol, toluene, and o-xylene. The rapid decrease of removal efficiency in sub-ppm levels indicates that applying high challenge concentration to accelerate air cleaner testing is not suitable. It was also observed that the performances of oxidation-based air cleaning systems tend to be more sensitive to humidity under 40% RH; hence, low humidity conditions should be avoided as the standard test condition. In addition, some selected PCO systems were tested for ozone removal, and commercial PCO systems showed poor ozone removal efficiency.

Based on the test results, a recommended test protocol was developed by aiming at multifaceted performance evaluations considering two different challenge levels (for indoor air quality application and lightly polluted industrial setup), by-product generation, and the effects of residue on air quality. The developed test protocol for full-scale testing has then been applied in 14 commercial in-duct air cleaning units under the recommended test conditions: 7 PCO units, 3 units combining PCO and adsorption media, 2 NTP units, and 2 ozonation units. The test results indicate that the proposed test protocol can capture different characteristics in the performance of the different systems except for the NTP units, which showed a poor performance throughout the study.

Considering large variations in the efficiency of oxidation-based air cleaning systems and their toxic by-product generation, developing a proper standard test method is urgent. The developed test protocol can serve as a starting point or as an interim test method. Commercial non-thermal plasma units tested in this study showed poor performance, which needs to be further investigated. The test results indicate that the efficacy of by-product scrubbers needs to be studied more for optimum design of air cleaning systems.

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LIST OF ACRONYMS, INITIALISMS AND ABBREVIATIONS

ASHRAE	American Society of Heating, Refrigerating, and Air Conditioning Engineers
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
ATD	Automatic Thermal Desorber
BASE	Building Assessment Survey and Evaluation
CADR	Clean Air Delivery Rate
CIMS	Chemical Ionization Mass Spectrometry
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
DAS	Data Acquisition System
DNPH	2,4-Dinitrophenylhydrazine
EDS	Energy Dispersive Spectroscopy
EE	Energy Efficiency of Non-Thermal Plasma
EPA	U.S. Environmental Protection Agency
FID	Flame Ionization Detector
FTIR	Fourier-Transform Infrared Spectroscopy
GAC	Granular Activated Carbon
GC	Gas Chromatography
He	Helium
HPLC	High-Performance Liquid Chromatography
IAQ	Indoor Air Quality
IAQP	Indoor Air Quality Procedure of ASHRAE Std. 62.1
IPC	In-Plasma Catalyst
IRSSST	Institut de recherche Robert-Sauvé en santé et en sécurité du travail
ISO	The International Organization for Standardization
KI	Potassium Iodide
MEK	Methyl Ethyl Ketone
MS	Mass Spectrometry
NIOSH	National Institute for Occupational Safety and Health
NO _x	Nitrogen Oxides
NTP	Non-Thermal Plasma
O ₃	Ozone
PC	Plasma Catalyst
PCO	Photocatalytic Oxidation
ppb	Parts per Billion
ppbv	Parts per Billion by Volume

PPC	Post-Plasma Catalyst
ppm	Parts per Million
ppmv	Parts per Million by Volume
PTFE	Polytetrafluoroethylene
PTR-MS	Proton Transfer Reaction-Mass Spectrometer
RH	Relative Humidity
ROHS	Regulation respecting Occupational Health and Safety (<i>Règlement sur la santé et la sécurité du travail [RSST]</i>)
SEM	Scanning Electron Microscope
SIE	Specific Input Energy of Non-Thermal Plasma
TiO ₂	Titanium Dioxide
TVOC	Total Volatile Organic Compounds
UV	Ultraviolet Radiation
UVA	Ultraviolet A Radiation
UVC	Ultraviolet C Radiation
UV-PCO	Ultraviolet-Photocatalytic Oxidation
VOC	Volatile Organic Compound
VRP	Ventilation Rate Procedure of ASHRAE Std. 62.1
VUV	Vacuum Ultraviolet Radiation
WHO	World Health Organization
XRD	X-Ray Diffraction Method

1. INTRODUCTION

1.1 Occupational exposure to volatile organic compounds (VOCs)

Limiting workers' exposure to chemicals released from various manufacturing processes, accidental spills and leakages is a priority in planning occupational health and safety. Farms, hospitals, and industrial laboratories as well as manufacturing facilities are susceptible to this form of exposure since they are dealing with a wide range of toxic chemicals. Many of these toxic chemicals such as solvents, chemical reactants, additives, plasticizers, adhesives, disinfectants, etc. can be classified as Volatile Organic Compounds (VOC). VOCs are ubiquitous and numerous air contaminants encompassing various chemical groups: alkanes, chlorinated hydrocarbons, alcohols, aldehydes, ketones, esters, terpenes, ethers, aromatic hydrocarbons, and heterocyclic hydrocarbons. Due to the high volatility, VOC can easily vaporize under ambient conditions and inhalation is a major route of exposure. The potential harmful health effects of VOC are irritations of the upper respiratory system, eye and skin, sinus infection, allergic reaction, asthma, headache, fatigue, poor concentration, nausea, dizziness, and cancer (Maroni, Selfert, & Lindvall, 1995).

A document from the Institut de recherche Robert-Sauvé en santé et en sécurité du travail (IRSST), reporting the results of the chemical analyses produced at IRSST for the 2001-2008 period, provides a list of the chemicals found in high concentrations in different industries in Quebec (Ostiguy, Morin, Bensimon, & Baril, 2011). It includes VOCs like toluene, styrene, methyl ethyl ketone (MEK), methanol, n-hexane, etc. For example, MEK levels were potentially higher than the 8-hour time-weighted average concentration limit in 79% of cases in tiles, slabs, and linoleum industry and 37% of cases in hardwood parquet industry. Eighty percent of soap and cleaning compound industry cases have potentially high methanol concentrations.

The exposure to VOCs is not limited to manufacturing or industrial setups. VOC used in manufacturing various goods can off-gas from the end products, resulting in elevated concentrations even in non-industrial environments like offices, schools, retails, etc. The indoor VOC concentrations are mostly higher than the ambient outdoors (American Society of Heating, Refrigerating and Air-Conditioning Engineers [ASHRAE], 2017). A field study of VOC levels in both indoor and outdoor air of office buildings in Montreal has shown that indoor total VOC (TVOC) levels are 2 to 4 times higher than outdoor (Lee et al., 2009). U.S. Environmental Protection Agency (EPA)'s Building Assessment Survey and Evaluation (BASE) investigated indoor and outdoor air pollution profiles of 100 randomly selected public and private office buildings across the USA and showed that all detectable VOCs had median indoor to outdoor concentration ratio greater than one suggesting that all detectable VOC had indoor sources. The BASE study identified 25 VOCs with 100% of detection frequency in indoor air. The VOCs with high concentrations among them are ethanol, 2-propanol, acetone, toluene, formaldehyde, d-limonene, and xylenes (EPA, 2018a).

More than 300 VOCs have been identified in indoor air (ASHRAE, 2017). Even though VOC concentrations are relatively low in non-industrial environments, the high potential for many VOCs' presence in indoor air to cause symptoms is a result of both additive and synergistic effects (Godish, 2001). VOCs are one of the identified causal factors for Sick Building Syndrome (SBS) (EPA, 2013). The World Health Organization (WHO) estimated that 30% of the newly built or

renovated buildings have characteristics related to SBS and between 10 and 30% of the occupants are affected with this syndrome (WHO, 1986). Since then there have been many reported cases of SBS (Ghaffarianhoseini et al., 2018). Considering the fact that 80% of Quebec's labor force is in service sectors (Government of Canada, 2018), working in institutional and commercial buildings, reducing VOC exposure in such environments is an important workers' health issue.

Ventilation is the generally adopted engineered solution to control the concentrations of chemicals in the air. The quantity of outdoor air brought into the building can have a direct effect on the energy cost of building operations. There is a cost to heat, cool, humidify or dehumidify the outdoor air depending on the location and the season. This leads to a balancing act between occupants' health and ventilation cost.

The strategy of diluting indoor contaminants with outdoor air assumes that the outdoor air is clean; this is not the case in many large cities or near industrial complexes. Most ventilation systems have a form of particulate filtration to protect heating or cooling equipment from fouling and to protect occupants; however, it does not do anything to remove gaseous contaminants like VOC. With the climate changes, the levels of ambient air pollutants such as ozone, VOC, and particulate matter are expected to increase along with more frequent and severe air pollution episodes (Adam-Poupart et al., 2013). As the median service life of air distribution equipment is more than 24 years (ASHRAE, 2015a), a ventilation system designed today should be able to cope with the changes in climate and air pollution occurring within the next quarter century. The need for good indoor air quality (IAQ), high energy cost, poor outdoor air quality, and the risk of a chemical release have increased the need and interest in air purification systems to filter gaseous contaminants from the air.

1.2 Air cleaning technologies for VOCs removal

The air cleaning market is growing fast. Prior to the 2008 recession, the annual market growth in Canada for air pollution abatement is 9%, higher than the average global growth rate of 7% (United States International Trade Commission [USITC], 2005). Due to the recession causing a slowdown in the construction industry, the North American market growth was reduced to the lowest value of 3.7% in 2009 but recovered back to normal from 2010 (Global Industry Analysts, 2011), and the global market is projected to reach US\$20.7 billion by 2020 (Markets and Markets, 2018).

There are traditional systems for filtering gases and vapors based on the adsorption process, i.e., activated carbon and/or potassium permanganate alumina pellets in trays or deep beds, particulate filters incorporating very thin beds of activated carbon or alumina pellets, and carbon cloth (Bastani, Lee, Haghghat, Flaherty, & Lakdawala, 2010; Haghghat et al., 2008). These adsorption-based technologies have long been used in wide range of applications, so their performance and efficiency under various conditions are well researched and understood. Currently available standards for the evaluation of gas-phase air cleaning devices are limited for those applying adsorption-based technologies (ASHRAE 2015a, 2016a).

There are newer technologies such as ultraviolet irradiation (UV), UV with catalyst, plasma, plasma with catalysts, and ozone generators, which are generally based on oxidation technologies (Zhang et al., 2011; Zhong & Haghghat, 2011). While the adsorption-based

technologies transfer the air pollutants to adsorbents hence the adsorbents need to be changed or regenerated regularly, oxidation-based technologies can decompose the pollutants resulting in fewer maintenance requirements. Upon complete oxidation, hydrocarbon VOC can be converted into carbon dioxide and water. Oxidation-based technologies, however, can generate intermediates such as carbon monoxide, formaldehyde, acetaldehyde, and acetic acid in cases of incomplete oxidation as well as generating pollutants like ozone and nitrogen oxides inherently depending on the system (Bahri & Haghghat, 2014; Zhong, Haghghat, Lee, & Lakdawala, 2013). In Quebec, the *Regulation respecting occupational health and safety* (ROHS, c. S-2.1, r. 13) prohibits the recirculation of air containing toxic substances like formaldehyde, acetaldehyde, and ozone. Due to the potential for the generation of these highly toxic by-products, the use of oxidation-based air-cleaning devices needs to be carefully examined to prevent unexpected exposure.

Compared to the adsorption-based air cleaning systems, the oxidation-based systems are generally easier to maintain and have lower flow resistance resulting in the savings from the reduced fan sizes in air-handling systems and energy cost. With these merits, oxidation-based air cleaning devices are quickly penetrating the market and presently there are several manufacturers and suppliers in Quebec. A Quebec manufacturer has estimated an average of 20% annual growth in sales of ozonation-based air cleaning systems in Quebec and the main applications are office buildings, schools and other industrial odor controls¹. As more air-cleaning devices using the new oxidation-based technologies enter the market, it would be essential to develop an evaluation method for comparing their effectiveness and overall performances.

1.3 Standards for the performance evaluation of air cleaning systems

American Society of Heating, Refrigerating, and Air Conditioning Engineers (ASHRAE) Standard 62.1 (2016c) specifies the requirements of ventilation system design and there are three design approaches: ventilation rate procedure (VRP), indoor air quality procedure (IAQP), and natural ventilation procedure. The mechanical ventilation system should be designed through the VRP and/or the IAQP. The VRP is a prescriptive ventilation design approach that sets the minimum requirement for outdoor air ventilation rates for various space types. In the VRP, the outdoor air ventilation rate of space is generally determined by simply adding the occupant-related demand and the building-related demand from the tabulated data. The IAQP is a performance-based ventilation design procedure requiring explicit contaminant load calculation and engineering analysis to meet the contaminant limits determined by cognizant authorities. While the VRP accounts for only dilution ventilation for indoor air quality control, the IAQP allows implementing all contaminant control methods: source control, dilution ventilation, and air cleaning. The use of proper air cleaning systems can reduce the required outdoor air ventilation rate (Diekmann, McKenney, & Brodrick, 2009). In spite of the great potential for improved indoor air quality and energy-saving (Johnson, 2005), the IAQP has not been widely applied. Lack of proper standards to evaluate the effectiveness of air-cleaning systems, especially for gaseous contaminants, may be part of the cause, along with the lack of IAQ regulations and the significantly more decision-making required for the engineers when using IAQP (Mendell & Apte, 2011; Stanke, 2012).

The need for the development of a standard testing method for gas-phase air cleaning systems has long been discussed. ASHRAE has developed two laboratory test standards:

¹ Salama, A., Personal communication, July 5, 2013

- ANSI/ASHRAE Standard 145.1-2015 Laboratory Test Method for Assessing the Performance of Gas-Phase Air Cleaning Systems: Loose Granular Media (ASHRAE, 2015b); and
- ANSI/ASHRAE Standard 145.2-2016 Laboratory Test Method for Assessing the Performance of Gas-Phase Air Cleaning Systems: Air Cleaning Devices (ASHRAE, 2016b).

These standards, however, clearly state that the applications are limited to traditional air cleaning systems using sorptive media.

ISO has developed similar standard test methods. The ISO 10121 standard, entitled *Test methods for assessing the performance of gas-phase air cleaning media and devices for general ventilation*, is divided into two parts:

- Part 1: Gas-phase air cleaning media (GPACM) (ISO 10121-1:2014)
- Part 2: Gas-phase air cleaning devices (GPACD) (ISO 10121-2:2013)

The ISO 10121-2:2013 standard does not constrain its application to adsorption-based technologies; however, the design of the standard test methods is essentially based on adsorption-based technologies. Both ASHRAE standard 145.2 and ISO 10121-2 norm are designed for the evaluation of full-scale in-duct air cleaning systems.

For the evaluation of photocatalysts, ISO has developed the standard ISO 22197 Fine ceramics (advanced ceramics, advanced technical ceramics) – Test method for air-purification performance of semiconducting photocatalytic materials, divided into 5 parts, depending on the challenge gas/vapor²: Part 1 for the removal of nitric oxide; Part 2 for acetaldehyde; Part 3 for toluene; Part 4 for formaldehyde; and Part 5 for methyl mercaptan. The purpose of this standard is to evaluate the performances of different photocatalysts under identical reaction conditions. A small piece of photocatalyst (100 mm × 50 mm) is tested in the given photoreactor under the irradiation of ultraviolet A (UVA) only. ISO 22197 is limited to bench-top small-scale testing,

² ISO (2007) ISO 22197-1: 2007, Fine ceramics, advanced technical ceramics – Test method for air-purification performance of semiconducting photocatalytic materials – Part 1: removal of nitric oxide. Geneva: International Organization for Standardization.

ISO (2011) ISO 22197-2:2011, Fine ceramics (advanced ceramics, advanced technical ceramics) - Test method for air-purification performance of semiconducting photocatalytic materials - Part 2: Removal of acetaldehyde. Geneva: International Organization for Standardization. Geneva: International Organization for Standardization.

ISO (2011) ISO 22197-3:2011, Fine ceramics (advanced ceramics, advanced technical ceramics) -- Test method for air-purification performance of semiconducting photocatalytic materials -- Part 3: Removal of toluene. Geneva: International Organization for Standardization.

ISO (2013) ISO 22197-4:2013, Fine ceramics (advanced ceramics, advanced technical ceramics) -- Test method for air-purification performance of semiconducting photocatalytic materials -- Part 4: Removal of formaldehyde. Geneva: International Organization for Standardization.

ISO (2013) ISO 22197-5:2013, Fine ceramics (advanced ceramics, advanced technical ceramics) -- Test method for air-purification performance of semiconducting photocatalytic materials -- Part 5: Removal of methyl mercaptan. Geneva: International Organization for Standardization.

unable to evaluate the different reactor designs applied in ultraviolet-photocatalytic oxidation (UV-PCO) air cleaning systems.

For the evaluation of PCO systems for air treatments, the French standard XP B44-013, *Photocatalyse - Méthode d'essais et d'analyses pour la mesure d'efficacité de systèmes photocatalytiques pour l'élimination des composés organiques volatils/odeurs dans l'air intérieur en recirculation - Test en enceinte confinée* (Association française de normalisation [AFNOR], 2009) was developed; however, it specified static chamber test methods monitoring the decay of an initially introduced challenge gas mixture of acetone, acetaldehyde, heptane and toluene. This standard was suitable for evaluating stand-alone room air cleaning devices. This standard requires for the measurements of reaction by-products.

This standard was updated to the European standard EN 16846-1:2017: *Photocatalysis - Measurement of efficiency of photocatalytic devices used for the elimination of VOC and odor in indoor air in active mode – Part 1 Batch mode test methods in a closed chamber* (AFNOR, 2017). However, it still adopts the decay test method in an environmental chamber. Formaldehyde was added to the challenge gas mixture. The concentrations are $50 \pm 25\%$ parts per billion by volume (ppbv) for each compound for measuring reaction by-products, and $1000 \pm 10\%$ ppbv for measuring photocatalytic activity and monitoring of the mineralization of VOCs into CO₂.

While the performances of traditional adsorption-based technologies are well studied and documented, those of new oxidation-based technologies have not been sufficiently investigated. This lack of thorough understanding of the performances of new technologies hinders the development of proper test procedures. At present, there are no test standards that can be applied for in-duct air cleaning systems using oxidation-based technologies. As a result, design engineers only have data from testing done by manufacturers. Since each manufacturer develops its own test procedures, it is not possible to compare the performances of air cleaning products by different manufacturers. Also, essential information like by-product generation is not reported. This lack of standards and convincing proof of actual performance greatly limits the proper use of oxidation-based air cleaning systems.

2. STATE OF KNOWLEDGE ON OXIDATION-BASED AIR CLEANING SYSTEM

Oxidation-based air cleaning technologies that can be applied for VOC abatement include catalytic oxidation, thermal oxidation, photocatalytic oxidation, thermal plasma, non-thermal (or cold) plasma, plasma catalysis, and ozonation. However, some of the technologies require high temperature and/or high concentration to be efficient and economical. The oxidation technologies that can be applied in conjunction with ventilation at ambient conditions are photocatalytic oxidation, non-thermal plasma, non-thermal plasma catalysis, and ozonation. These oxidation-based air cleaning technologies usually pose less flow resistance (lower pressure drop) than other conventional adsorption-based techniques leading to easier implementation especially in existing ventilation systems, and better energy efficiency.

2.1 Photocatalytic oxidation (PCO) air cleaning systems

Among the emerging gas-phase air cleaning technologies, air cleaning through photocatalytic oxidation (PCO) has been heralded as a promising technology that can convert toxic gaseous contaminants into harmless products like carbon dioxide and water, and inactivate microbial agents (Ginestet, Pugnet, Rowley, Bull, & Yeomans, 2005; Hager & Bauer, 1999; Jacoby et al., 1996; Kim & Hong, 2002; Lin & Li, 2003; Zhong & Haghghat, 2015). Since Fujishima and Honda's discovery of PCO during their water cleavage experiment on titanium dioxide (TiO_2) electrodes in the late 1960s, it has been applied more for water treatments (Fujishima, Rao, & Tryk, 2000). With the development of immobilized TiO_2 catalysts, PCO applications could be expanded to air purification (Anderson & Bard, 1995). PCO techniques for air purification can be implemented under room temperature and pressure, which makes PCO technology suitable for general building applications.

PCO uses semiconductor materials like titanium dioxide where electron transition from the valence band to the conduction band results from the absorption of light usually in the ultraviolet radiation (UV) range (Zhong & Haghghat, 2011). The subsequent generation of positive holes and their interactions with water lead to the formation of hydroxyl radicals as shown in Figure 2-1. These act as powerful oxidizing agents and can be used in the mineralization of organic molecules on the catalyst surface. In addition, claims have been made with respect to the use of PCO devices utilizing UVA generating black lamps in enhanced inactivation rate for the removal and destruction of microorganisms (Lin & Li, 2003).

In the past three decades, many studies have been conducted to develop better photocatalysts and more effective reactor designs. These studies have demonstrated high removal efficiency of PCO (Huang et al., 2016; Jeong, Sekiguchi, Lee, & Sakamoto, 2005; Verbruggen, 2015). However, these results were usually obtained under ideal oxidation conditions (e.g., long residence time under extremely high UV radiation) and/or using small bench-top scale test rigs, which are all different in design. Also, many studies used static test methods of which results are difficult to translate into dynamic performance of the in-duct systems that can be used in combination with ventilation. Previous tests conducted in dynamic setups to measure single-pass efficiency, show wide variation in the test conditions, making it difficult to compare the results directly from one study to another. Table 2-1 presents dynamic test results (i.e., single-pass efficiency) and conditions of some PCO studies, and it clearly demonstrates the aforementioned

differences in testing. Even the studies using commercial photocatalysts without modification in dynamic test setups have adopted widely different test conditions, prohibiting direct comparison of the results (Table 2-2). The majority of studies have applied small bench-top scale reactors and there are wide differences in residence time. The residence times of most PCO studies are unfeasibly long considering the nominal residence time of 0.1 second used in adsorption-based technologies.

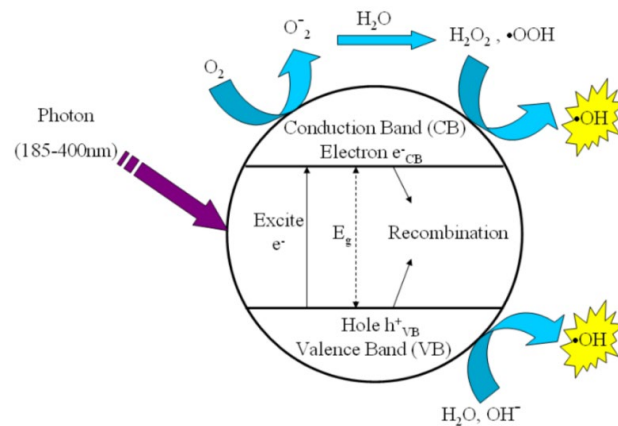


Figure 2-1. Primary mechanism of photocatalytic reaction (Zhong et al., 2010).

The performance of PCO air cleaning depends on the light source type and intensity, properties of photocatalyst, the properties of the PCO reactor, challenge compounds and concentrations, and airstream characteristics like temperature, humidity level, air velocity, and mixing, and so on (Haghighat, Haghighat, & Lee, 2017). Due to the large variance of these parameters, the single-pass efficiency reported in previous research varies from 0 to 100%.

As the essential component of the PCO reaction process, UV light (wavelength and intensity) has a great effect on the PCO reaction rate. Germicidal lamp (UVC, 254 nm) and fluorescent black-light lamp (300-400 nm) are the most utilized light sources in PCO studies. Some studies employed UV light-emitting diodes (wavelength usually centered at 365 nm) due to a long lifetime and a high efficiency (Sharmin & Ray, 2012; Tokode, Prabhu, Lawton, & Robertson, 2015). For the same photon energy distribution, i.e. light wavelength, increasing the light intensity leads to the generation of a larger number of photons and consequently e⁻-h⁺ pairs. However, high UV intensity is often applied to get higher PCO efficiency but too much UV power can increase the air temperature making the PCO system uneconomical or unsuitable for general building applications. Stokke, Mazyck, Wu, and Sheahanb (2006) proposed a pilot PCO system for emission control and tested it at two different UV intensities. Ambient air at 22-24°C was introduced, and the outlet air temperature increased to 59.6°C at 6.5 mW/cm², and to 69.8°C at 11.5 mW/cm². On the other hand, it should be mentioned that even though the increase in light intensity brings about higher pollutant removal efficiency, excessive light intensity diminishes quantum efficiency and imposes unnecessary energy cost. In this regard, Tang and Yang (2012) suggested a novel method to determine the maximum required light intensity based on the VOC molecule type, average reaction rate, optical absorption coefficient of photocatalyst, and light wavelength. Investigations on PCO of formaldehyde, benzene, and toluene at low concentrations over P25 (< 600 ppb) revealed that the removal rate follows the order of ozone-generating vacuum UV (VUV) > UVC > UVA (Jeong *et al.*, 2005; Kibanova, Sleiman, Cervini-Silva, & Destailats,

2012), likely due to the low-energy photons in the case of UVA and positive involvement of ozone in the PCO reactions for ozone-generating VUV lamp.

Table 2-1. Examples of PCO dynamic test conditions and efficiency from the literature

Reference	Reactor volume [liter]	UV type	UV Intensity [mW/cm ²]	Residence time [second]	Challenge VOC	Challenge Concentration [ppm]	Single-pass Efficiency [%]
Ao et al. (2003)	57	UVA	0.6	228	Benzene Toluene Ethylbenzene o-xylene	0.035	37.4 62.8 72.1 75.2
Zhang et al. (2003)	1.44	UVC	5.8	86.4 28.8 17.3	Toluene	4.7-5.2	87 83 70
Einaga et al. (2004)	0.042	UVA	-	25	Benzene	125 250	80 15
Jeong et al. (2004)	0.55	UVA UVC VUV	- - -	33	Toluene	0.6	83 84 99
Stokke et al. (2006)	448	UVC	6.5 11.5	4.3	Methanol	50	27.5 66
Yang et al. (2007)	105.6	UVC	2.8	1.47 0.47	Formaldehyde	0.26-0.29	20 <5
Hodgson et al. (2007)	-	UVC	6.5	0.03	Mixture of Ethanol Acetone Toluene m-Xylene Hexanal	0.016 0.014 0.009 0.003 0.001	69 51 16 23 31
Sleiman et al. (2009)	0.085	UVC	4.3	48	Toluene	0.12	95
Korologos et al. (2011)	0.0395	UVC	-	30	Benzene Ethylbenzene Toluene m-xylene	3.3 9.5 9.5 15	30 85 35 40
Destailats et al. (2012)	49	UVA	6.1	0.159	Mixture of Benzene Toluene Formaldehyde o-xylene Acetaldehyde	0.001 0.003 0.024 0.005 0.018	14 38 13 81 25
Zhong et al. (2013)	-	UVC	2.7-3.6	0.019	Ethanol Hexane Octane Acetone MEK Toluene p-Xylene	0.5	34 14 15 25 28 20 22

Table 2-2. Summary of reactor design and test conditions of commercial TiO₂ powders

Photo-catalyst	Reactor type and volume [L]	Pollutant	Concentration [ppmv]	RH [%]	Residence time	Light primary wavelength and intensity [W/m ²]	Reference
P25	Glass-plate photoreactor	Toluene	0.09–0.8	3-70	0.2 s	254 nm; 43	Mo et al., 2013
P25	Tubular-flow reactor	Toluene	0.01-0.5	0-66	0.1-2 s	254 nm; 30	Quici et al., 2010
P25	Stainless steel plate-type photoreactor	Toluene	0.450-8	47-50	0.2 s	254 nm; 4.3-9.5	Mo et al., 2009
P25	Cylindrical flow reactor with coated Raschig rings	Toluene	0.17	10-66	0.9 s	365 and 254+185 nm; 7.7-28	Kibanova et al., 2009
P25	-	Benzene	80-260	0-65	25 s	365 nm; -	Einaga et al., 2004
P25	Cylindrical reactor with coated Raschig rings	Benzene	0.1–0.5	0–66	0.05-0.500 s	365, 254 and 254 + 185 nm; 7.7-44.5	Kibanova et al., 2012
P25	Annular photoreactor	Acetone	504.2	10	12.6-25.2 s	365 nm; 0-40	Vincent et al., 2008
P25	-	Acetylene	100	zero	2 s	365 nm; 80-100	Thevenet et al., 2014
P25	Annular photoreactor; 0.0664	1-propanol	100–300	0-30	11.8-25.2 s	365 nm; 0.78-39.4	Vincent et al., 2009
P25	Annular photoreactor	Benzene, ethyl-benzene, xylene	0.004-0.034	10-100	5 s	352 nm; 38	Jo and Park, 2004
P25	Plug flow photoreactor; 0.405	TCE, octane, acetone, methanol, MEK, propanol	400-600	23	2.025 min	365 and 254 nm; -	Alberici and Jardim, 1997
P25	Annular photoreactor; 0.02	BTE, xylenes	0-34	0	50-210 s	254.7+184.9 nm; -	Boulamanti et al., 2008
P25	-	BTE, xylenes	0.02	10-82	0.6-3.7 min	365 nm; 7.5	Ao and Lee, 2004
P25	Cylindrical flow reactor with coated Raschig rings; 0.55	Toluene, benzene	0.6-10	0-90	8.3-33 s	365, 254 and 254+185 nm; -	Jeong et al., 2005

Photo-catalyst	Reactor type and volume [L]	Pollutant	Concentration [ppmv]	RH [%]	Residence time	Light primary wavelength and intensity [W/m ²]	Reference
P25	Tubular-flow reactor	Benzene, ethyl benzene, xylenes	0.021-0.093	18–78	0.7-5.1 s	352 nm; 22-58	Jo et al., 2002
P25	Annular photoreactor; 0.02	Pentane, i-pentane, hexane, i-hexane, heptane	0-100	0-90	50-85 s	254.7+184.9 nm	Boulamanti and Philippopoulos, 2009
PC500	Stainless steel annular flow-through; 0.085	Toluene	0.02-0.4	0-70	0.8–4 min	43	Sleiman et al., 2009
PC500	Stainless steel annular flow-through; 0.05	2-propanol	0.100–0.7	0-60	6-30 s	32	Vildoza et al., 2010
PC500	Continuous flow-through reactor; 0.085	2-propanol	0.05-0.7	0-80	17-102 s	43	Cazoir et al., 2012
PC500	Stainless steel tubular flow-through photoreactor; 0.05	2-propanol, toluene	0.08–0.4	0-60	10 s	32	Vildoza et al., 2011
PC500	Annular photoreactor; 0.22	PCE	600–2200	3-40	> 44 s	280-400 nm; 18.9–38.4	Monteiro, Silva et al., 2015
P25, PC500	Annular photoreactor; 0.22	n-decane, PCE	75-2738	3-40	44-130 s	18.9-38.4	Monteiro, Miranda et al., 2015
UV100, P25	Annular Pyrex reactor made of coaxial tubes	MEK	1500	50	7.6-19 s	380 nm; 33	Alonso-Tellez et al., 2012

- NR: not reported; Conc.: Concentration; Res.: Residence
- BTE: benzene, toluene, ethylbenzene; RH: Relative humidity
- In all works, experiments were conducted at room temperature unless stated otherwise

Most studies tested PCO system for the removal of a single challenge compound; however, different VOCs were used, and the challenge levels varied in several orders of magnitude, from low ppb levels to 100s of ppm. Sub-ppm levels or parts per billion (ppb) concentrations are commonly associated with indoor VOCs. Extrapolation of the oxidation data collected at concentrations much higher than the intended application may not be totally valid for air purification applications on indoor air. As a consequence, it is necessary to investigate the catalytic performance of catalysts at low pollutant levels. However, there are limited studies on the photodegradation of VOC pollutants at typical indoor levels.

The humidity level is one of the most influential operating parameters in photocatalytic oxidation in the gaseous phase (Haghighat et al., 2017). Other operating parameters such as initial challenge compound concentration and residence time as well as the photocatalyst type can significantly affect the final impact of humidity on the performance of the photocatalytic air purifiers. As a consequence, there are numerous discrepancies between the results obtained from different works, which stated that the relative humidity can be beneficial or disadvantageous and, in some cases, both behaviors can be observed. Figure 2-2 attempts to demonstrate that even though these studies use the same photocatalyst (i.e., commercial Degussa P-25) and pollutant (i.e., toluene), the impact of relative humidity (RH) on toluene removal efficiency does not follow a unique trend and varies based on specific operating conditions employed in each research.

In general, water vapor can have two sets of conflicting functions (Einaga, Ibusuki, & Futamura, 2004; Obee & Hay, 1997; Quici et al., 2010;):

1. (a) Adsorbed water molecule is oxidized to hydroxyl radicals, which improves the PCO reactions; (b) RH maintains the oxidation rate by replenishing surface hydroxyl groups; and (c) surface hydroxyl groups can trap holes and hinder e^-h^+ recombination, and
2. (a) Water molecules adsorbed on the surface of TiO_2 via hydrogen bonding with hydroxyl groups form a multi-layer film which impedes pollutants from contacting TiO_2 surface or reactive species in the boundary layer; (b) water molecules compete with VOCs for adsorption on active sites of TiO_2 ; and (c) at very high RH, water vapor can lower the light intensity on photocatalyst surface by blocking the UV radiation.

Taking into consideration the opposing effects of RH, there could be an optimal value of RH before which hydroxyl radical population determines the PCO rate (i.e. efficiency ascends with RH) and after that, the inhibiting effect of competitive adsorption dominates the oxidation rate (i.e. efficiency descends with RH). Another impact of the level of relative humidity is on the catalyst deactivation (Alberici & Jardim, 1997; Boulamanti, Korologos, & Philippopoulos, 2008). There is an overall consensus that the presence of water vapor decreases the deactivation rate and, as a consequence, increases the catalyst lifetime. This has been explained by a retarding effect of water on the formation of less reactive surface-bound intermediates and a promoting effect on their degradation (Debono et al., 2013; Vildoza, Portela, Ferronato, & Chovelon, 2011).

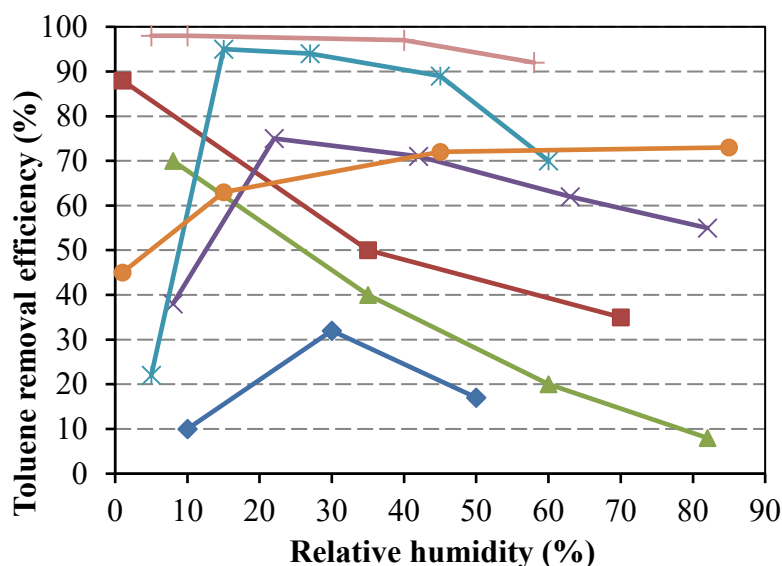


Figure 2-2. Influence of relative humidity on toluene photocatalytic removal over P25.

Data extracted from *Jafarikojour et al., 2015* (◆), *Jeong et al., 2013* (■), *Ao and Lee, 2003* (▲), *Obee and Brown, 1995* (×), *Mo et al., 2013* (* and +), *Jeong et al., 2005* (●)

One of the main concerns in the applications of PCO technology in buildings is the formation of undesired by-products. Unintended oxidation intermediates and by-products can be toxic or irritating and may be more unacceptable for human health and comfort than their precursors. By-product formation is a function of the PCO reaction mechanisms and contaminants types. Table 2-3 summarizes the main intermediates detected during photocatalytic degradation of VOCs in previous studies and also lists some of the prevalent analytical methods employed for intermediates identification/quantification. As shown in Table 2-3, the oxidation by-products of VOC are aldehydes, ketones, carboxylic acids, etc. Oxidation intermediates can also chemisorb onto the catalyst surfaces causing deactivation of catalysts, which reduces the efficiency of UV-PCO devices.

Deactivation of photocatalysts (i.e. loss of photocatalyst active sites) can stem from several sources: adsorption of reaction intermediates/by-products onto the photocatalyst surface (i.e. blockage of the active sites), photo-polymerization of species on the surface, fouling and aggregation of TiO₂ nanoparticles, and deposition of SiO₂ onto the surface due to the presence of siloxane group materials in the environment (Ardizzone, Bianchi, Cappelletti, Naldoni, & Pirola, 2008; Cao et al., 1999; Hay, Obee, & Thibaud-Erkey, 2010; Mo, Zhang, Xu, Zhu, Lamson, & Zhao, 2009). Additionally, some studies pointed out that the dehydroxylation of TiO₂ surface due to the consumption of hydroxyl radicals can remarkably reduce the lifetime of the photocatalyst. This phenomenon can be effectively prevented by keeping the humidity content in the reactor high enough to continuously rehydrate the photocatalyst surface (Haghighat et al., 2017). When PCO is challenged with toluene, the oxidation intermediates like benzoic acid and benzaldehyde are considered to be responsible for the TiO₂ deactivation resulting in the color change from white to yellow (Cao et al., 2000).

Several individual treatments or a combination of them have been reported to recover the catalyst activity (d'Hennezel, Pichat, & Ollis, 1998; Einaga, Futamura, & Ibusuki; Obee, 1996; Piera, Ayllón, Doménech, & Peral, 2002; Thevenet, Guillard, & Rousseau, 2014). The treatments include (a) exposing the catalyst to pure air or humid air; (b) irradiating the catalyst with simultaneous UV irradiation; (c) treating the catalyst with a vaporized H₂O₂ solution and heating the surface to different temperatures; (d) ozone-purging in the presence of humidity. By employing ozone in the regeneration process, Krichevskaya, Preis, Moiseev, Pronina, and Deubener (2017) could significantly shorten the required time for the restoration of P25 activity from hours of treatment (up to 15 h) with UVA at elevated temperatures (up to 180 °C) to 20 minutes using UVA + O₃. Piera et al. (2002) examined a number of surface treatments in order to recover the activity of P25 used in PCO of ethanol. Exposure to UV irradiation, clean air (dry or humid), air containing H₂O₂, hot air flow (80-150 °C) or a combination of these processes for a long period of time (15-56 h) were investigated in this study.

Overall, no systematic studies have been carried out regarding comprehensive PCO performance under the conditions relevant to the real applications. Furthermore, although a number of such devices are available on the market, the comparative evaluation of the commercial devices has never been carried out. Also, many questions remain about the parameters influencing their efficiency and the formation of harmful by-products.

Table 2-3. Summary of by-products of PCO reactions for different challenge VOCs in the literature

Challenge VOC	Intermediates/by-products	Analytical technique	Reference
Toluene	Acetone, acetaldehyde, formaldehyde, benzaldehyde, o-cresol	GC/MS, HPLC	Debono et al., 2011
	Benzene, benzyl alcohol, benzoic acid	FTIR	Schmidt et al., 2007
	Formaldehyde, acetaldehyde and methanol, propylene, acetone, acetic acid, benzene	PTR-MS	Mo et al., 2013
	Acetone, acetic acid, butyraldehyde, benzene, pentanal, benzaldehyde, benzoic acid	PTR-MS, GC/MS	Mo et al., 2009
	Benzoic acid, benzyl alcohol, and benzaldehyde, formic acid, acetic acid	GC/MS, HPLC	d'Hennezel et al., 1998
	Benzaldehyde, benzene, formaldehyde, MVK, cresol, phenol, benzyl alcohol	GC/MS, HPLC	Sleiman et al., 2009
	Benzyl alcohol, benzaldehyde, benzoic acid	GC	Tang & Yang, 2012
	Benzyl alcohol, benzoic acid, benzaldehyde, hydroquinone, cresol	FTIR	Bianchi et al., 2014
Benzene	Hydroquinone, 4-benzoquinone, phenol, formic, acetic acids	GC/MS, HPLC	d'Hennezel et al., 1998
	1,5-hexadien-3-yne, 2,4-hexadiyne, 1,3-hexadien-5-yne, formic acid	GC/MS, FTIR	Wang & Ku, 2003
	2-propenoic acid, 2-methyl-1-propanol	GC	Tang & Yang, 2012
Acetone	Acetaldehyde, methyl and isopropyl alcohol, MEK, ethyl acetate, acetic acid, mesityl oxide, diacetone alcohol	GC/MS, GC-FID	Vincent et al., 2008
	Formic acid, acetic acid, mesityl oxide, diacetone alcohol	CIMS	Schmidt et al., 2007
MEK	Acetone, ethanol, acetaldehyde, acetic acid, methanol, formaldehyde, formic acid	GC/MS, GC-FID	Raillard et al., 2006
Acetaldehyde	Formaldehyde, acetic acid	GC-FID, FTIR	Nimlos et al., 1996
	Acetic acid, formic acid, formaldehyde	FTIR	Hauchecorne et al., 2011
Ethanol	Acetaldehyde, formaldehyde, acetic acid, formic acid	GC-FID, FTIR	[Nimlos et al., 1996]
	Acetaldehyde, acetic acid, formaldehyde, formic acid	TPD-TPO	[Muggli et al., 1998]
n-Butanol	n-Butanal, crotonaldehyde, propanal, acetaldehyde	GC-FID	Kirchnerova et al., 2005
	Butanal, butanoic acid, 1-propanol, propanal, ethanol, acetaldehyde	GC/MS	Benoit-Marquié et al., 2000

* CIMS: Chemical ionization mass spectrometry; HPLC: High-performance liquid chromatography; FID: Flame ionization detector; PTR-MS: proton transfer reaction-mass spectrometer

2.2 Plasma-based air cleaning systems

2.2.1 Non-thermal plasma

Another emerging air cleaning technology for VOC removal is using non-thermal plasma (NTP). NTP technique acts based on creating a quasi-neutral environment including ions, radicals, electrons, neutrals, and UV photons (Bahri & Haghghat, 2014). Because of the lower mass, electrons are accelerated selectively by an electric field reaching the temperature in the range of 10,000–250,000 K (1 - 25 eV). Unlike thermal plasma, where all components of air including electrons, ions, atoms, and molecules are in thermal equilibrium, in NTP, only electrons are heated and the rest are not in thermal equilibrium. Hence the temperature increase of the processed air in NTP is very small like only a few degrees and the energy requirement is lower than thermal plasma. High energy free electrons in NTP result in the generation of reactive ions and free radicals such as hydroxyl radicals leading to oxidation reactions. NTP can be generated through various techniques: pulsed corona discharge, dielectric barrier discharge, surface discharge, ferroelectric (dielectric) packed-bed, electron beam, and flow-stabilized DC discharge processes (Khono et al., 1998).

Previous studies showed that NTP has a capability for abatement of VOC, acid gases, particulate matters, and bacteria at ambient temperature (Bahri and Haghghat, 2014; Oda, 2003). NTP has a high removal efficiency for particulate matters ranging from 76 to 99% (Zhang et al., 2011), but the performance for VOC removal is controversial. While several studies reported high removal efficiency for VOC removal as shown in Table 2-4, Schmid, Jecklin, and Zenobi (2010) tested a commercially available NTP device for VOC and its degradation efficiency was $11 \pm 1.6\%$ for cyclohexene, $<2\%$ for benzene, $11 \pm 2.4\%$ for toluene, $3 \pm 1\%$ for ethylbenzene, $1 \pm 1\%$ for o-xylene, and $3 \pm 0.4\%$ for m-xylene.

In NTP studies, the specific input energy (SIE, J L⁻¹) and energy efficiency (EE_i, g kWh⁻¹) are defined as:

$$SIE = \frac{60UI}{Q} \quad (2-1)$$

$$EE_i = \frac{3.6 C_{in} \cdot \eta \cdot M}{24.4 SIE} \quad (2-2)$$

where, U is the applied voltage (kV); I is the discharge current (mA); Q is the gas flow rate (L min⁻¹); C_{in} and η are the inlet concentration (ppm) and the conversion of the compound, respectively; M indicates the compound molar mass (g mol⁻¹); 24.4 is the gas molar volume (L mol⁻¹) under the defined condition and finally 60 and 3.6 are the conversion coefficients. As summarized in Table 2-4, NTP has poor energy efficiency (EE_i) especially for low concentrations of VOCs.

RH can affect VOC removal performances of NTP; however, its effect tends to be discordant among different studies. The presence of water vapor can promote the generation of hydroxyl radical, which is a strong VOC oxidizing agent; hence, increasing the VOC removal efficiency. At the same time, increasing the relative humidity level could have a negative effect on the removal efficiency due to decreasing electron density and quenching of the reactive species in the reactor (Bahri, Haghghat, Rohani, & Kazemian, 2017). In DC corona discharge reactors, Wan, Fan, and Zhu (2011) showed the increased formaldehyde removal efficiency when RH increased to 70%,

while Van Durme, Dewulf, Sysmans, Leys, and Van Langenhove (2007a) showed that toluene removal efficiency peaked at 26%.

In NTP systems, incomplete oxidation of target VOC pollutants is generally reported, and this can result in the formation of carbon monoxide (CO) and some other organic by-products (Schmid *et al.*, 2010; Van Durme *et al.*, 2007a). Furthermore, the formation of nitrogen oxides (NO_x) and ozone (O₃) as a consequence of plasma inducing in NTP reactors is inevitable (Meichsner, Schmidt, Schneider, & Wagner, 2013).

2.2.2 Plasma-catalyst systems

To resolve the problems of NTP, the combination of NTP and catalysts, so-called plasma catalysis (PC), has been developed. PC approach is promising for air cleaning applications as it enhances the removal efficiency and the total oxidation leading to reduced by-product generation (Bahri & Haghghat, 2014; Inoue, Okano, Yamagata, Muraoka, & Teraoka, 2011; Van Durme, Dewulf, Leys, & Van Langenhove, 2008;). The synergic effect of NTP and catalysts results in a higher removal efficiency compared to the sum of each process efficiency.

In a plasma catalyst reactor, catalyst and plasma can be combined in two different ways as shown in Figure 2-3:

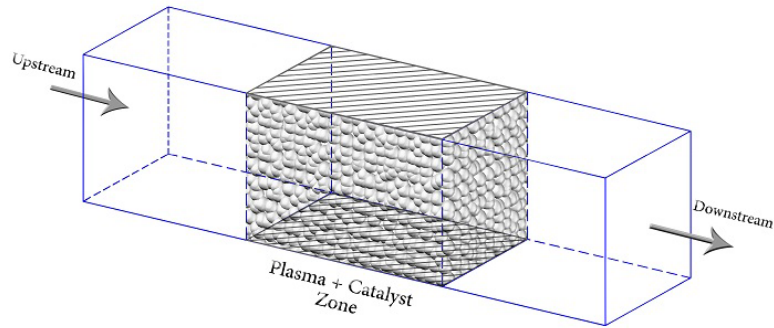
- 1) In-plasma catalyst (IPC): In this method, a catalyst is introduced to the discharge zone of the reactor
- 2) Post-plasma catalyst (PPC): In a two-stage plasma catalyst method, the catalyst can be placed either at the upstream or downstream of the discharge zone. However, the installation of the catalyst in the downstream of the plasma (PPC) is more efficient, since the generated reactive species in the plasma zone participate in oxidation reactions in the catalyst zone, leading to better mineralization reactions (Chen *et al.*, 2009; Van Durme, Dewulf, Sysman, Leys, & Van Langenhove, 2007b).

Figure 2-4 shows a schematic of the possible reactions in a PPC reactor. In a plasma zone, the dominant reactions for VOC removal include the formation of reactive species. The presence of catalyst suppresses these types of reactions and enhances the heterogeneous oxidation reactions, resulting in higher CO₂ selectivity (Bahri & Haghghat, 2014).

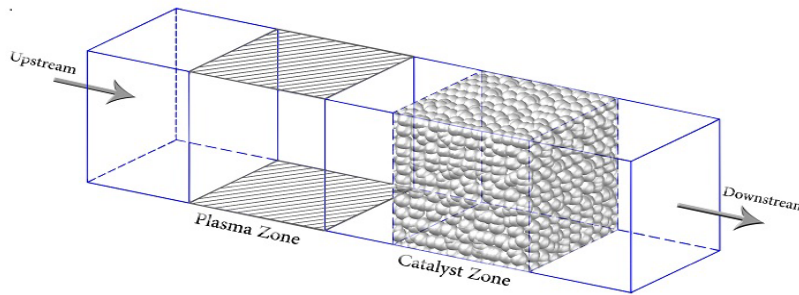
The presence of the catalysts increases the probability of surface reactions between the reactants and reactive species, which leads to more selective reactions and higher removal efficiency of the system. Therefore, the catalyst surface textural properties including specific surface area, pore volume, pore size, and size distribution, as well as particle size and shape have an important role on the plasma catalyst performance (Parvulescu, Magureanu, & Lukes, 2012; Rousseau, Guaitella, Röpcka, Gatilova, & Tolmachev, 2004).

The performance of a catalytic plasma process is also related to the catalyst storage capacity. To have a high VOC removal efficiency, VOCs should form strong bonds with the catalyst surface. Formation of these bonds becomes more important in low concentration levels (Bahri, Haghghat, Kazemian, & Rohani, 2017; Zhao, Li, Shi, Fan, & Zhu, 2011;). A catalyst with a great ability to absorb VOCs as well as formed reactive species in the presence of plasma increases the removal efficiency of these compounds. Dual functional adsorbent/catalysts are favorable catalysts when

generated reactive species under plasma catalyst conditions are not enough for decomposition of the pollutants (Bahri, Haghghat, Kazemian, & Rohani, 2017). In fact, the storage material capacity increases the reaction time as well as the probability of collision between the VOCs compounds and reactive species on the surface of the catalyst (Chen et al., 2009). Earlier studies have reported the positive effect of employing a dual functional adsorbent/catalyst on energy efficiency and eliminating the formation of harmful by-products (Demidiouk, Moon, & Chae, 2003; Ogata et al., 2003).



a) In-plasma catalyst (IPC) reactor



b) Post-plasma catalyst (PPC) reactor

Figure 2-3. Types of plasma-catalyst reactors (adapted from Bahri & Haghghat, 2014).

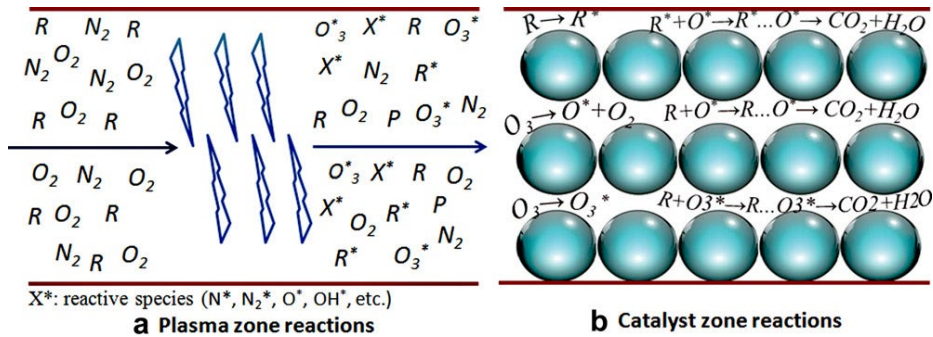


Figure 2-4. Reactions in post-plasma catalyst (PPC) system.

Porous adsorbents, including alumina (Al_2O_3) (Ogata, Shintani, Mizuno, Kushiyama, & Yamamoto, 1999; Song, Kim, Choi, & Yamamoto, 2002) were the first materials considered for such application. Zeolites feature more permanently in the literature because of their greater storage capacity of VOCs (Inoue et al., 2011; Oh et al., 2005). The catalyst properties and plasma activity can be enhanced by coating the porous materials with metals (i.e. Ag, Pt, Pd, Rh, Ni, Cu, Co, Mg, Ti) or metal oxides (TiO_2 , V_2O_5 , WO_3 , etc.) as support (Fan, Zhu, Wang, & Li, 2009; Magureanu, Mandache, Eloy, Gaigneaux, & Parvulescu, 2005; Van Durme, Dewulf, Demeestere, Leys, & Van Langenhove, 2009; Zhu, Li, Liang, & Jin, 2009). However, in some studies decreasing the removal efficiency was reported as a consequence of adding a support and decreasing the specific surface area of the catalyst (Harling, Demidyuk, Fischer, & Whitehead, 2008; Kim, Ogata, & Futamura, 2006). Recently, the application of metal organic frameworks (MOFs) has been considered as dual-functional adsorbent/catalysts in NTP-catalyst systems (Bahri, Haghghat, Rohani, & Kazemian, 2017; Bahri, Kazemian, Rohani, & Haghghat, 2017).

Table 2-5 summarizes PC test results available in the literature (Bahri & Haghghat, 2014). Most test flow rates in Tables 2-4 and 2-5 are very low and far from the real operational conditions because NTP or PC reactors are in small bench-top scales and/or have a long residence time for better oxidation. In addition, other test conditions are all different making the inter-comparison difficult.

It is noteworthy that the application of the catalyst in commercial plasma systems has not been reported so far. Also, very few studies have conducted their experiments with the low concentration levels of the VOCs. Therefore, developing a full-scale system that challenges the ppb levels of VOCs is an important step towards commercializing the PC method. The formation of by-products is another important concern in employing any air cleaning system for an indoor environment (Bahri and Haghghat, 2014). Thus far, very few studies quantitatively investigated the amount of formed inorganic by-products (i.e., O_3 , NO_x , CO) as well as organic by-products.

Table 2-4. Summary of NTP evaluation results for VOC removal (modified from Bahri and Haghighat, 2014)

Reference	Reactor type	Target pollutant	Carrier gas	Conc. [ppm]	Flow Rate [Lmin ⁻¹]	Removal efficiency [%]	CO ₂ yield [%]	SIE [J L ⁻¹]	EEi [g kWh ⁻¹]	Reported by-product	Conc.	
Urashima et al., 1997	Corona	Toluene	Air	2000	1	90	N/A	N/A	26	Aerosol particles	N/A	
		Trichloroethylene				40			13			Aerosol particles, Cl ₂
Demidiouk et al., 2003	Wire cylinder pulse	Toluene	Air	280	5	< 97	20	N/A	N/A	CO	500 ppm	
		Butyl acetate		120	20	< 75				Aerosol	N/A	
Sugasawa et al., 2009	Ferro-electric Packed-bed	Toluene	N ₂ + 20%O ₂	100	0.5	~85	~60	450	~2.6	CO	N/A	
		CH ₂ Cl ₂		109		~85	~40		~2.6	CO, formaldehyde, acetic acid		
		(Toluene+ CH ₂ Cl ₂)		100+ 109		N/A	~60		---	Chloroform (CHCl ₃) Benzene	0.5 ppm 0.4 ppm	
Quoc An et al., 2011	DBD	Toluene	N ₂ + O ₂	800	0.07	60	N/A	N/A	N/A	O ₃ , CO, CO ₂ , NO _x (NO, NO ₂), formic acid, acetic acid, benzene	N/A	
Wan et al., 2011	DC-Corona	Formaldehyde	Dry Air	2.2	6	42	N/A	80	0.05	O ₃	282 ppm	
						Air+ 30% RH			54		0.06	162 ppm
						Air+ 70% RH			57		0.07	157 ppm
Delagrangé et al., 2006	DBD	Toluene	20% O ₂ + 80%N ₂	240	0.315	36	6	172	6.8	CO	8%	
Yu-fang et al., 2006	DBD	Toluene	N ₂ , 5%O ₂	50	100	~ 52	61	600	0.6	CO	N/A	
			N ₂ , 5%O ₂ , .2%H ₂ O			73.1	72		0.8			
Wang et al., 2009	DBD	Acetone	Air+ N ₂	200	2.5	38	N/A	402	2.9	N/A	N/A	
		Benzene				56			5.8			
		Tetrachloroethylene				74			16.3			
		m-xylene				98			13.9			
		Mix				N/A			29.3			
Fan et al., 2009	DC-tooth wheel cylinder	BTX mix (Benzene, toluene, p-xylene)	Air	1.5	6	~ 60	~ 45	300	N/A	CO, O ₃ NO _x (NO, NO ₂ , N ₂ O, N ₂ O ₅) Formic acid, benzaldehyde, benzyl alcohol	>35% 46.7 ppm (0, 1380 ppb, 0,0) N/A	
				1.4		~ 93						
				1.2		~ 100						
Van Durme et al., 2007b	DC-Corona	Toluene	Dry air	0.5	10.8	70	N/A	60	0.09	O ₃ NO NO ₂	49.9 ppm <10 ppb 1500 ppb	
			Air+27% RH		10.8	~ 80			N/A	0.1	O ₃ NO NO ₂	31.2 ppm <10ppb 800 ppb
Van Durme et al., 2007a	DC-Corona	Toluene	Dry air	0.5	10	46	N/A	28.8	0.12	Ozone, 4-Nitrophenol, 4-Methyl-2-nitrophenol, formic acid, benzaldehyde, benzoic acid, benzyl alcohol, 4-Methyl-2-propyl furan, 3-Methyl-4-nitrophenol 2-Methyl-4,6-dinitrophenol	55-75 ppm N/A	
			Air+ 26% RH			57			0.15			
			Air+ 50% RH			26			0.07			

Table 2-5. Summary of plasma-catalyst evaluation results for VOC removal (Modified from Bahri and Haghightat, 2014).

Reference	Reactor Type	Catalyst	SSA (m ² g ⁻¹)	Target pollutant	Carrier Gas	Conc. [ppm]	Flow Rate [L min ⁻¹]	Removal efficiency [%]	CO ₂ yield [%]	SIE [J L ⁻¹]	EEi [g kWh ⁻¹]	By-product	Conc.
Delagrangre et al., 2006	DBD/ PPC	MnO ₂ -FeO ₃	219	Toluene	20%O ₂ + 80%N ₂	240	0.315	76	23.5	172	14.4	O ₃ , CO	3.9 ppm, 16.5%
		MnO ₂ /γ-Al ₂ O ₃	169					88	18		16.7		14.6 ppm, 14.0%
		MnO/AC	1024					99.7	30.2		18.9		8 ppm, 24.8%
Oh et al., 2005	Surface Discharge /PPC	NaY	750	Toluene	80% N ₂ + 20% O ₂ + 0.5% H ₂ O	200	0.5	78	60	600 ^b	3.54	O ₃ /CO	0.2 * 10 ⁻³ mol, N/A
		HY	520					87	38		3.94		0.3 * 10 ⁻³ mol, N/A
Holzer et al., 2002	DBD/IPC	γ-Al ₂ O ₃ α-Al ₂ O ₃	133 0.26	Carbowax ethane-1,2-ol (C ₂ H ₆ O ₂)	Air	200	0.1	77	96	2400 ^b	0.64	O ₃	0
	DBD/PPC	γ-Al ₂ O ₃ α-Al ₂ O ₃ + γ-Al ₂ O ₃	133 N/A					100	61		0.83		N/A
Ayrault et al., 2004	DBD/IPC	Pt/Al ₂ O ₃	N/A	2-Heptanone	Dry air Air+ 3% H ₂ O	180	0.42	98	64	34	87.4	CO, O ₃ , NOx	36%, N/A, < 10ppm
								86	56		76.7 ^c		26%, N/A, < 10ppm
Karuppiah et al., 2010	AC DBD/ IPC	3 wt% MnO _x /SMF ¹	N/A	Isopropanol	Air	100	0.5	100	100	195	4.55	O ₃	N/A
Yu-fang et al., 2006	DBD/IPC	Co ₃ O ₄ /Al ₂ O ₃ /Ni	N/A	Toluene	N ₂ + 5%O ₂	50	0.1	96	75	500	1.30	CO	N/A
Wan et al., 2011	DC Corona /PPC	MnO _x /Al ₂ O ₃	N/A	Formaldehyde	Air+ 30% RH	2.2	6	87	N/A	20	0.43	O ₃	14 ppm
Fan et al., 2009	Tooth wheel cylinder plasma-DC/ PPC	MnO _x /Al ₂ O ₃	200	BTX mix (Benzene Toluene p-Xylene)	Air +25% RH	1.5 1.4 1.2	6	94 97 95	100	10	1.63 1.85 1.80	O ₃ NO ₂	1.9 ppm 40 ppb
Van Durme et al., 2007b	DC Corona /PPC	CuOMnO ₂ /TiO ₂	50	Toluene	Dry air	0.5	10.8	78	N/A	2.5	2.2	O ₃ NO NO ₂	24 ppm N/A 553 ppb
	DC Corona /IPC	TiO ₂	49					82 ± 2	N/A		17		0.35
Fan et al., 2010	DC tooth wheel cylinder Plasma/PPC	MnO _x /Al ₂ O ₃ 5 wt.% Mn	N/A	Benzen	Air+ 30% RH Air+ 50% RH	0.470	6	100 ~0.63	20-35	10	0.54 0.34	O ₃ CO	27.3- 30ppm N/A
				Toluene	Air+ 30% RH Air+ 50% RH	0.810		100 ~0.95			1.1 1.05		
				p-Xylene	Air+ 30% RH Air+ 50% RH	0.730		95 ~95			1.08 1.08		
Van Durme et al., 2009	DC Corona /PPC	Pd/Al ₂ O ₃	230-280	Toluene	Air Air+ 74% RH	0.5ppm	10	94	N/A	10	0.64	O ₃	2.9 ppm
								39			0.27		2.0 ppm

¹SMF: sintered metal fiber

2.3 Ozonation air cleaning systems

Ozone is a strong oxidant that can react with both biological and chemical compounds. Ozone generators are widely used in water treatments, some ozone generator manufacturers produce devices for air treatments as well. Due to the harmful health effects of ozone, U.S. EPA deprecates the use of ozone generators for air cleaning in occupied spaces (EPA, 2018b). In addition, the California Environmental Protection Agency has banned the use of air cleaners that generate ozone at the level of more than 50 ppb; however, this regulation does not apply to in-duct air cleaning systems (Cal. Code Regs. tit. 17, § 94800-94810 (2020)). In spite of governmental efforts, ozone generators are still available in the market and there are at least two manufacturers in Quebec.

The efficiency of ozone generators for the removal of VOC depends on the ozone level. Ozone generally reacts slowly with saturated hydrocarbons, but relatively fast with unsaturated hydrocarbons. But these reactions can produce carboxylic acids, aldehydes, epoxides, organic peroxides, and ketones (Britigan, Alshawa, & Nizkorodov, 2006) as well as secondary organic aerosols in ultrafine and fine sizes (Corsi, Siegel, Karamalegos, Simon, & Morrison, 2007). EPA (2013) concluded that ozone generators are generally ineffective at concentrations which do not exceed the public health standards. Britigan et al. (2006) tested commercial ozone generators for the ozone output, which was varied from 42 mg/hr to 220 mg/hr depending on the device. When the tested ozone generators were continuously operated in an office with 11.1 m² of floor area, the increase of ozone concentration in the office was 140 ppb to 276 ppb. There is little study for in-duct systems applications.

It is noteworthy that ozone generators are commonly subclasses of two other aforementioned oxidation-based technologies; in fact, in these systems ozone is generated by means of either UV lamps or plasma methods (Chao, Kwong, & Hui, 2007; Zhong & Haghghat, 2014). The removal performance of ozone generators has been widely investigated in different studies. However, according to several reports, typical exposure limits of ozone concentration in an indoor environment (in the range 50–100 ppbv) does not show an effective performance for many of the VOC pollutants (Luengas et al., 2015). Furthermore, ozone generators could contribute to the formation of organic aerosols, especially when terpenes (an ingredient of deodorants and cleaning agents) are present in indoor environment (Hubbard, Coleman, Sarwar, & Corsi, 2005).

To enhance the VOCs removal capacity and removal efficiency by ozonation, the application of different types of porous adsorbents and catalysts in these systems has been suggested (Onuki et al., 2015; Samarghandi et al., 2014). Usually, the same porous catalysts available for plasma-catalyst technologies exhibit high VOCs removal performances for this method as well. For instance, Sekiguchi, Sanada, and Sakamoto (2003) used a VUV lamp for ozone generation and utilized TiO₂ as a catalyst to enhance the decomposition efficiency of toluene during the ozonation. The advantage of the implementation of the catalyst in this system was not only enhancing the toluene decomposition efficiency, but also decreasing the concentration of the ozone downstream of the system.

In a different study ozone was generated by means of a non-thermal plasma (corona discharge) system (Chao et al., 2007). The result of this study stated an inverse relationship between the concentration of ozone and the required time for the complete decomposition of toluene. Also, the presence of the zeolite as a catalyst decreased the formation of by-products. Application of

different types of microporous zeolites and mesoporous MCM-41 (Mobil Composition of Matter No. 41) as adsorbents in the presence of ozone was performed by Kwong, Chao, Hui, & Wan (2008) also demonstrated that the combined use of ozone and these media could enhance the oxidizing capability of ozone significantly. The utilized ozone generator in this study was also a corona discharge system (Kwong et al., 2008).

Overall, there is a lack of systematic studies on the actual performances of emerging oxidation-based air cleaning technologies. Very limited data is available to industrial hygienists, HVAC engineers, building managers, and end-users to make an informed decision regarding the appropriate cleaning device for a given situation. The oxidation-based air cleaning systems are penetrating the market rapidly due to higher energy efficiency as they have much less flow resistance compared to adsorption-based technologies. A fair evaluation of new oxidation-based technologies under realistic application conditions is necessary for the development of standard test methods for such devices.

Finally, when it comes to the utilization of the catalyst in oxidation-based systems, for improving the removal performance and elimination of hazardous by-products, most of the studies are available for small-scale systems, in which the operational conditions are far different from the real conditions. There is no systematic approach to upgrade catalytic-oxidation methods for full-size HVAC systems. The presence of these deep gaps between the research and the real-life application of catalytic-oxidation-based systems necessitates -more specific attention to this aspect.

3. RESEARCH OBJECTIVES

The main objective of this research is to develop and validate a test protocol to evaluate the performance of air-cleaning devices based on oxidation technologies such as photo-catalyst, non-thermal plasma, and ozonation. The main objective was achieved through sub-objectives defined as follows:

- 1) Identify the capacities of commercial oxidation-based air cleaning devices in removing different contaminants in the range expected in actual applications;
- 2) Investigate the by-product generated from the oxidation-based air-cleaning devices;
- 3) Investigate the effects of operational conditions like airflow and relative humidity on the overall performances of oxidation-based air-cleaning devices.

This research will assist in developing standards, advanced technologies, and providing information to enable industrial hygienists, HVAC engineers, building managers, and operators to develop a methodology for design and operation of a healthy and safe indoor environment. The research could also be used to develop a rating system for pollutant mitigating devices. The outcomes of this research can also provide a strong push for the development and integration of a technology that has the potential to significantly increase our health, safety and security while also improving the indoor air quality and the sustainability of buildings.

4. EXPERIMENTAL METHODS

4.1 Test setups

A full-scale test rig and a smaller-scale one comprised of four identical test ducts were used in this research. The smaller scale four-parallel test rig has been used in obtaining preliminary performance data and parametric study of oxidation-based air cleaning technologies necessary for the development of test method protocol. The developed method was verified and refined through testing in the full-scale test rig.

4.1.1 *Four-parallel air cleaner test rig*

We have designed and built a test rig consisting of four identical test ducts with 0.3m x 0.3m of cross-sectional area each. The rig was originally designed for testing different UV-PCO devices. The biggest challenge in designing the rig was the space limitation because the laboratory is located in downtown Montreal and a full-scale test rig complying with the ASHRAE Standard 145.2-2016 was already occupying large space in the laboratory. The maximum available room was only about 1.3m×3.8m. Bench-top scale setup was not considered because regular sizes of UV lamps cannot be used in such a system. Then test results could be questionable and may not be transferrable to full-scale system performances. With the given limitations, the test duct size allowing reasonable scaling-up was decided as 0.3 m × 0.3 m. To run many tests in a time-efficient manner, it was decided to develop four parallel ducts; hence, four tests can run at the same time.

Figure 4-1 shows the picture and the schematic of the 4-parallel test rig. It has 3.56 m of total length and 1.20 m width. The test rig is made of aluminum which has the highest reflectance of UV. Pre-filtration (①), contaminant gas introduction and mixing (②), followed by upstream air sampling, and temperature and relative humidity measurement station are located in the 1.20 m × 1.21 m main duct. The main duct is connected to four separate 0.3 m × 0.3 m ducts. Each 0.3 m × 0.3 m duct contains an airflow measurement section (③), test air cleaner section (④), downstream air sampling, airflow, temperature, and relative humidity measurement station (⑤), a clean-up media bed (⑥), a variable speed fan (⑦), and the final filtration and ozone scrubber.

The airflow rate of each duct can go up to 340 m³/hr. Due to the size of the rig, the laboratory air was used as carrier air and air filtration was applied before the introduction of the challenge air contaminant. From the challenge contaminant introduction point to the upstream air sampling section is only about 1.2m, which is not enough to have a good mixing; therefore, a fan and a custom-designed air mixer were applied. Cross-shaped averaging air sampling tubes were used for both upstream and downstream air sampling. All the probes and tubing used in air sampling are either stainless steel or polytetrafluoroethylene (PTFE).

Various geometries of air cleaning systems are available in the market. The test air cleaner section was designed to be able to accommodate different UV-PCO systems and to be easy to install and modify. Different air cleaning devices can result in different flow resistance. To be able to control the airflow rate, each duct has a variable speed fan with its control system.

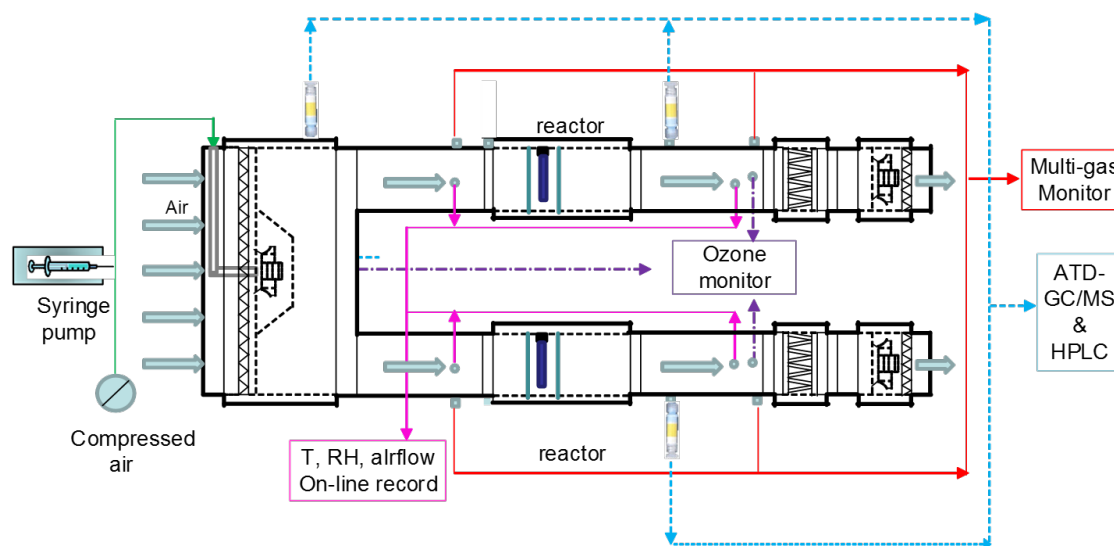
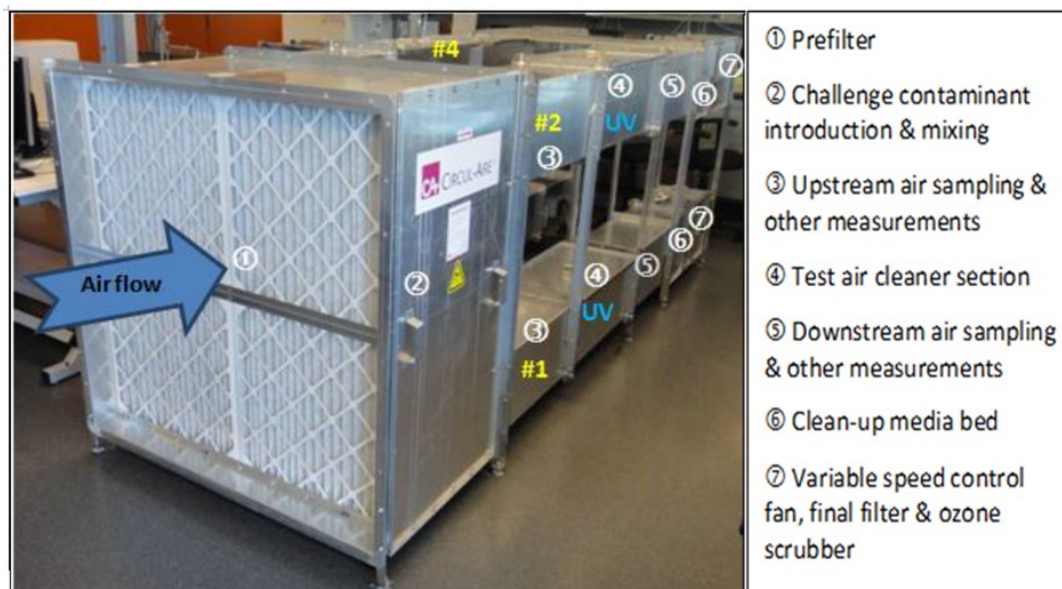


Figure 4-1. Four-parallel test duct system.

The designed test rig is for single-pass testing and the carrier air containing challenge air contaminants as well as potential by-products generated from oxidation-based air cleaning systems are exhausted into the laboratory. To clean up these potentially harmful contaminants, a final clean-up adsorbent media bed is installed in each duct before the variable speed fan. The adsorbent media are regularly changed for safety. And after the fan, there are final filtration and ozone scrubbers.

To verify that the test rig is capable of providing reliable air cleaner performance measurements, we have carried out extensive qualification tests of the rig after the rig was built. The prequalification tests include air leakage test, air velocity uniformity, and stability test, concentration uniformity test, and no-filter test (Lee, Zhong, Farhanian, Flaherty, & Haghighat,

2012). Among them, the air leakage test and concentration uniformity test were conducted again as these performances can deteriorate with the advancing years of the setup. Tracer gas test was conducted twice using ethanol and the leakage rate results were 0.47% and 0.57%, which are less than the 1% limit. The concentration uniformity test conducted with n-octane resulted in less than 2% as a coefficient of variation.

4.1.2 Full-scale air cleaner test rig

A full-scale system was designed and constructed based on ASHRAE Standard 145.2-2016, which incorporates an air-cleaning device like its actual field use. The cross-sectional area of the duct is 610 mm x 610 mm and made of stainless steel with smooth interior finishes to reduce sink effects due to adsorption. The length of the duct is 11.6 m and the full-loop length is 24.3 m. The test system can be run in recirculation (closed-loop) mode or once-through (open loop) mode exhausting outside after passing through the exhaust clean-up bed.

Figure 4-2 presents the photo and the schematic of the full-scale test rig. The laboratory air is introduced to the system through the inlet damper (Point B shown on the schematic). Ultra-low leakage positive pressure dampers (M&I Air Systems Engineering) were used in both inlet and outlet, which enables testing in recirculation mode. The carrier lab air goes through cooling coils and a steam humidifier section (Point C) for temperature and humidity control before the blower. A radial fan (Rosenburg America, DKNB-355), which can provide a 1.0 m³/s airflow rate at 2 kPa pressure drop, was used with a fan speed control (Point D). A clean-up media bed (Point E) and a HEPA filter (Point F) are mounted downstream of the fan to remove gaseous contaminants and particulate matters from the carrier air.

The challenge gas injection port is located downstream of the clean-up bed and the HEPA filter. A mixing baffle consisting of a 30 cm diameter orifice plate (Point G-1) and a 15 cm diameter 40% perforated plate (Point H-1), ensures the uniform dispersion of the challenge gas. An identical mixing baffle (Points G-2 and H-2) is installed downstream of the bend in the duct. This combination ensures that the challenge contaminant and the air are fully mixed in the upstream and downstream zones of the filter and allows a single center-point air sampling from each zone. To have even velocity and concentration profiles across the cross-sectional area, an undisturbed ducting of 2.9 m was installed between the mixing baffle and the upstream air sampling and measurement location. There are three sections for test air cleaner installation (Points I-1 to I-3) to be able to test different sizes and types of air-cleaning devices, and multiple stage air cleaning systems.

Temperature and relative humidity in upstream and downstream of the tested filter are monitored by temperature and relative humidity transmitters (Vaisala HUMICAP series HMT100). These probes are mounted at the same locations (Points J-1 and J-2) as the challenge gas concentration sampling ports. They are connected to a data acquisition system (DAS) (Agilent 34970A Data Acquisition/Switch Unit). The airflow rate is measured using an ASME long-radius flow nozzle (Point G) as used in ASHRAE standard 145.2-2016. A pressure difference transmitter (Huba type-694) and two static taps are mounted before and after the flow nozzle (Points H-1 and H-2) to measure the pressure drop created by the nozzle. The exhaust of the system is directly vented to the exhaust duct of the laboratory. The air is cleaned by a final clean-up bed (Point H) before exhausting.

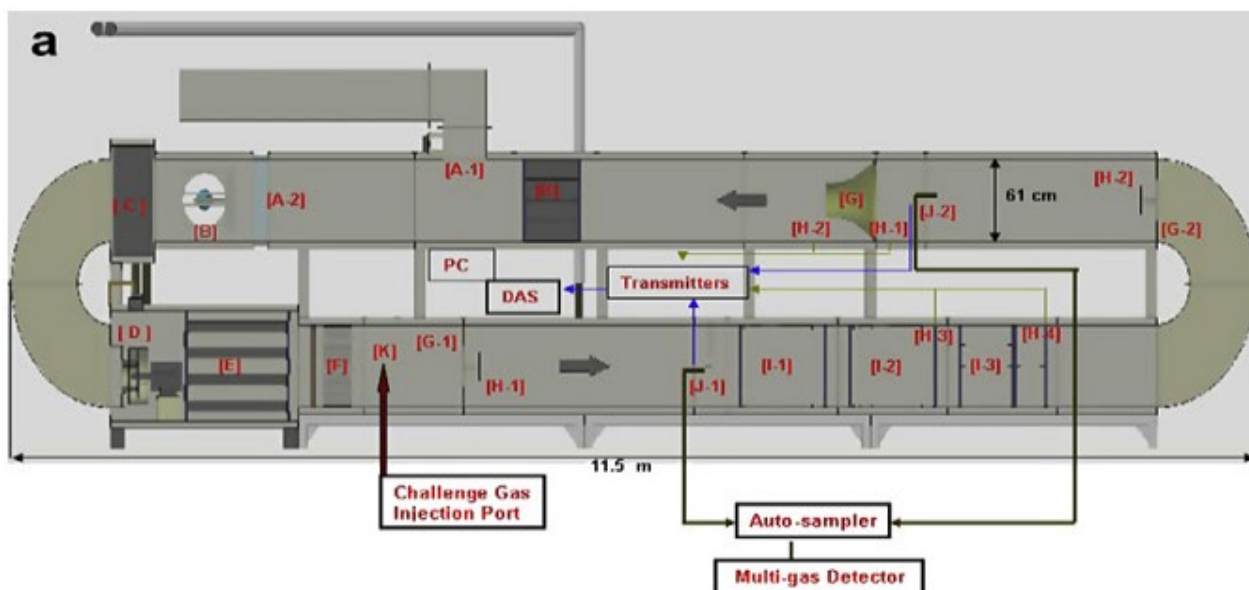


Figure 4-2. Full-scale test rig complying with ASHRAE Standard 145.2-2016.

A series of qualification tests of the system have been conducted following the requirements by the ASHRAE Standard 145.2-2016 (Bastani *et al.*, 2010). Table 4-1 summarizes the qualification test results conducted after the rig was built. Since then the rig has not been modified at all. The only concern is leakage as the rig gets older the gaskets and seals applied can weaken. Therefore, test duct leakage tests were conducted twice using n-octane as the tracer gas and both tests showed less than 0.2% of air leakage, complying with the ASHRAE Std. 145.2-2016 criterion.

In both test rigs, the challenge VOC was generated using an automatic syringe pump (KD Scientific). VOC was constantly injected into a compressed air stream using PTFE tubing. This carrier air flow rate was controlled by a mass flow controller (Omega FMA 5400/5500) to ensure the evaporation of injected VOC but limited to less than 1% of the air cleaner test flow rate not to disturb the test conditions.

Table 4-1. Full-scale test rig original qualification test results

Qualification Test	Requirement	Result
Test duct velocity uniformity	CV < 10%	8.6-9.0% (2000cfm) 6.5-8.6% (500 cfm) (OK)
Test duck leakage: Ratio of leak rate to test airflow rate	<1%	0.082% (OK)
Test duct leakage: Total allowable leak	<PEL (Toluene 100 ppm)	80 ppb (OK)
Contaminant dispersal uniformity	CV < 15%	4.76-5.67% (2000cfm) 4.78-4.98% (500cfm) (OK)
Downstream mixing	CV < 10%	2.01-2.02% (2000cfm) 2.77-3.12% (500 cfm) (OK)
Gas contaminant generation system airflow rate	< 1% of lowest rig flow	0.014% (OK)
Gas analyzer calibration (0, 10, 50 & 100% of challenged conc.)	Use traceable gas standard and zero air	<u>B&K: Toluene</u> (OK) R ² = 0.99 @ 50%RH (0/2/5/10/20/50/100 ppm)
Contaminant generator & duct response time	No predetermined level	306 seconds (OK)
No filter test and overall system check	Calculated efficiency for no filter test < 5% Calculated conc. within 10% of measured.	Average absolute efficiency = 2.75% (OK)

4.2 Air sampling and analysis methods

4.2.1 Direct reading instruments

A photo-acoustic analyzer (Innova, Type 1312) combined with an automatic multi-channel sampler (CBISS MK3) were used to monitor the air contaminant concentration in real time at the upstream and downstream of the test air cleaning system in a 4-duct test rig. The photo-acoustic analyzer is equipped with photo-acoustic filters for total hydrocarbon (THC, calibrated as toluene), aldehydes (calibrated as formaldehyde), carbon monoxide (CO), and carbon dioxide (CO₂). Since it has different sensitivity for different hydrocarbons or aldehydes, its results cannot be applied in evaluating the VOC removal efficiency of oxidation-based air cleaning technologies. Therefore, its main use is the test quality control to ensure the challenge gas introduction and upkeep of constant concentration. Originally we planned to use CO and CO₂ measurement data to evaluate the mineralization (i.e., complete oxidation) rate of oxidation-based air cleaning systems. From the actual test, we have realized that this plan is impractical due to: 1) our testing device is large, so the carrier air is filtered laboratory air unlike other previous works using compressed air. CO and CO₂ levels fluctuate in indoor air and CO₂ is generated by occupants, making it difficult to isolate the generation by the oxidation-based air cleaning test unit; 2) the CO and CO₂ generation rates by the commercial oxidation-based air cleaning systems are not high due to the relatively low challenge VOC concentrations considered in this study and/or low conversion efficiency.

Two ozone monitors (Teledyne Instruments 6-channel industrial hygiene ozone analyzer and 2B Technologies model 202 ozone monitor) were applied in this study to measure ozone generation from the oxidation-based devices. These ozone monitors are based on UV absorption technology, which is one of the U.S. EPA-approved ozone measurement technologies. These monitors have sufficient detection ranges from low ppb to high ppm sufficient for this project. A 6-channel monitor was applied in the 4-duct test rig to alternately monitor upstream, downstream of each duct and exhaust air after the ozone scrubber. The other monitor was applied in full-scale testing, monitoring ozone levels in downstream of the air cleaner test unit, comparing before and after the unit is turned on.

Other measurements included in this study are air flow rate, temperature, and relative humidity. Airflow rates in 4-duct test rigs were measured at the exhaust using an automatic volume flow meter with pressure compensation (DIFF automatic, Observer instruments), which is suitable for measuring low flow rate ranges (10 – 400 m³/hr) with an accuracy of $\pm 3\%$ of the readings. The reliability has been verified through a Lawrence Berkeley National Laboratory study (Stratton, Turner, Wray, & Walker, 2012). In a full-scale test rig, the flow rate was obtained by measuring the pressure difference across ASME long-radius flow nozzle as prescribed in ASHRAE Standard 145.2-2016. The pressure difference across the flow nozzle and the pressure drop due to the test air cleaner were measured using differential pressure transmitters (Cuba control pressure difference transmitter type-694). Temperature and relative humidity in upstream and downstream of the tested filter were monitored by temperature and relative humidity transmitters (Vaisala, HMT100) in both full-scale and 4-parallel test rigs. These transmitters are connected to a data acquisition system (Agilent 34970A Data Acquisition/Switch Unit) to collect relevant data.

4.2.2 Active sampling for VOCs and ATD-GC/MS analysis methods

To analyze challenges VOCs and other VOCs generated as oxidation by-products, air samples were collected on multi-bed adsorbent tubes (SUPELCO AirToxic®) for thermal desorption at 50 ml/min of air sampling flow rate using calibrated personal air sampling pumps (GilAir-3/5, Sensidyne). Originally, the pump flow rate was measured on the bench before each test; however, some minor variations (i.e., less than $\pm 5\%$) were observed due to the pressure changes when the pump is connected to the test ducts. To minimize the test uncertainties, the actual sampling flow rates during the testing were monitored alternately using a flow calibrator (Bios Definer 220) connected to its own data acquisition software (Bios Drycal). The air sampling duration was varied depending on the challenge VOC concentration to avoid overloading the sampling tubes. The sampling interval was evenly distributed for the given challenge concentration. The sampling tubes used in this study are stainless-steel tubes filled with Carbotrap B followed by Carbosieve adsorbent, which are formulated for capturing C3- C12 VOCs as in the EPA TO-17 method (EPA, 1999a). Prior to sampling, the tubes were conditioned for at least 30 minutes at 320 °C under 50 mL/min of helium (He) flow, and then they were sealed. After sampling, tubes were sealed at both ends with gas-tight caps made of brass containing PTFE ferrules, then wrapped in aluminum foils, and stored in LDPE bags at room temperature.

Two different analysis systems were used in this study. In the first system, the VOCs, collected on adsorbent tubes, were released by automatic thermal desorber (Perkin-Elmer TurboMatrix® 650 ATD) and introduced to GC/MS (Perkin-Elmer Clarus® 500) with a specialty capillary GC column (Perkin-Elmer Elite-VMS, 60m, 0.32 mm I.D., and 1.8 μ m of film thickness) for qualification/quantification analysis of VOCs. The applied thermal desorption methods are as

follows: initial dry purge at helium flow of 50 ml/min at room temperature for moisture removal followed by primary desorption of a sample tube at 240 °C for 4 minutes at 20 ml/min of He flow with inlet split of 60 ml/min. During the primary desorption, the trap (Perkin Elmer AirToxic® trap) was held at -20 °C, then increased to 300 °C at a rate of 40 °C/s for the secondary desorption of the trap. During secondary desorption outlet split of 48 ml/min was applied. The value and the transfer line temperatures were held at 225 °C and 220 °C, respectively. The GC oven temperature started at 40 °C for 5 min, increased at 5 °C/min to 110 °C, then increased at 20 °C/min to 200 °C and was held for 15 min. Helium (He) was the carrier gas and the GC column flow was 2.0 ml/min. The mass spectrometer scanned from 40 to 150 m/z with a scanning time of 0.25 min and an inter-scanning delay of 0.01 s, between retention time of 5.0 and 25.0 min. Five-point calibration has been applied for the challenge VOCs quantification analysis.

In the other system, VOCs sampled on adsorbent tubes were released by helium gas in an automatic thermal desorption unit (Perkin-Elmer TurboMatrix® 650 ATD) and then introduced to GC/MS (Agilent Technology, 7890B/5977B MSD). The sequence of thermal desorption method was as follows: initial dry purge at helium flow of 50 mL/min at room temperature for moisture removal followed by loading of internal standard; primary (tube) desorption at 300 °C for 10 minutes at 25 mL/min of helium flow with inlet split of 35 mL/min and outlet split of 40 mL/min. Next in secondary (trap) desorption (Perkin Elmer AirToxic® trap), the trap temperature was held at 27 °C, then increased to 300 °C at a rate of 40 °C/s for 5 min. During the secondary desorption, both value and the transfer line temperatures were held at 150 °C. By introducing the analytes to GC/MS, analytes were separated on HP-5MS UI GC-column, 30m, 0.250 mm I.D., and 0.25 µm of film thickness (Agilent J&W). The GC oven temperature started at 35 °C for 4 min, increased at 8 °C/min to 100 °C, then increased at 110 °C/min to 300°C and held for 5 min. Helium was used as carrier gas and GC was operated in split mode. The MS source temperature was kept at 230 °C (maximum 250 °C) and the MS quad temperature was held at 150 °C (maximum 200 °C). The MS scanned from 30 to 290 m/z. Five-point calibration has been applied for the challenge of VOCs for quantification analysis.

Ozone interference in VOC sampling was a concern, so we have tested two different commercial ozone scrubbers: one is manganese dioxide coated on stainless steel meshes and the other is 1.5 grams of granular potassium iodide (KI) ozone scrubber (Supelco) originally designed for carbonyl compound sampling using 2,4-dinitrophenylhydrazine (DNPH) cartridges. The problem we found is that the ozone scrubbers we tested not only remove ozone but also can reduce the collection efficiency by more than 50% on AirToxic adsorbent tubes. Due to the adverse effects of the ozone scrubber, we have not applied the ozone scrubber in VOC sampling. Measuring interference of ozone on VOC sampling in our testing methods is not simple, as it requires separating the homogeneous ozone reactions with VOC in the air inside the duct from the heterogeneous ozone reaction with VOC collected inside the adsorbent tube. Tests conducted under unfavorable homogeneous reaction conditions such as high flow rates and high challenge VOC concentrations, show very low VOC removal efficiency (i.e., less than 5%) for toluene despite of high ozone concentration (i.e., 1.1 ppm). This can demonstrate the ozone interference in VOC sampling through heterogeneous reactions of ozone and collected VOC in the tubes is inconsequential. This might be caused by the fact that the solvent tubes we used do not contain Tenax®, which is more prone to ozone interferences (Cao & Hewitt, 1994; Woolfenden, 1997).

4.2.3 Active sampling for aldehydes and ketones, and HPLC analysis method

Air sampling and analysis methods for aldehydes and ketones of this study were developed based on the EPA TO-11A method (EPA, 1999b). Samples were collected periodically from the upstream and downstream sampling ports on 2,4-dinitrophenylhydrazine (DNPH) cartridges (SUPELCO, LpDNPH S10L) to convert trapped carboxylic compounds to the hydrazone derivatives. For the measurement of by-product generation, at least 50 liters (i.e., in preliminary testing) but nominally 90 liters of air were sampled using air sampling pumps calibrated at about 1 L/min of sampling flow rate. When ketones like acetone and 2-butanone were used as challenge VOCs, the sampling volume was varied depending on the challenge concentration. Since some oxidation-based air cleaning technologies considered in this study can generate ozone, which can decompose the analytes collected in DNPH cartridges, the potassium iodide (KI) based ozone scrubber was placed before the DNPH cartridge in each sampling line and regularly changed according to the direction by the manufacturer.

The sampled cartridges were stored in the refrigerator until they were eluted with 4 ml of acetonitrile. The storage duration is generally less than one week. The eluted samples were then analyzed using HPLC with LC-18 column (SUPELCO, Supelcosil™ LC-18, 25 cm × 4.6 mm, 5 μm), auto-sampler and UV/Vis detector (Perkin-Elmer Flexar). The injection volume was 20 μL. The isocratic method using 72% acetonitrile and 28% of deionized water as mobile phase at a total of 1 ml/min of flow rate for 10 minutes was used. The HPLC was calibrated with six component carbonyl-DNPH mixture (formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, and crotonaldehyde) with each analytical concentration of 15 μg/mL and MEK-DNPH of 100 μg/mL. The calibration curve was performed by a series of calibration points covering the concentration range of interest for quantitative results with HPLC. A single-point calibration was periodically run as an unknown to check the integrity of the calibration.

4.3 General test procedures

For the four-duct testing, the general test procedures were as follows:

- 1) **Start-up:** First, the fans were turned on and a monitoring program using VEE pro software was started to monitor and record the data from all the transducers connected to the data acquisition system.
- 2) **Flow set and background monitoring:** The multi-gas analyzer and the ozone monitor were started to measure the background concentrations for a minimum of 30 min. Then the fan speed was set and the airflow rate of each duct was checked using an airflow meter (DIFF automatic, Observator instruments).
- 3) **Low concentration VOC injection start:** When the experimental conditions became stable, injection of the challenge VOC at a lower injection rate was started and the total hydrocarbon (THC) reading was monitored in the multi-gas analyzer to ensure the stability of the challenge VOC concentration.
- 4) **Activation of test air cleaning systems:** Ten minutes after the VOC injection started, test oxidation-based air cleaning systems were activated by switching on UV lamps and NTP. The UV output was monitored using a radiometer installed in each duct to gauge its stability.

- 5) **Air sampling in low concentration test:** Once the UV output became stable, which took about 5 minutes, air sampling was started. When ketones were considered as challenge gas (VOCs), only DNPH sampling was carried out. For the other challenge VOCs, both AirToxic and DNPH sampling were conducted. The details of air sampling methods are presented in the previous section. For challenge VOC sampling, two to three sets of air sampling were conducted at an even interval, depending on the challenge concentrations, and DNPH sampling for by-product measurements was conducted for one set of air sampling due to the requirements of long sampling duration. The low concentration tests were carried out for a minimum of 2 hours.
- 6) **Regeneration period and desorption sampling:** Then VOC injection was stopped for one hour to prepare for high concentration test, and this period provided an opportunity to regenerate PCOs for high concentration tests. When UV-PCO systems were using substrates with high adsorption capacities, air sampling was conducted to measure any generation of challenge VOC and other by-products desorbed from photocatalyst.
- 7) **High concentration VOC injection start:** The challenge VOC was injected for high concentration testing, which lasted for a minimum of 2 hours.
- 8) **Air sampling in high concentration test:** After waiting for about 15 minutes after the VOC injection for the high concentration test, air sampling was started in the same manner as for the low concentration test.
- 9) **Desorption sampling:** To measure the VOC concentration or other reaction intermediates, which were released from PCO, air sampling was conducted for 1 hour after the VOC injection was stopped.
- 10) **Switch-off of test air cleaning systems:** Test air cleaning systems were turned off and the multi-gas analyzer and the ozone monitor were continued to observe the returning to background levels.
- 11) **Finish-up:** Before turning off the fans, the airflow rates were checked once again by the flow meter for airflow assurance. For instruments with built-in data storage, the recorded data were transferred at the end of the experiments. All test systems and equipment were then turned off. The air samples were sealed and stored.

Most tests done with the 4-duct rig were conducted with two different challenge VOC concentrations, and the total test duration was about 7 hours. For some tests investigating the effect of challenge VOC concentrations, three different levels were tested in a day. To avoid potential overloading and/or deactivation issues in the UV-PCO test systems, tests were always conducted from the lowest concentration to higher ones.

The full-scale testing was conducted in a similar manner, except for the start-up and flow measurement processes. The fan was turned on and the flow was first set. Since the test rig uses an ASTM flow nozzle for flow rate measurements, the differential pressure was continuously measured and recorded by the data acquisition system. Hence, there was no need for separate flow measurements. Once the flow rate was set, the humidifier was turned on if necessary. Because the test conditions could change a lot after starting up the humidifier, the test conditions

were closely monitored until they became stable. Then the VOC injection was started. The details of the recommended full-scale test methods are presented in Chapter 6.

4.4 Data analysis methods

The performances of oxidation-based air cleaning technologies in this study were primarily evaluated in terms of VOC removal efficiency and by-product generation rates. The challenge VOC removal efficiency (E) is calculated as follows:

$$E(\%) = \frac{C_{up} - C_{down}}{C_{up}} \times 100 \quad (4-1)$$

where C_{up} and C_{down} are challenge VOC concentrations at upstream and downstream of test air cleaner, respectively.

Clean Air Delivery Rate (CADR) was originally developed for rating room air cleaner performance by the Association of Home Appliance Manufacturers (AHAM, 2015). Due to its wide use, reports evaluating air cleaning systems have adopted the CADR concept (Siegel, 2016; Zhang et al.). For single-pass dynamic testing like this study, CADR can be determined as:

$$CADR = \eta \cdot Q \quad (4-2)$$

where η is the removal efficiency expressed in fractions; and Q is the airflow rate through the test air cleaner [m^3/hr].

The generation rate (G_i) of by-product compound i was calculated as follows:

$$G_i = (C_{i,down} - C_{i,up}) \cdot Q \quad (4-3)$$

where $C_{i,up}$ and $C_{i,down}$ are upstream and downstream concentrations of by-product i [mg/m^3].

Ozone generation was simply depicted as the concentration difference between the downstream and upstream of the air cleaner, because it is then easier to compare with the acceptable ozone levels.

Previous studies on the performance of oxidation-based air cleaning technologies have applied mineralization ratio (M) to measure the level of complete oxidation, which is defined as follows:

$$M(\%) = \frac{[CO_2] + [CO]}{N_C([C_{up}] - [C_{down}])} \times 100 \quad (4-4)$$

where $[CO_2]$ and $[CO]$ are the molar concentrations of CO_2 and CO generated by the tested oxidation-based air cleaning device, respectively; $[C_{up}]$ and $[C_{down}]$ are the molar concentrations of challenge VOC at upstream and downstream of the test air cleaner, respectively; and N_C is the carbon number of the challenge VOC. For example, N_C of toluene is 7.

The mineralization ratio, however, could not be included in the data analysis of this study for the following reasons:

- 1) Due to high airflow rates applied in this study, filtered laboratory air was used as carrier air, unlike bench-top-scale tests done in literature, where pure air or nitrogen oxygen mixture was used as carrier air. Scrubbing CO₂ and CO in low concentrations and in room temperature is technologically challenging, especially in the given dimensions of the test rigs. Therefore, CO₂ and CO levels in the carrier air were not controlled. In addition, the presence and variability of occupancy in the laboratory affect indoor CO₂ levels greatly, and
- 2) As the challenge VOC concentrations were low compared to general indoor CO₂ and CO concentrations, the amounts of CO₂ and CO generated by the test air cleaning system were generally within the error ranges of the measurement accuracy of the multi-gas monitor (i.e., 1% of measured value). For example, when CO₂ concentration is 600 ppm, the error becomes ± 6 ppm. If toluene is the challenge VOC and the challenge concentration is 1 ppm, upon complete oxidation, 7 ppm of CO₂ would be generated. However, the tested air cleaning devices normally have less than 50% of toluene removal efficiency; therefore, even for 100% mineralization, the CO₂ generation becomes within the error range of CO₂ monitor.

4.5 Test materials

All chemicals used in this study were either GC or HPLC grade purchased from Fisher Scientific or Sigma Aldrich. Table 4-2 presents the list of VOCs initially selected for challenge compounds for this project and the basis for the selection. Through the development and calibration of GC/MS analysis methods and preliminary testing of some oxidation-based air cleaning systems, it was found that the ATD-GC/MS analysis of ethanol and iso-propanol cannot provide the reliability and the sensitivity required in this study. The unsuitability of iso-propanol in thermal desorption has been reported (Zhu, Yao, Li, & Chan, 2014). The coefficients of variation of these compounds were greater than 12%. Since some oxidation-based air cleaning units have low efficiency (i.e., less than 10%), the analysis method requires higher precision. IRSST analysis methods for methanol and those two compounds (Drolet & Beauchamp, 2013) were considered; however, they have too high minimum reporting values for this study as IRSST methods are primarily designed for air sampling in workplaces. For the low challenge concentrations considered in this study, the IRSST method requires more than 30 hours of sampling duration. Due to these limitations, the aforementioned compounds were excluded and iso-butanol (CAS number: 78-83-1), which is one of the challenge VOCs in ASHRAE Standard 145.2-2016, was included instead as a representative of the alcohol group. Iso-Butanol has 74.121 g/mol of molar mass and 10.02 eV of ionization energy.

The air cleaning systems or parts used in this study are commercially available ones that were either purchased or supplied by different manufacturers. Due to the proprietary nature, the manufacturers do not reveal any detailed information on the products, and the confidentiality agreement with the manufacturers prohibits exposing the product names.

Only one photocatalyst (PCO-F) was prepared in our laboratory for comparison with commercial PCOs. Fibrous activated carbon felt was dipped into a 5% by weight solution of anatase-phase titanium dioxide (TiO₂) nano-powders with particle size less than 25 nm (Sigma-Aldrich Co.) in deionized water, then air dried in the ambient indoor conditions.

Table 4-2. Initial selection of challenge VOCs for testing


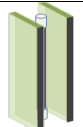



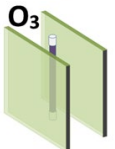
VOC	Family	CAS number	Molar Mass [g/mol]	Ionization Energy [eV]	Quebec ROHS Schedule I TWAEV* [ppm]	IRSST Report R-712 (2011)	U.S. EPA BASE Study Detection Frequency [%]	ASHRAE Std. 145.2-2016
Toluene	Aromatic	108-88-3	92.04	8.83	50	√	100	√
o-Xylene	Aromatic	95-47-6	106.17	8.56	100	√	100	√
Styrene	Aromatic	100-42-5	104.15	8.46	50	√	99	-
Acetone	Ketone	67-64-1	58.08	9.70	500	√	100	√
Methyl Ethyl Ketone (MEK)	Ketone	78-93-3	72.11	9.52	50	√	99	√
Methanol	Alcohol	67-56-1	32.04	10.84	200	√	-	-
Ethanol	Alcohol	64-17-5	46.07	10.48	1000	-	100	√
2-Propanol	Alcohol	67-63-0	60.10	10.17	400	-	100	√
n-Hexane	Alkane	110-54-3	86.18	10.13	50	√	98	√
n-Octane	Alkane	111-65-9	114.23	9.80	300	-	99	-

* TWAEV: Time weighted average exposure value

The commercial ozone generation systems utilize corona discharge or vacuum UV (VUV) lamp technologies. Corona discharge units have higher ozone outputs, so this technology is generally applied for in-room emergency treatment purposes. Since in-duct ozone generators require to limit ozone outputs not to endanger the occupants, VUV lamps are generally utilized. Therefore, VUV lamps (Atlantic Ultraviolet Co., Model G18T5VH-U) were tested as ozonation systems in this study. O3-A and O3-B denote one VUV lamp and two lamps, respectively. In practice, an ozone monitor is installed in occupied space to modulate ozone generation amount not to exceed the ozone concentration limit, which is normally 50 ppb. For the given test setup this modulation has not been adopted to measure the removal efficiency under constant ozone concentrations.

Table 4-3 summarizes the oxidation-based air cleaning systems tested in 4-duct test rig. Due to the limitation of test duct size, most in-duct commercial air cleaners do not fit in the test section. For PCO systems, five commercial photocatalysts were tested under the comparable UV light conditions. Since UV-PCO technology is adopted more in the market with diverse configurations and light conditions, more UV-PCO systems were tested in this study. While PCO-A to PCO-F were installed to cover the whole cross-sectional area of the test duct perpendicular to the airflow direction, PCO-G and PCO-H are stick-type PCO that has one straight UV lamp in the center and photocatalysts are mounted in limited areas near the lamp. When photocatalyst "A" is applied with UVC lamps, it is denoted as "PCO-A", and "PCO-A1" is for VUV lamps. Photocatalyst "B" was also tested with the UV lamps supplied by the manufacturer and named as "PCO-B2" for UVC lamp and "PCO-B3" for VUV lamp. The UV lamps supplied by manufacturers as a part of their UV-PCO systems (i.e., PCO-G, PCO-H, PCO-B2 and PCO-B3), there was little information on the lamps. Due to the size limit and low flow ranges applied in the 4-duct test rig, the regular in-duct NTP system could not be tested, so small NTP units normally used in room air cleaners were tested instead.

Table 4-3. Summary of oxidation-based air cleaning systems tested in 4-duct test setup

Technology Group	Notation	Air Cleaning System Information		
		Light source	PCO Substrate	Configuration
Photo-catalytic oxidation (PCO)	PCO-A	Two U-shaped low pressure mercury UVC lamps (Atlantic Ultraviolet Co., Model G18T5L-U)	Fiber glass pad	
	PCO-B		Expanded aluminum mesh panel	
	PCO-C		Expanded aluminum mesh panel	
	PCO-D		Nickel foam	
	PCO-E		Aluminum honeycomb	
	PCO-F		Activated carbon fiber pad	
	PCO-G	One straight UV lamp (no information)	Metal honeycomb	
	PCO-H	One straight UVC lamp (no information)	Activated carbon monolith	
	PCO-A1	Two U-shaped low pressure mercury VUV lamps (Atlantic Ultraviolet Co., Model G18T5VH-U)	Fiber glass pad	
	PCO-B1		Expanded aluminum mesh panel	
	PCO-C1		Expanded aluminum mesh panel	
PCO-B2	One straight low pressure mercury UVC lamp (no information)	Expanded aluminum mesh panel		
PCO-B3	One straight low pressure mercury VUV lamp (no information)	Expanded aluminum mesh panel		
Non-thermal plasma (NTP)	NPT-A	3 small barrier discharge NTP AC units		Perpendicular to airflow direction
	NPT-B	3 small barrier discharge NTP DC units		
	NPT-C	2 medium size barrier discharge type NTP units		
Ozonation	O3-A	One U-shaped low pressure mercury VUV lamp		
	O3-B	Two U-shaped low pressure mercury VUV lamps		

For ozonation, low-pressure mercury VUV lamps (Atlantic Ultraviolet Co., Model G18T5VH-U) were applied. Some of PCOs were tested for ozone removal performances, and a different number of PCO layers were tested as shown in Figure 4-3: for one-layer PCO, two lamps were installed upstream of PCO; for two-layer PCO, PCO were installed both upstream and

downstream at 5 cm distance from two UV lamps; and for three-layer PCO, four UV lamps were installed in two rows and PCO were installed upstream, between the rows and downstream of UV lamps.

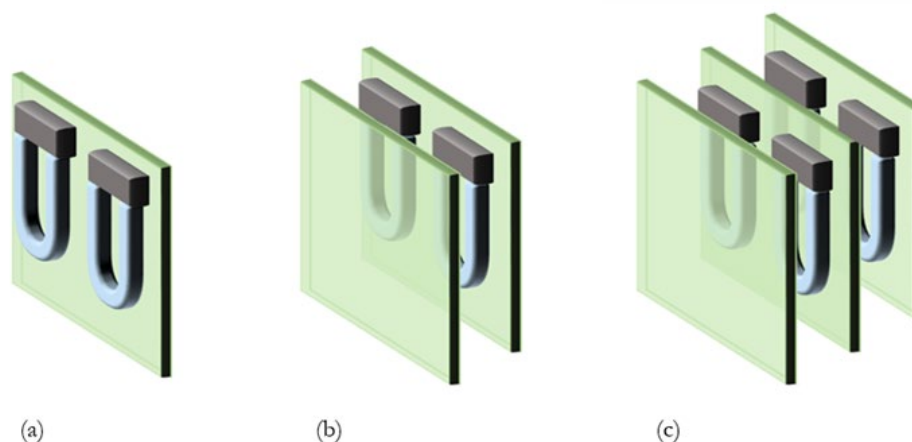


Figure 4-3. UV-PCO setups in different layers applied in ozone removal testing: (a) 1-layer PCO, (b) 2-layer PCO and (c) 3-layer PCO.

Table 4-4 summarizes the air cleaning units tested in the full-scale test rig. The tested systems include 7 PCO systems, 3 systems using PCO combined with adsorption-based scrubbers, 2 ozone generators, and 2 non-thermal plasma units. Since there are few size limitations in full-scale test duct, the tested units were mostly regular commercial units. However, when the nominal length of UV lamps in commercial UV-PCO units is 0.9 m, which does not fit even for full-scale test rig, the manufacturers have provided equivalent UV lamps that can fit into the full-scale test rig. Five different types of commercial catalysts (i.e., type 1, 2, 3, 4, and “A”) were tested, and type 4 was tested in 1-layer (denoted as PCO-4a) and 2-layer configurations (denoted as PCO-4) following the manufacturer’s applications. Photocatalyst type “A”, which was tested with the 4-duct setup as shown in Table 4-3, was applied again with the full-scale setup in two light conditions: with 4 UVC lamps (PCO-Af) or with 4 VUV lamps (PCO-Af1). PCO-1 to PCO-3 were supplied by the same manufacturer, so the light conditions were the same in 2 UVC lamps and 2 VUV lamps. PCO-4 and PCO-4a use only UVC lamps. Two PCO manufacturers also supplied adsorption-based by-product scrubbers, which are used in conjunction with their PCO units. PCO-2 and PCO-4 were tested with the supplied scrubber installed downstream of PCO section.

Table 4-4. Summary of oxidation-based air cleaning systems tested in full-scale setup

Technology Group	Notation	Air Cleaning System Information		
		Light source	PCO Substrate	Configuration
Photo-catalytic oxidation (PCO)	PCO-Af	4 UVC lamps	Fiber glass pad	2 layers of PCO and the lamps located in the middle
	PCO-Af1	4 VUV lamps	Fiber glass pad	
	PCO-1	2 UVC & 2 VUV lamps	Expanded aluminum mesh panels	
	PCO-2	2 UVC & 2 VUV lamps	Expanded aluminum mesh panels	
	PCO-3	2 UVC & 2 VUV lamps	Expanded aluminum mesh panels	
	PCO-4	4 UVC lamps	Metal honeycomb	
	PCO-4a	4 UVC lamps	Metal honeycomb	1 layer of PCO installed downstream of lamps
Photo-catalytic oxidation (PCO) with by-product scrubbers	PCO-2+Sc	2 UVC & 2 VUV lamps	Expanded aluminum mesh panels	Granular activated carbons in V-shape modules installed downstream of PCO-2
	PCO-4+Sc1	4 UVC lamps	Metal honeycomb	Combination panel filter type 1 with activated carbon and permanganate media, installed downstream of PCO-4
	PCO-4+Sc2	4 UVC lamps	Metal honeycomb	Combination panel filter type 2 with activated carbon and permanganate media, installed downstream of PCO-4
Non-thermal plasma (NTP)	NPT-1	Barrier discharge plasma		Perpendicular to airflow direction
	NPT-2	Needle point plasma		
Ozonation	O3-1	2 VUV & 2 UVC lamps		
	O3-2	4 VUV lamps		

5. FOUR-DUCT SYSTEM AND PARAMETRIC STUDY RESULTS

The methods, developed for the 4-duct system as described in Chapter 3, were evaluated for their reliability through side-by-side testing and for their repeatability. Then different oxidation-based air cleaning products were tested to understand the VOC removal performance and the ranges of by-product generation rates. Based on these results, a few systems were selected for further investigation on the parameters affecting the air cleaner performance. This chapter presents the results of the aforementioned test systems in terms of removal efficiency and by-product generation rates, and any findings to be considered for the development of a proper test protocol are discussed.

5.1 Examination of test methods

To examine the reliability of the developed methods for the 4-duct system, PCO-A in the same configuration was tested side-by-side in Duct #3 and Duct #4 of the 4-duct rig. It was challenged with 100 ppb of MEK at 180 ± 4 m³/hr of air flow rate (or 0.54 ± 0.01 m/s of air velocity) for each duct under 21.4 ± 0.2 °C and $49 \pm 2\%$ RH. Figure 5-1 shows the results of the MEK removal efficiency and the by-product generation rates. When MEK is the challenge VOC, formaldehyde, acetaldehyde, and acetone are the by-products identified in this study. The absolute differences between the two test results are minor - 0.85% in efficiency; 0.15 mg/hr in formaldehyde generation rate; 0.36 mg/hr for acetaldehyde; and 0.02 mg/hr for acetone.

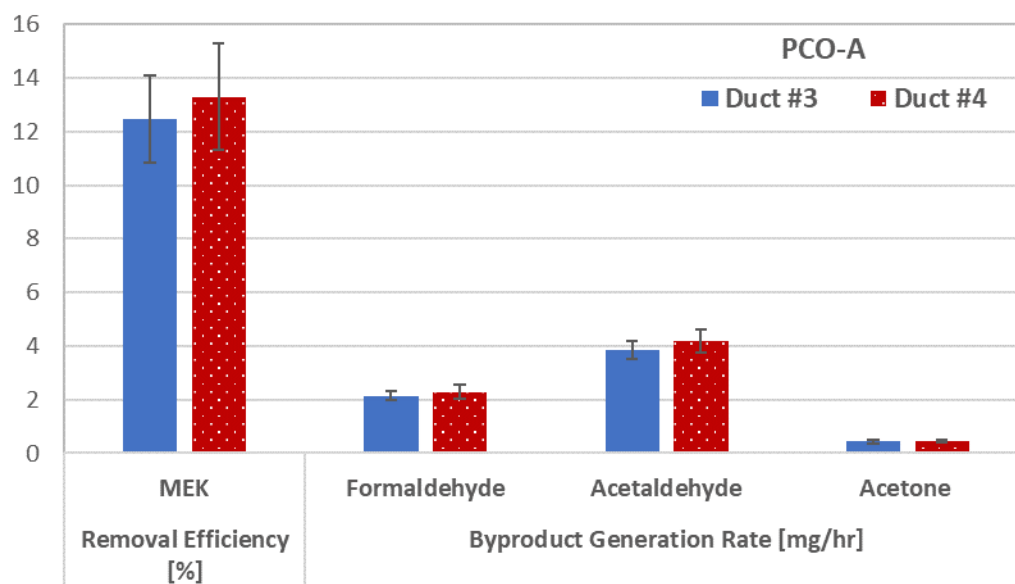


Figure 5-1. Evaluation of test method: Side-by-side results of PCO-A.

The reliability of the developed methods was further examined by conducting a repeat test. These tests were conducted 9 months apart on February 4, 2015 and November 17, 2015. The persons who conducted the tests were not identical – half of the team members were changed. PCO-A was tested in Duct #4 of the 4-duct rig in both testings. The test conditions were 100 ppb of

acetone as a challenge gas (97 ± 2 ppb) at 173 ± 4 m³/hr of air flow rate (or 0.52 ± 0.01 m/s) for each duct under $17 \pm 1\%$ RH. There were slight differences in temperature: 23.6 ± 0.2 °C and 20 ± 0.2 °C in February and November tests, respectively. Figure 5-2 presents the repeatability results in terms of acetone removal efficiency and the generation rates of two identified by-products, formaldehyde and acetaldehyde. The absolute differences are 0.25% in efficiency; and 0.57 mg/hr and 0.97 mg/hr of generation rate for formaldehyde and acetaldehyde, respectively. Due to the low activity of PCO-A in the removal of acetone, the difference can be perceived to be large; however, when the difference in the by-product generation rates is translated into a by-product concentration, the difference is only 2.4 ppbv for formaldehyde and 3.3 ppbv for acetaldehyde.

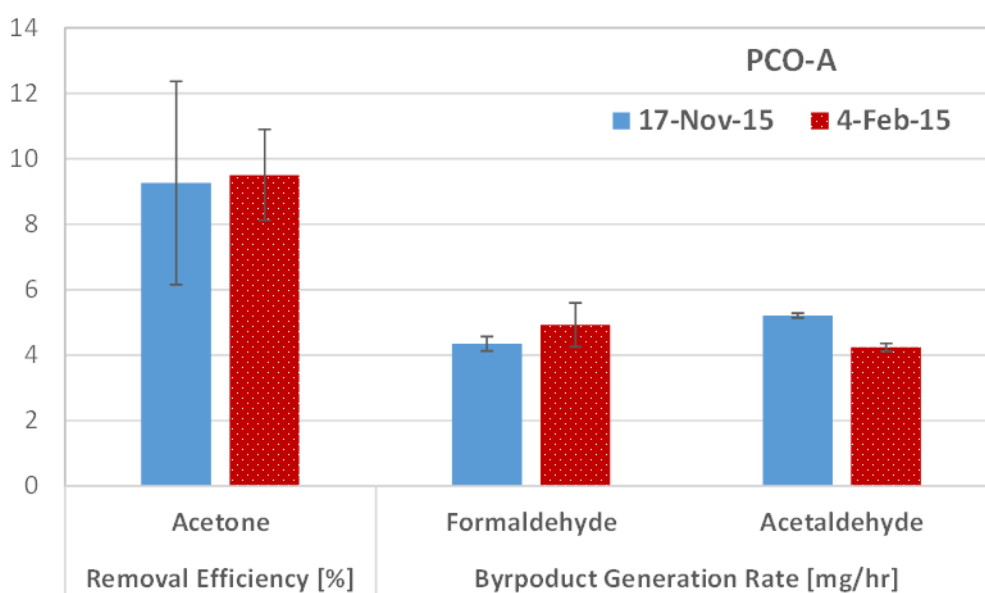


Figure 5-2. Repeatability test for PCO-A.

5.2 Performance of different oxidation-based air cleaning systems

Farhanian and Haghghat (2014) have tested three different UV-PCO systems for the removal of 1-butanol, hexane, octane, acetone, MEK, toluene, and p-xylene measured individually through single challenge gas testing, and the VOC that give the median removal efficiency are MEK for two PCO and acetone for the other PCO. Hodgson, Sullivan, and Fisk (2005) developed a pilot UV-PCO system and tested for VOC mixtures in low ppb ranges representing for office VOC, cleaning products, and building product mixtures. Fifty-two efficiency data for 45 different VOC were reported in the range of 85% and 19%, and MEK removal efficiency (i.e., 55%) was in the mid-range and near the average efficiency (i.e., 52%). Based on this, MEK was selected for the comparison of different oxidation-based air cleaning systems evaluated in the 4-duct test rig. This is also used for screening purposes for further investigation on the parameters affecting the air cleaner performance.

Eight different photocatalysts were employed in total of 12 configurations with the main changes in the light source (i.e., germicidal low-pressure mercury UVC lamps or ozone generating low-pressure mercury vacuum UV (VUV) lamps) as described in Chapter 3. All photocatalysts except PCO-F are commercially available and/or supplied by manufacturers. PCO-F was prepared in-house laboratory using activated carbon fiber as a substrate to increase the adsorption. The details of the preparation are given in Chapter 3. Two different types of small NTP units, normally used in room air cleaners, were tested due to the size limitation of the 4-duct system. For ozonation, VUV lamps (Atlantic Ultraviolet Co., Model G18T5VH-U) were applied. O3-A and O3-B denote for one VUV lamp and two lamps, respectively, and the resulting average ozone levels measured at the downstream sampling ports were 435 ppb and 1310 ppb, respectively.

Sixteen different air cleaning systems were tested for 100 ppb of MEK (95 ± 3 ppb) at 21 ± 0.2 °C and 26 ± 1 % RH. PCO-B and PCO-C were tested at 37 ± 0.5 % RH. Eight systems were tested at 135 ± 7 m³/hr of air flow rate (or 0.40 ± 0.02 m/s of air velocity) and twelve systems were tested at 176 ± 8 m³/hr (or 0.53 ± 0.02 m/s). PCO-A, PCO-D, PCO-E, and NTP-A were tested in both flow conditions.

Figure 5-3 shows the average single-pass MEK removal efficiency of the tested oxidation-based air cleaning systems. Removal efficiency varies significantly from one system to another, between 0 and 37%. PCO systems show a clear disparity. While PCO-F, PCO-A1, and PCO-C1 have greater than 20% removal efficiency, PCO-B, PCO-D, PCO-E, PCO-G, and PCO-H have less than 5% of efficiency. In general, PCO systems with VUV lamps (i.e., PCO-A1, PCO-B1, PCO-B3, PCO-C1) tend to have higher efficiency as the presence of ozone can enhance the MEK oxidation. PCO-F, which is the only non-commercial photocatalyst, has the highest efficiency at 34%; however, it is because of the higher adsorption capacity of activated carbon fiber used as the substrate. As the large standard deviation marked in Figure 5-3 indicates, the removal efficiency of PCO-F was decreasing with time – 61% of efficiency measured in the 1st hour was decreased to 20% after 5 hours of testing. This indicates that adsorption is the dominant removal mechanism in PCO-F. The stick-type PCO units (PCO-G and PCO-H) have low efficiency due to a considerable bypass of the air; therefore, PCO units adopting stick or rod type design were excluded in the further investigation. While PCO-G showed zero efficiency, PCO-H has 4.7% of efficiency. PCO-G uses metal honeycomb as the substrate, but PCO-H uses activated carbon monoliths.

NTP units have less than 5% of removal efficiency, which is much lower than the efficiency reported in the literature, as presented in Chapter 2. NTP intrinsically generates ozone as a by-product. Unlike pilot NTP units studied in the literature that show high ozone output (i.e., 10's or 100's ppm), ozone generation by the tested commercial units was less than 70 ppbv probably to comply with the regulation and guidelines regarding ozone generating air cleaners (Cal. Code Regs. tit. 17, § 94800-94810 (2020); EPA, 2018b). The reduced plasma output in commercial units may have resulted in the reduced performances.

Ozonation tested using VUV lamps shows high removal efficiency: 21% for O3-A and 37% for O3-B. The ozone emission rates are 123 mg/hr and 467 mg/hr for O3-A and O3-B, respectively. Similar ozone emission rates were reported for UV-based ozone generators (Morrison, Shaugnessy, & Siegel, 2014). It should be noted that the ozone levels generated in this testing may not represent the actual applications of ozone generators. Due to the high toxicity of ozone, in-duct ozone generators are generally connected with ozone sensors installed in the occupied

zones. The ozone generator output is controlled or turned off whenever the ozone level in the occupied zones exceeds the set point, which is normally 50 ppb or less. The test setup used in this study cannot apply this safety feature, so ozone generators were tested under a full ozone output. Therefore, the removal efficiency measured in this study may be overestimated considerably compared to actual applications.

Figure 5-4 shows the calculated Clean Air Delivery Rates (CADR) using the average efficiency of the tested air cleaning units for MEK removal. The CADR were 68 m³/hr or less. Hodgson et al. (2005) reported between 89 and 366 m³/hr of CADR for MEK for a pilot UV-PCO system. In their study, the challenge MEK concentrations as a part of VOC mixture were between 0.95 ppb and 9.7 ppb. The removal efficiency generally decreases as the challenge concentration increases, which will be covered more in detail in the following section; however, the concept of CADR does not consider this. Therefore, CADR concept can penalize testing under high challenge concentration, which can be a limitation as an air cleaner rating value.

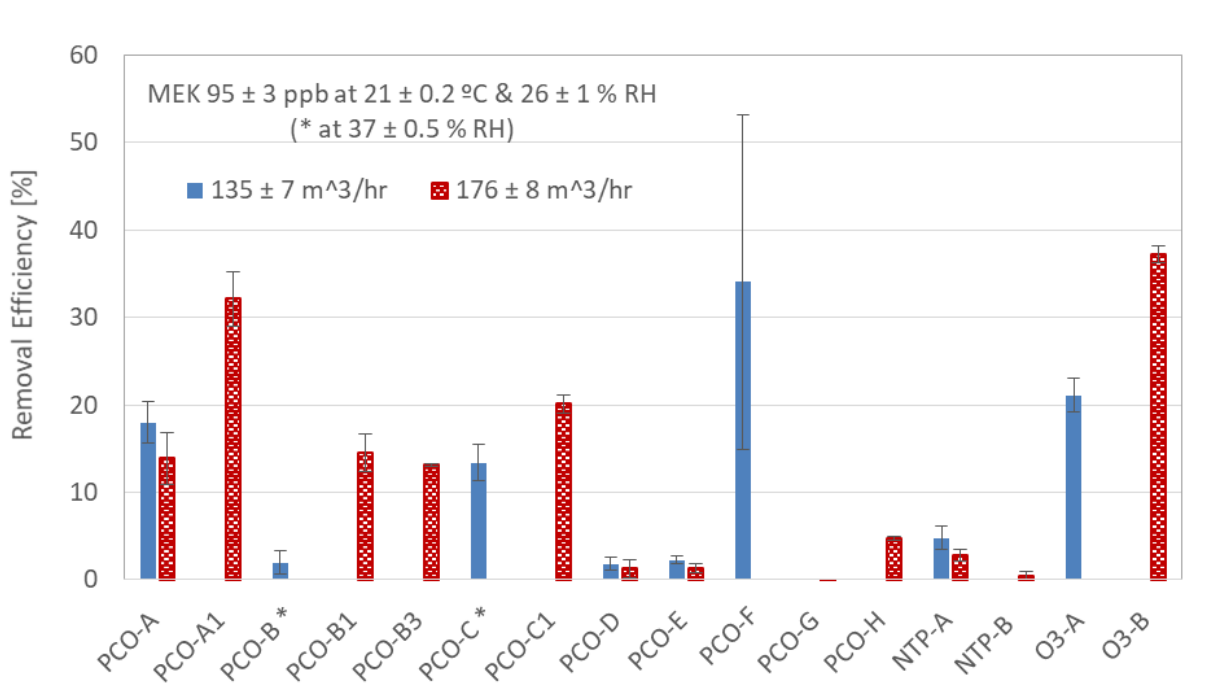


Figure 5-3. MEK removal efficiency of 16 tested oxidation-based air cleaning systems.

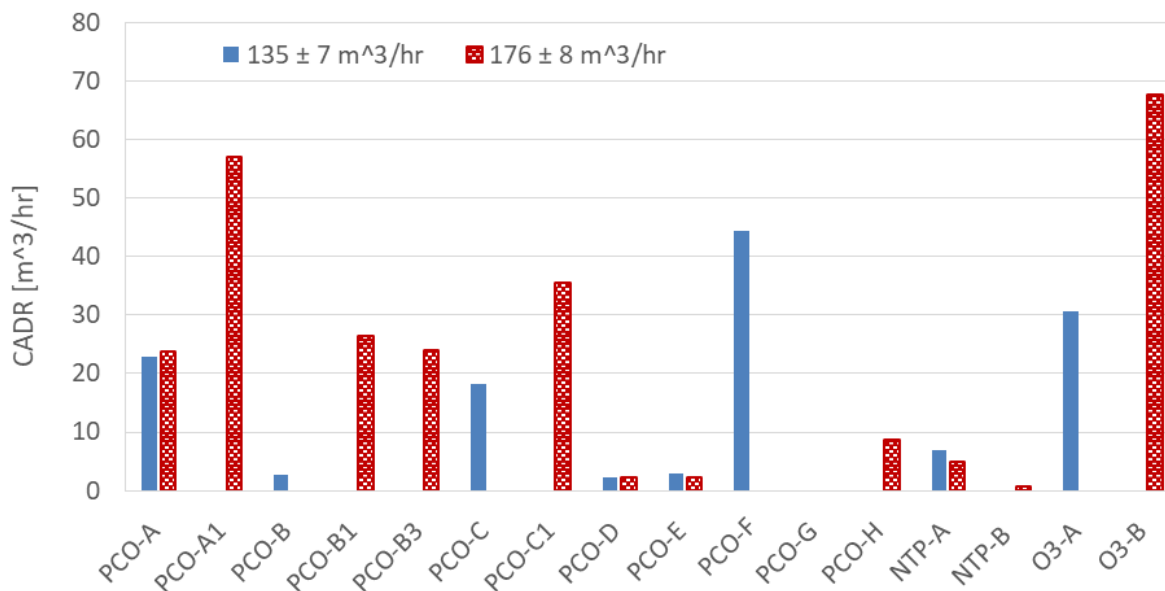


Figure 5-4. CADR of 16 tested oxidation-based air cleaning systems.

Table 5-1 summarizes by-product generation from the 16 tested air cleaning systems for MEK removal. Ozone generation is reported as the concentration difference between downstream and upstream ozone levels. Three identified by-products – formaldehyde, acetaldehyde, and acetone, are reported in terms of mass generation rate in mg/hr. The ozone emitted by PCO units using VUV lamps was in the range of 340 ppb and 1282 ppb. Since ozone is reactive, PCO with UVC lamps can remove ozone without any ozone generation, so the downstream ozone levels are lower than the upstream concentration. Mild ozone generation was measured for the tested commercial NTP units. The air cleaning systems with low removal efficiency are not able to decompose MEK, generating less by-products accordingly. Photocatalyst type “A” tends to generate more organic by-products. PCO-A1 generates the most formaldehyde, acetaldehyde, and acetone. PCO-A has similar removal efficiency as PCO-B1, PCO-B3 and PCO-C; however, its generation rates for formaldehyde and acetaldehyde were higher. In spite of the higher removal efficiencies efficiency of ozone generators, the organic by-product generation rates tend to be lower.

Table 5-1. By-product generation of 16 different oxidation-based air cleaning systems tested for MEK removal

	Flow rate [m ³ /hr]	Efficiency	STDEV	Ozone		Formaldehyde		Acetaldehyde		Acetone	
				Cdn-Cup [ppb]	STDEV	Generation rate [mg/hr]	STDEV	Generation rate [mg/hr]	STDEV	Generation rate [mg/hr]	STDEV
PCO-A	127	17.99	2.40	-13.61	1.88	2.78	0.11	3.69	0.21	0.36	0.10
PCO-A	172	13.87	2.91	-6.03	1.12	2.85	1.01	3.28	0.66	0.36	0.03
PCO-A1	178	32.11	3.12	602.11	15.49	4.60	0.44	6.43	0.57	1.78	0.15
PCO-B*	135	1.99	1.36	-1.85	1.11	0.33	0.05	0.31	0.02	0.14	0.03
PCO-B1	182	14.54	2.15	1104.37	47.42	0.46	0.20	2.19	0.17	1.27	0.12
PCO-B3	183	13.12	0.10	340.35	32.27	0.52	0.15	0.52	0.15	1.36	0.25
PCO-C*	136	13.40	2.04	-2.49	2.13	0.50	0.21	0.96	0.10	0.08	0.06
PCO-C1	177	20.09	1.08	1282.09	46.53	0.70	0.29	2.45	0.21	1.20	0.16
PCO-D	129	1.82	0.76	-1.45	1.41	0.13	0.04	0.08	0.01	-0.04	0.11
PCO-D	172	1.28	1.09	-0.76	0.98	0.05	0.04	0.06	0.01	0.00	0.02
PCO-E	130	2.24	0.47	-1.53	1.42	0.32	0.01	0.49	0.05	-0.05	0.19
PCO-E	171	1.28	0.53	-0.98	1.00	0.35	0.23	0.39	0.12	0.03	0.02
PCO-F	130	34.02	19.06	-23.31	0.94	1.61	0.15	2.98	0.31	0.17	0.51
PCO-G	186	-1.66	1.39	0.00	1.88	0.05	0.03	0.02	0.01	0.03	0.01
PCO-H	183	4.71	0.22	-0.45	1.96	0.20	0.06	0.14	0.02	-0.01	0.03
NTP-A	145	4.81	1.30	65.25	8.47	-0.06	0.02	0.15	0.03	0.12	0.01
NTP-A	175	2.82	0.70	57.25	6.42	-0.09	0.00	0.05	0.02	0.05	0.02
NTP-B	157	0.51	0.40	21.85	5.91	-0.06	0.01	0.03	0.01	0.03	0.08
O3-A	145	21.11	1.94	433.49	47.50	0.41	0.08	1.46	0.11	0.36	0.09
O3-B	182	37.25	0.97	1310.32	24.32	0.75	0.22	1.60	0.09	0.31	0.11

Cdn-Cup: Difference between downstream and upstream concentrations

STDEV: Standard deviation

5.2.1 PCO performances under UVC irradiation

Since the light source can affect the PCO performances, the photocatalyst type from "A" to "F" were tested further for acetone removal using the same light source (i.e., two U-shaped UVC lamps) to compare the activity of the photocatalyst itself. Only PCO-B2 was tested under lower light intensity using a straight UVC lamp. Tests were conducted for 97 ± 1 ppb of acetone at 176 ± 3 m³/hr of air flow rate (or 0.53 ± 0.01 m/s of air velocity) for each duct under 22.3 ± 0.2 °C and $17 \pm 1\%$ RH.

Figure 5-5 presents the average acetone removal efficiency of 7 different PCO units. The acetone removal efficiency is low, being less than 10%. Acetone is harder to oxidize than MEK - the lifetime of acetone due to the reaction with hydroxyl radicals in the atmosphere is estimated to be 817 hr, while that of MEK is 114 hr. The photocatalyst activity is highest in PCO-A followed by PCO-F > PCO-C > PCO-E > PCO-D > PCO-B. In MEK removal (Figure 5-3), PCO-F showed better performance than PCO-A due to the higher adsorption capacity given by activated carbon fiber substrate. In physical adsorption, which is the main mechanism of activated carbon media, acetone has generally a weaker van der Waal's force than MEK. This may result in a considerable reduction in the removal efficiency of acetone compared to MEK. According to the energy dispersive spectroscopy (EDS) results reported in Chapter 3, TiO₂ content in the coated area of the tested photocatalysts is the greatest in PCO-C followed by PCO-E > PCO-A > PCO-F > PCO-B > PCO-D. Due to the differences in substrates, EDS results in themselves cannot directly indicate the PCO performance. For example, PCO-E has high TiO₂ content, but its performance is poor. Also, PCO-A and PCO-F use glass fiber media and activated carbon fibers as the substrate, respectively. In contrast, the other PCO units use metallic media with limited surface area. Therefore, in spite of the fact that PCO-A and PCO-F have medium TiO₂ contents, they showed better performances. In addition, XRD results presented in Chapter 3 show that the TiO₂ content of PCO-A and PCO-F is 100% and 80% anatase-phase, respectively. Anatase-phase TiO₂ generally shows higher PCO performances. PCO-B and PCO-C, provided by the same manufacturer, use the same expanded aluminum mesh substrate. TiO₂ content of PCO-C is almost twice of PCO-B. This may explain the higher performance of PCO-C measured in both MEK and acetone tests.

The by-products generated by the tested PCO systems are formaldehyde and acetaldehyde. Figure 5-6 presents the by-product generation rates as a function of acetone removal efficiency for 7 different PCOs under UVC irradiation. It shows linear trends that the generation rates of both formaldehyde and acetaldehyde generally increase with increasing removal efficiency. The outlier points that give lower by-product generation rates are of PCO-C. This would be a desirable feature as harmful by-product generation is one of the main concerns for oxidation-based air cleaning technologies.

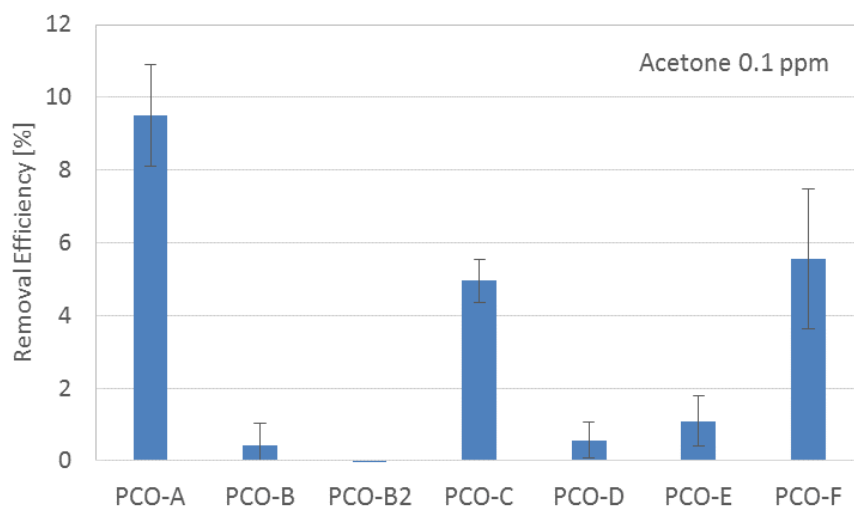


Figure 5-5. Acetone removal efficiency of 7 different PCO units with UVC lamps.

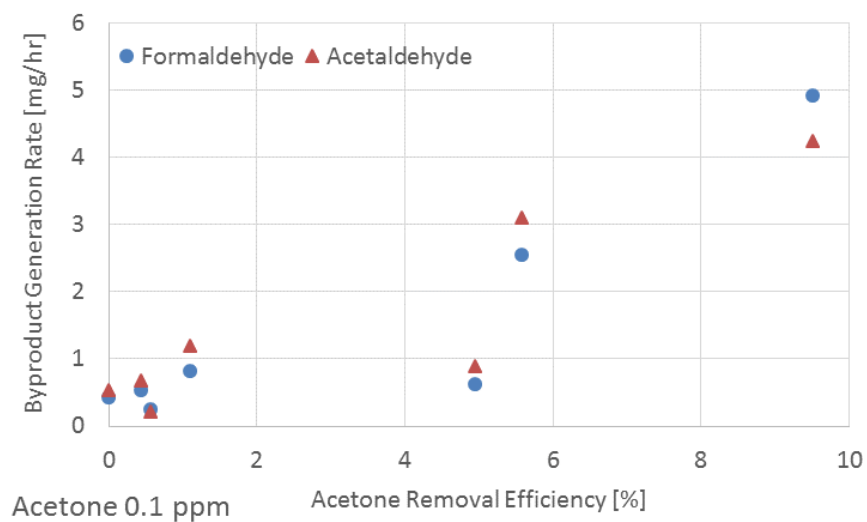


Figure 5-6. By-product generation rates of 7 different PCO units with UVC lamps.

5.2.2 PCO Performances: UVC lamps versus VUV lamps

The removal efficiency is higher when ozone-generating vacuum UV lamps are used because of the additional oxidation of ozone generated from VUV lamps. Based on the above PCO activity test results, three photocatalysts were selected to investigate the effects of the light source: photocatalyst type “A” for the best removal efficiency, “B” for the worst efficiency; and “C” for lower by-product generation compared to its efficiency. PCO-A, PCO-B, PCO-B2, and PCO-C use UVC lamps, and PCO-A1, PCO-B1, PCO-B3, and PCO-C1 use VUV lamps. The tests were conducted for acetone at two challenge concentrations (i.e., 96 ± 2 ppb and 955 ± 20 ppb) at 177 ± 3 m³/hr of air flow rate (or 0.53 ± 0.01 m/s of air velocity), 21 ± 0.2 °C and 18 ± 1 % RH.

Figure 5-7 presents the effects of the light source on the acetone removal efficiency of the tested PCO units. The removal efficiency of the PCO using VUV lamps is higher than the one using UVC lamps. The rate of increase in removal efficiency tends to be higher at higher acetone challenge concentrations. Generally, the removal efficiency of a PCO is higher at lower challenge concentration (more evidence can be found in the following section). However, the opposite trends were observed in PCO-B, B1, B3, and C1. Acetone is a common oxidation by-product of various VOCs. Due to the high flow requirement of the test setup used in this study, laboratory room air is filtered and supplied as carrier air for the testing, and the complete removal of VOC in the air stream is impractical. Other VOCs present in trace levels can be decomposed by PCO and generate acetone as a by-product. This can affect the acetone removal efficiency measurement, especially when the acetone challenge concentration is low like in the case shown in Fig. 5-7 and PCO performances are higher like in the cases with VUV lamps. Therefore, testing with 0.1 ppm of acetone for PCO with VUV lamps can underestimate the removal efficiency. It should be noted that the repeatability test presented in section 4-1 was conducted with PCO with UVC lamps; hence, the above-mentioned effect was believed to be negligible so good repeatability results were obtained.

This suggests that selecting a common oxidation by-product like formaldehyde, acetaldehyde, acetone, formic acid, and acetic acid as a standard challenge compound for testing oxidation-based air cleaning systems, should be avoided especially in large or full-scale testing. A similar recommendation was made by Gunschera, Markewitz, Bansen, Salthammer, and Ding (2016), who investigated the performance of portable photocatalytic air cleaners by environmental chamber testing. However, the challenge contaminant mixture set by European standard for photocatalysis EN 16846-1:2017 includes acetone, formaldehyde, acetaldehyde, heptane, and toluene (AFNOR, 2017). Adopting these challenge compounds is not suitable for this study, so acetone, formaldehyde, and acetaldehyde are excluded from the potential challenge compound list.

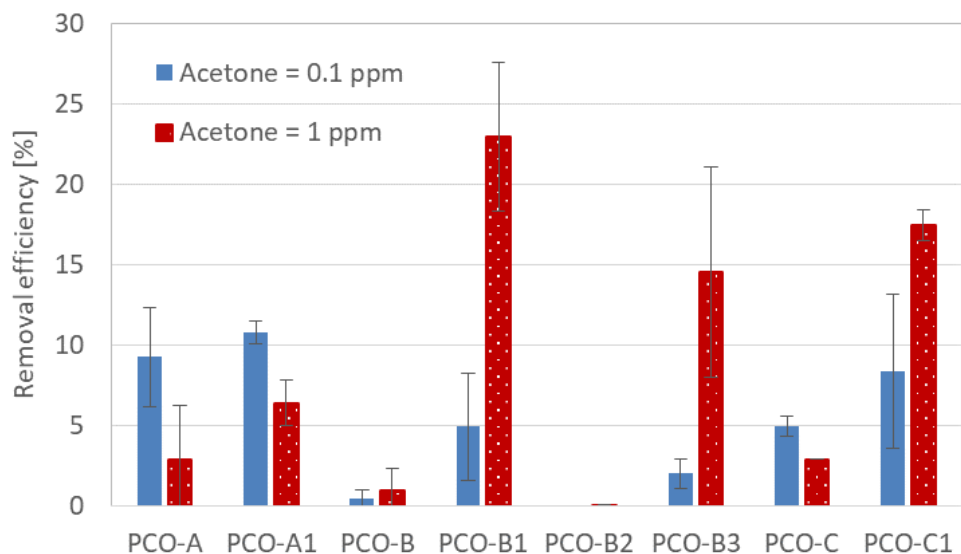


Figure 5-7. Effects of light source on acetone removal efficiency of PCO.

Based on the MEK and acetone test results of the oxidation-based air cleaning systems, PCO-A, PCO-A1, O3-A, and NTP-A were selected for further testing. Photocatalyst “A” shows the best photocatalytic performance. So PCO-A is selected to represent PCO technology. Since some commercial PCO systems use ozone-generating VUV lamps for the light source, PCO-A1 is also selected. For ozonation, one VUV lamp case (O3-A) was selected to have ozone concentration as low as possible. NTP-A was chosen to represent NTP since it showed slightly better performance than NTP-B.

5.3 Effects of air velocity

For successful applications of these oxidation-based technologies, air-cleaning system should be designed and operated to ensure sufficient reactions. Unlike stand-alone room air cleaners operated in recirculation mode, in-duct air cleaning systems directly applied in air handling units (AHU) are operated in dynamic single-pass mode and tend to be subjected to a much shorter reaction time. The 4-duct test rig results reported in the previous sections were conducted at 180 m³/hr (or 0.54 m/s of air velocity) or less.

To investigate the effects of air-flow rates on VOC removal performances of oxidation-based air cleaning technologies, first we examined the time scale required to oxidize VOCs by major oxidizing agents and compared the effects of air-flow rates expressed in reactor residence time on single-pass VOC removal efficiency by PCO and NTP reported in the literature. Then we presented the experimental results of four oxidation-based air-cleaning systems selected from the previous sections. These units were tested side-by-side in the 4-duct test rig at three different air-flow rates (i.e., 121, 176, and 253 m³/hr) for toluene at 0.1 ppm and 1 ppm.

5.3.1 Lifetime of VOCs

The reaction processes of VOCs have long been studied in atmospheric chemistry to understand the fate of VOCs and partaking in air pollution. The major chemical reaction processes are the reactions with hydroxyl (OH) radical, ozone, and nitrite (NO₃) radical (Hester & Harrison, 1995). Table 5-2 presents the rate constants (k) of the challenge compounds in aldehydes and VOC groups of ASHRAE standard 145.2-2016 and other common VOCs (Atkinson & Arey, 2003; Atkinson et al., 2008).

With the given rate constant, the characteristic time scale or chemical lifetime (τ) is defined as

$$\tau_{VOC-i} = \frac{1}{k_{VOC-i} \cdot C_i} \quad (5-1)$$

where τ_{VOC-i} is the lifetime of specific VOC due to the reaction with reactive species i [s]; k_{VOC-i} is the rate constant of the reaction between VOC and species i [cm³/molecules/s]; and C_i is the concentration of species i [molecules/cm³]. The overall lifetime (τ_{all}) of a VOC due to the reactions with O₃, OH radical and NO₃ radical is given by

$$\frac{1}{\tau_{all}} = \frac{1}{\tau_{VOC-O_3}} + \frac{1}{\tau_{VOC-OH}} + \frac{1}{\tau_{VOC-NO_3}} \quad (5-2)$$

In the troposphere, OH radical is generated from the photolysis of O₃, the ground level OH radical concentration peaks during the daytime, which is in the order of 10⁶ – 10⁷ molecules/cm³. In contrast, NO₃ radical peaks during nighttime due to its high reactivity with photons and nitric oxide (NO). Nighttime ground level NO₃ concentration varies from less than 5 × 10⁷ to 1 × 10¹⁰ molecules/cm³ (Hester and Harrison, 1995). The lifetime for outdoor air (OA), presented in Table 5-2, was calculated using a 12-hr daytime average of 2.0 × 10⁶ molecules/cm³ for OH radical reactions; a 12-hr night-time average of 5 × 10⁸ molecules/cm³ for NO₃ radical reactions; and a 24-hr average of 7 × 10¹¹ molecules/cm³ for O₃, which is about 30 ppb (Atkinson & Arey, 2003).

There is limited information on the levels of reactive species in indoor environments. Ingrosso (2002) has reviewed the radical chemistry in the troposphere and indoor environments, and recommended the following indoor concentrations for lifetime calculation: a 12-hr daytime average of 1.0 × 10⁶ molecules/cm³ for OH radical reactions; a 12-hr night-time average of 5 × 10⁸ molecules/cm³ for NO₃ radical reactions; and a 24-hr average of 5 × 10¹¹ molecules/cm³ for O₃, which is about 20 ppb. These values were applied for the calculation of lifetime indoor air (IA) in Table 5-2.

Table 5-2. Rate constants and calculated lifetimes for common VOCs

VOC	k at 298K [cm ³ /molecule/s]			Lifetime [hr] due to OH		Lifetime [hr] due to O ₃		Lifetime [hr] due to NO ₃	Overall Lifetime [hr]	
	OH	O ₃	NO ₃	OA	IA	OA	IA	OA = IA	OA	IA
n-Hexane	5.2×10 ⁻¹²	<1×10 ⁻²³	1.1×10 ⁻¹⁶	27	53	>4.0×10 ⁷	>5.6×10 ⁷		27	53
Cyclopentane	4.97×10 ⁻¹²	<1×10 ⁻²³		28	56	>4.0×10 ⁷	>5.6×10 ⁷			
Cyclohexane	6.97×10 ⁻¹²	<1×10 ⁻²³	1.4×10 ⁻¹⁶	20	40	>4.0×10 ⁷	>5.6×10 ⁷	3968	20	39
Benzene	1.22×10 ⁻¹²	<1×10 ⁻²⁰	<3×10 ⁻¹⁷	114	228	>4.0×10 ⁴	>5.6×10 ⁴	>18519	113	224
Toluene	5.63×10 ⁻¹²	<1×10 ⁻²⁰	7.0×10 ⁻¹⁷	25	49	>4.0×10 ⁴	>5.6×10 ⁴	7937	25	49
m-Xylene	2.31×10 ⁻¹¹	<1×10 ⁻²⁰	2.6×10 ⁻¹⁶	6.0	12	>4.0×10 ⁴	>5.6×10 ⁴	2137	6	12
o-Xylene	1.36×10 ⁻¹¹	<1×10 ⁻²⁰	4.1×10 ⁻¹⁶	10	20	>4.0×10 ⁴	>5.6×10 ⁴	1355	10	20
p-Xylene	1.43×10 ⁻¹¹	<1×10 ⁻²⁰	5.0×10 ⁻¹⁶	10	19	>4.0×10 ⁴	>5.6×10 ⁴	1111	10	19
Styrene	5.8×10 ⁻¹¹	1.7×10 ⁻¹⁷	1.5×10 ⁻¹²	2.4	4.8	23	33	0.37	0.32	0.34
Formaldehyde	9.37×10 ⁻¹²	<1×10 ⁻²⁰	5.6×10 ⁻¹⁶	15	30	>4.0×10 ⁴	>5.6×10 ⁴	992	15	29
Acetaldehyde	1.50×10 ⁻¹¹	<1×10 ⁻²⁰	2.7×10 ⁻¹⁵	9.3	19	>4.0×10 ⁴	>5.6×10 ⁴	206	9	17
Hexanal	3.0×10 ⁻¹¹	<1×10 ⁻²⁰	1.6×10 ⁻¹⁴	4.6	9.3	>4.0×10 ⁴	>5.6×10 ⁴	35	4	7
Benzaldehyde	1.2×10 ⁻¹¹	<1×10 ⁻²⁰	2.4×10 ⁻¹⁵	12	23	>4.0×10 ⁴	>5.6×10 ⁴	231	11	21
Acetone	1.7×10 ⁻¹³	<1×10 ⁻²⁰	<3×10 ⁻¹⁷	817	1634	>4.0×10 ⁴	>5.6×10 ⁴	>18519	767	1462
2-Butanone	1.22×10 ⁻¹²	<1×10 ⁻²⁰		114	228	>4.0×10 ⁴	>5.6×10 ⁴			
Ethanol	3.2×10 ⁻¹²	<1×10 ⁻²⁰	<2×10 ⁻¹⁵	43	87	>4.0×10 ⁴	>5.6×10 ⁴	>278	38	66
Isopropanol	5.1×10 ⁻¹²	<1×10 ⁻²⁰	1.4×10 ⁻¹⁵	27	54	>4.0×10 ⁴	>5.6×10 ⁴	397	25	48
iso-butanol	9.3×10 ⁻¹²	<1×10 ⁻²⁰		15	30	>4.0×10 ⁴	>5.6×10 ⁴			
Dichloro- methane	1.0×10 ⁻¹³			1389	2778					
Tetrachloro- ethene	1.6×10 ⁻¹³	<1×10 ⁻²¹	<1×10 ⁻¹⁶	868	1736	>4.0×10 ⁵	>5.6×10 ⁵	>5556	749	1320
Limonene	1.64×10 ⁻¹⁰	2.1×10 ⁻¹⁶	1.22×10 ⁻¹¹	0.8	1.7	1.9	2.6	0.046	0.042	0.044
a-Pinene	5.23×10 ⁻¹¹	8.4×10 ⁻¹⁷	6.16×10 ⁻¹²	2.7	5.3	4.7	6.6	0.090	0.086	0.088

The results show that the reaction with OH radical is the main mechanism in the decomposition of most VOCs in both outdoor and indoor air. For highly reactive VOCs like limonene, a-pinene, and styrene, the reaction with NO₃ radical is dominant. The overall indoor lifetime varies from 160 seconds to 61 days for the considered VOCs. Figure 5-8 depicts the obtained lifetime of the common VOCs in indoor and outdoor air. The target VOCs selected for testing in this study have greater than 10 hr of a lifetime in indoor air except for styrene. Acetone has a much longer lifetime, which attributes to the low removal efficiency reported in previous sections. The calculated lifetime is several orders of magnitude longer in time scale compared to the residence time we can achieve from the applications of in-duct air cleaners. AHU, of course, would provide different reaction environments from normal occupied indoor environments. Nonetheless, to defy these limitations oxidation-based air cleaning systems should be able to generate huge amounts of oxidizing agents.

Considering OH radical as the main oxidant, the required OH concentration to achieve 0.1 second of residence time, which is the nominal residence time applied in testing adsorption-based air cleaning technologies like activated carbons, was calculated as shown in Figure 5-9. It shows that 10^{11} molecules/cm³ or higher concentrations of OH radicals are needed for most VOCs. There are few studies that investigated radical generation by oxidation-based air cleaning technologies. The concentrations of OH radicals generated by lab-scale NTP using dielectric barrier discharge (DBD) reactors have been reported in the range of $(5.9\text{--}23.6)\times 10^{13}$ molecules/cm³ (Guo, Liao, He, Ou, & Ye, 2010); and $(1.5\text{--}4.0)\times 10^{12}$ molecules/cm³ (Chen et al., 2016). These levels could considerably shorten the lifetime of VOCs and could be sufficient depending on the VOC. However, these can lead to high ozone generation, as Guo et al. (2010) reported, 18 – 215 ppm of ozone.

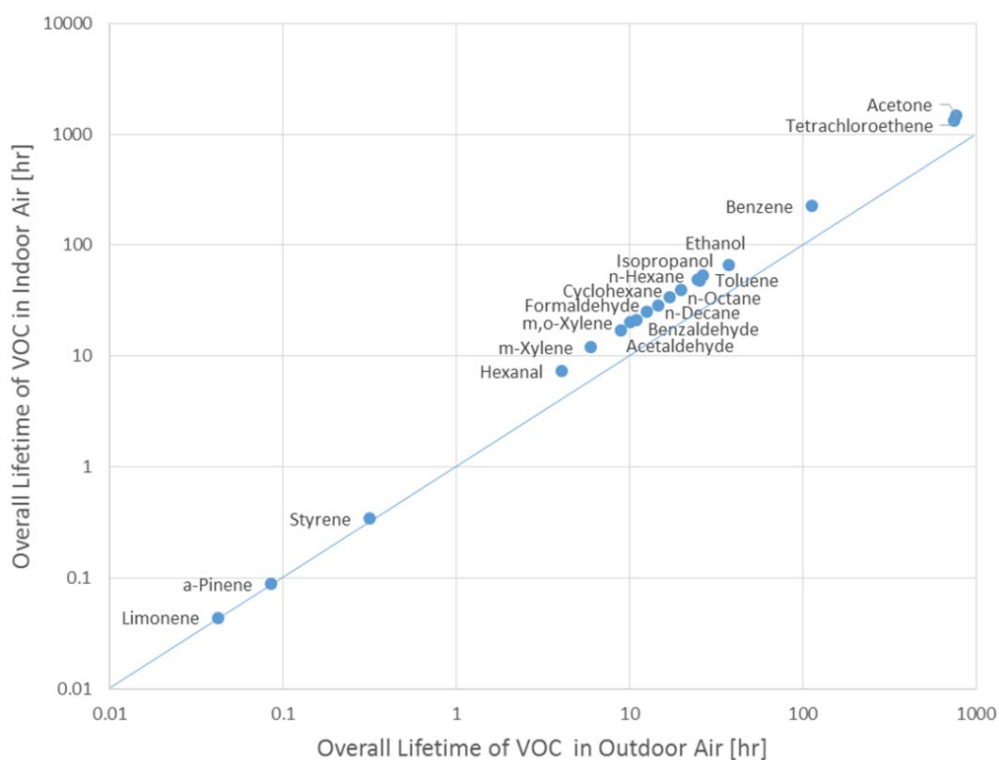


Figure 5-8. Figure 5-8 Overall lifetime of common VOCs in typical indoor and outdoor air.

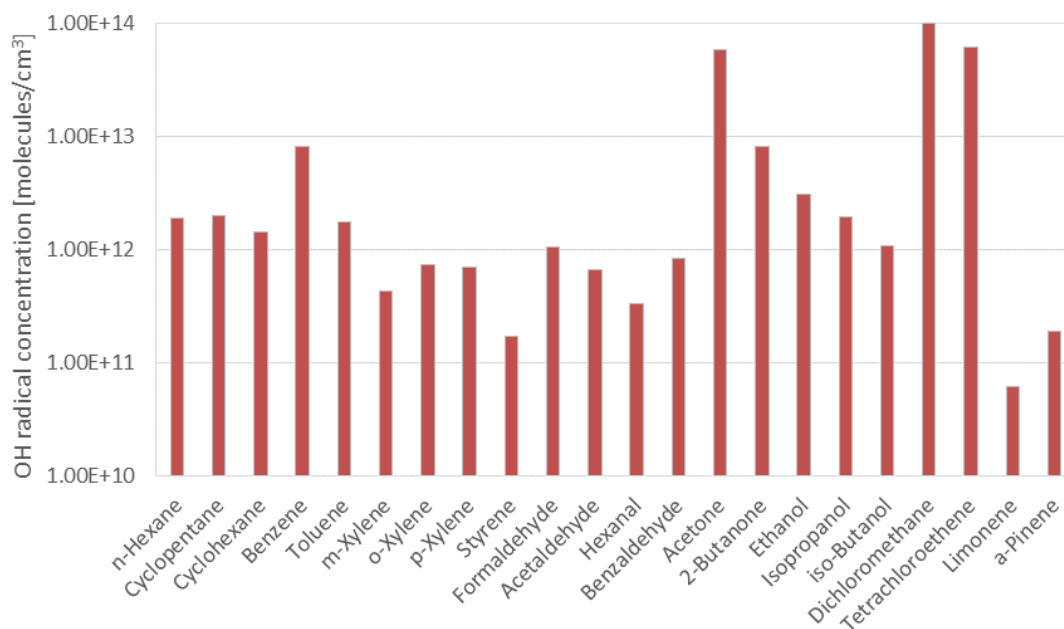


Figure 5-9. Figure 5-9 Hydroxyl radical concentration required for 0.1 s of lifetime of selected VOCs.

5.3.2 Effects of reactor residence time – Analysis of data in literature

In the absence of standard test methods, the experimental designs for PCO systems are all different from one study to another. For easier inter-comparisons among various studies, the studies which are reporting single-pass efficiency for toluene and xylene removal measured in test setups relevant to AHU applications were reviewed. To reduce the variations of photocatalysts and their substrates, the most studied photocatalyst, P-25 (Evonic Corp.) coated on the substrates with minimum adsorption effects such as glass and fiberglass filter was considered. Figure 5-10 presents the effects of reactor residence time, which is defined as the reactor volume divided by the airflow rate, on the performance of UV-PCO using the data compiled from various studies (Ao & Lee, 2003; Ao, Lee, Mak, & Chana, 2003; Jeong et al., 2004; Kibanova, Cervini-Silva, & Destailats, 2009; Mo, Zhang, & Xu, 2013; Quici et al., 2010; Sharmin & Ray, 2012). Since the performance of UV-PCO is affected by the humidity level, the test results in low humidity conditions were considered. It shows that the applied residence times in literature are diverse. When non-ozone generating UV lamps were used, UV-PCO showed similar removal performances for both toluene and xylene. The increase in efficiency with increasing residence time tends to be logarithmic, and a faster increase was observed with PCO using ozone-generating vacuum UV (VUV) lamps due to additional oxidation by ozone. For the cases using VUV lamps, the ozone levels were in the range of 0.1 – 0.25 ppm. The results suggest that in the absence of ozone, a voluminous PCO system is required for AHU applications to have sufficient efficiency. However, various approaches are continuously proposed to improve the UV-PCO efficiency through photocatalyst modification, various doping, the use of more effective coating technologies and substrates, and so on.

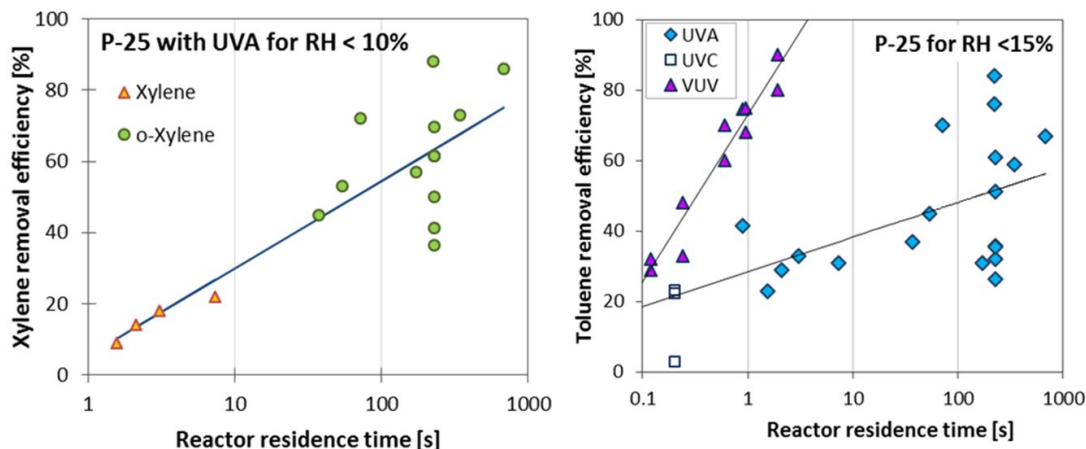


Figure 5-10. Effect of reactor residence time of UV-PCO using P-25 on removal efficiency.

Left - Xylene using UVA lamps at RH < 10% , Right - Toluene using different UV lamps at RH < 15% (Data are from Ao and Lee, 2003; Ao et al., 2003; Jeong et al., 2004; Kibanova et al., 2009; Mo et al., 2013; Quici et al., 2010; Sharmin and Ray, 2012).

Due to large variation in NTP generation methods and their design parameters, operational parameters, and test conditions, a direct comparison of NTP performance of VOC removal from one study to another was not feasible. Only a few studies have investigated the effects of air-flow on VOC removal performance of NTP (Byeon, Park, Jo, Yoon, & Hwang, 2010; Cal & Schluep, 2001; Wang, Li, Wu, Li, & Li, 2009), and these studies reported increased efficiency by increasing the residence time. However, it was found that excessive increase is not necessarily beneficial from the perspective of energy efficiency of NTP (Wang et al., 2009).

5.3.3 Effects of air velocity – 4-duct test rig results

Four different oxidation-based air cleaning systems (i.e., PCO-A, PCO-A1, O3-A, and NTP-A) were tested simultaneously in the 4-duct test rig. The tests were conducted in three different flow rates: $121 \pm 2 \text{ m}^3/\text{hr}$, $176 \pm 5 \text{ m}^3/\text{hr}$, and $253 \pm 5 \text{ m}^3/\text{hr}$, which are equivalent to the face air velocities of $0.36 \pm 0.01 \text{ m/s}$, $0.53 \pm 0.01 \text{ m/s}$, and $0.76 \pm 0.01 \text{ m/s}$. Considering the distance from the air cleaner to the air sampling port for the reactor volume, the corresponding reactor residence times were 2.5 s, 1.7 s, and 1.2 s, respectively. However, this calculation method would not be appropriate for PCO-A, which uses non-ozone generating UVC lamps so it involved only surface reactions. Considering the thickness of two layers of PCO, the corresponding residence times became 0.036 s, 0.024 s, and 0.017 s, respectively. The test was conducted with two different toluene challenge concentrations (i.e., $0.097 \pm 0.002 \text{ ppm}$ and $0.98 \pm 0.02 \text{ ppm}$) at $21 \pm 0.1 \text{ }^\circ\text{C}$ and $44 \pm 2\% \text{ RH}$.

The ozone generation by the tested system varied with flow rates as shown in Figure 5-11. Since ozone is reactive and PCO can remove ozone, ozone generated by PCO-A1 in spite of having two VUV lamps, is similar to that of one VUV lamp (O3-A). PCO-A also removes ozone without any ozone generation, so the downstream ozone levels were lower than the upstream concentration. Unlike the NTP results in the literature, ozone generation by the tested NTP-A was not significant.

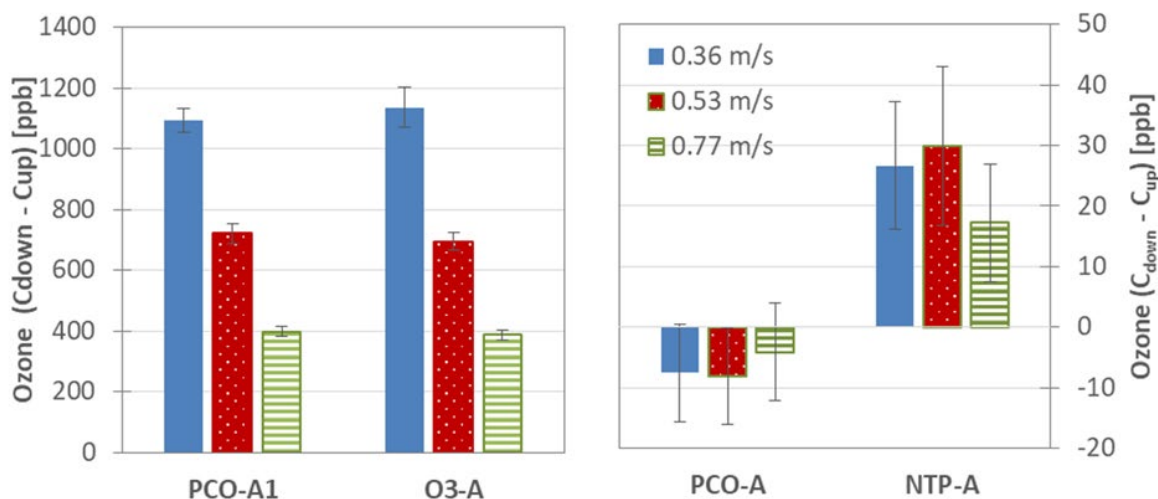
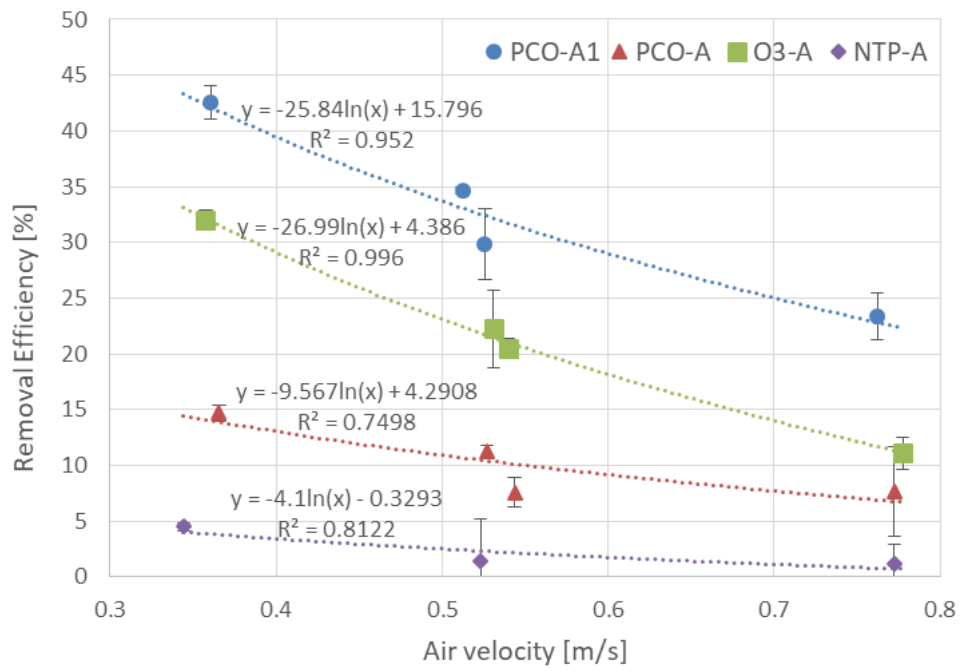


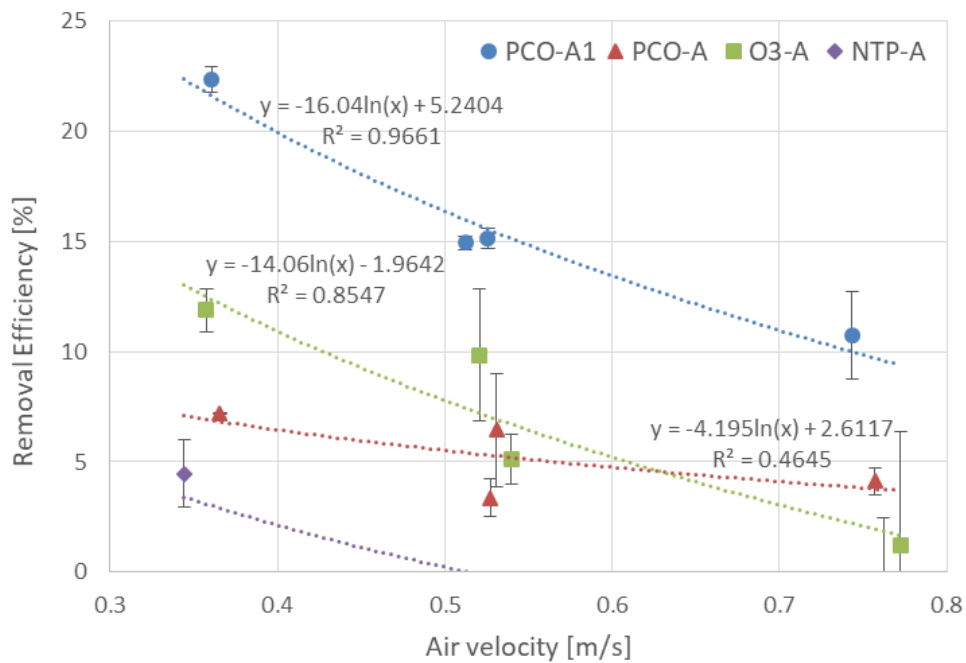
Figure 5-11. Figure 5-11 Ozone generation by the tested oxidation-based air cleaning systems.

The measured toluene removal efficiency for four different technologies is presented in Figure 5-12. PCO-A1 showed the best removal efficiency in all cases followed by O3-A > PCO-A > NTP-A. Based on the information found in Table 5-2, a 50-fold increase in ozone concentration from indoor air condition of 20 ppb can decrease the lifetime of toluene from 49 hr to 47 hr, which is not sufficient enough to explain the higher toluene removal efficiency by PCO-A1 and O3-A. This may indicate that more reactive species like OH radical, but not NO₃ radical due to UV light, were generated in these systems, and ozone generation can be a gauge for the generation of reactive species in oxidation-based air cleaning systems except for PCO systems using non-ozone generating light sources. Due to the size limit and low flow ranges applied in the test rig a regular in-duct NTP system could not be tested, so three small NTP units normally used in room air cleaners were tested instead. Therefore, the tested NTP-A capacity may not match with the test conditions applied here. The performance of commercial NTP units needs to be investigated further. As the air velocity increases, the efficiency decreases. The trends generally follow logarithmic functions as shown in Fig. 5-12. This indicates that pseudo-first order reactions can be applied. Similar to the results given in Fig. 5-10, the PCO-A1 is more sensitive to flow rate changes. Increasing challenge toluene concentration from 0.1 to 1 ppm resulted in about a 50% decrease in efficiency for PCO-A1 and O3-A; and about 70% decrease for PCO-A.

Formaldehyde, acetaldehyde, and acetone were the main by-products quantified by HPLC analysis. Figure 5-13 presents the by-product generation rates of these compounds for each technology, which show all different profiles. PCO systems tend to generate more by-products. PCO-A has lower efficiency than O3-A but by-product generation rates are greater. Formaldehyde generation rates are greater than other by-products in all test units except NTP-A. In O3-A and NTP-A, acetone generation rates are greater than acetaldehyde. In GC/MS analysis, benzaldehyde generation by PCO-A1 and O3-A, which have high ozone concentrations, were detected.

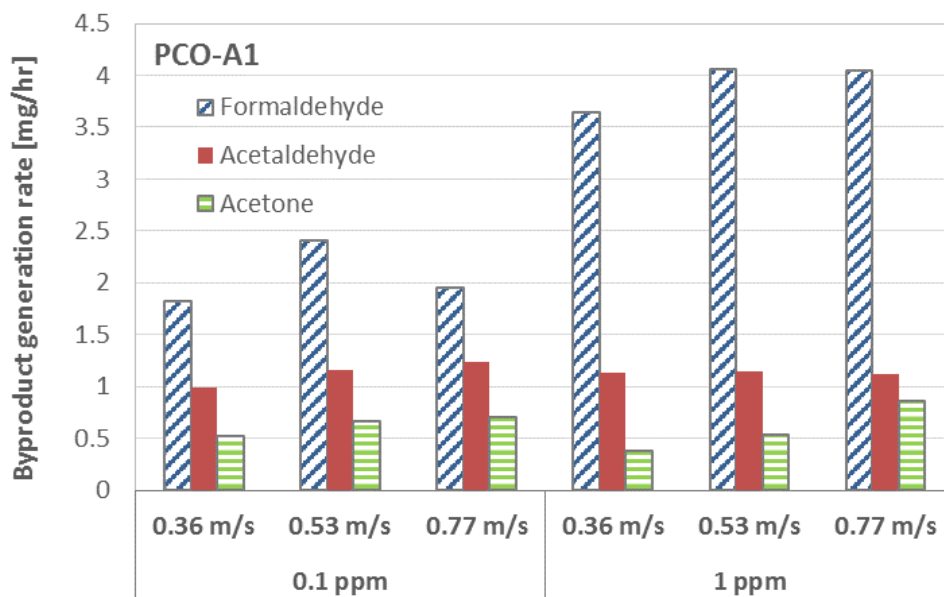


(a) 0.1 ppm

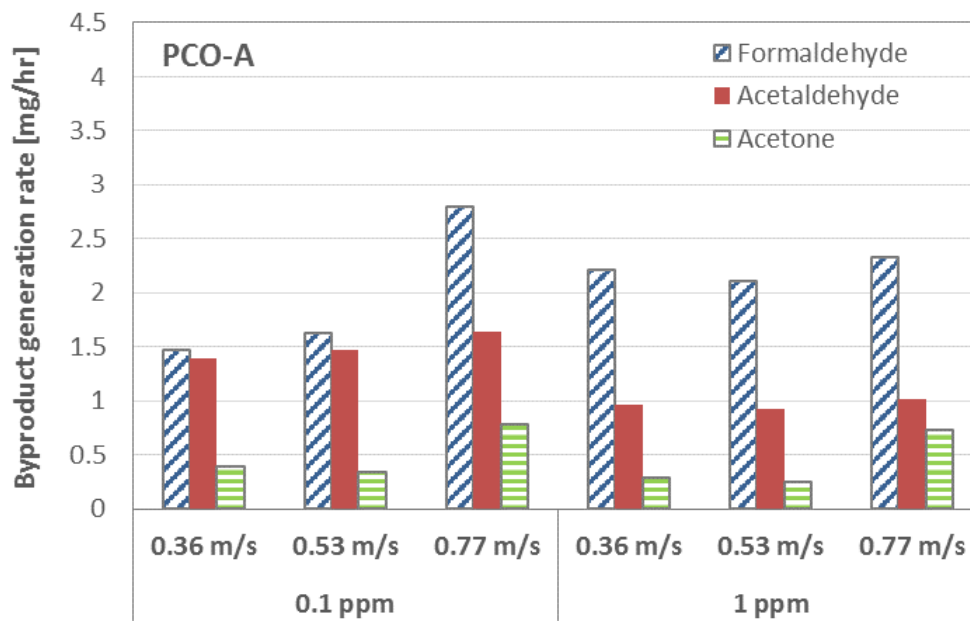


(b) 1 ppm

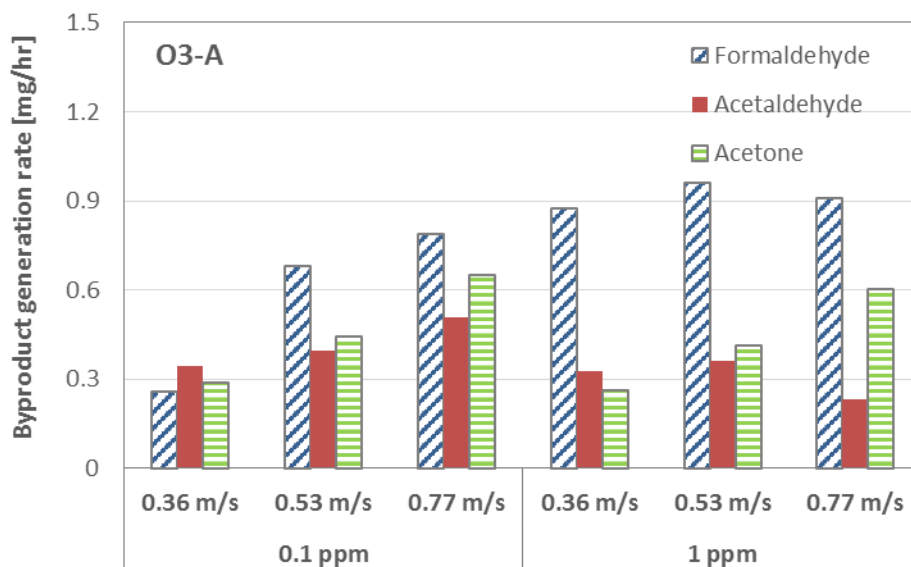
Figure 5-12. Effect of air velocity on toluene removal efficiency.



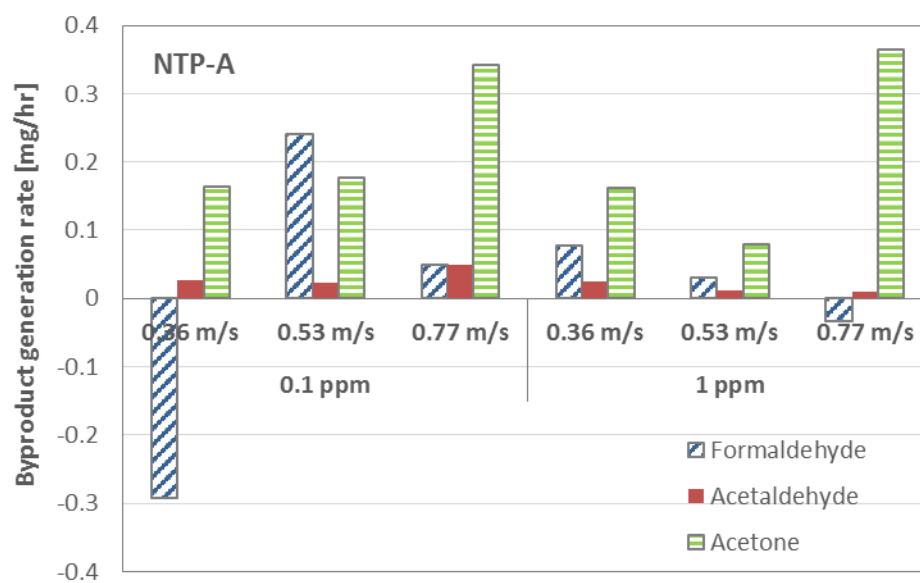
(a) PCO-A1



(b) PCO-A



(c) O3-A



(d) NTP-A

Figure 5-13. Effects of air velocity on by-product generation rates.

5.4 Effects of challenge VOC and concentrations

The target challenge compounds of this study were acetone, MEK, n-hexane, n-octane, toluene, o-xylene, styrene, and iso-butanol. MEK and acetone test results were presented in the previous section. The test results of the other challenge VOCs are presented here.

Four main oxidation technologies were selected for side-by-side testing in the 4-duct test rig for VOC removal testing. PCO-A, which uses UVC lamps, represents pure photocatalytic oxidation technology; O3-A represents for ozonation; PCO-A1 represents the combination of PCO technology and ozonation; and NTP-A or NTP-C non-thermal plasma. Originally, NTP-A was selected and tested for toluene, o-xylene, and styrene. Due to its low effectiveness, it was changed to NTP-C and tested for n-hexane, n-octane, and iso-butanol. Since the challenge concentration can affect the oxidation-based air cleaning performances and also may affect the integrity of the test methods as demonstrated in acetone test results, the tests were conducted in two target concentrations: 0.1 ppm and 1 ppm. The test conditions are 178 ± 11 m³/hr of air flow rates (or 0.53 ± 0.03 m/s of air velocity) at 21 ± 0.1 °C and 58 ± 1 % RH. The average challenge concentrations were 0.095 ± 0.002 ppm and 0.951 ± 0.025 ppm.

Figure 5-14 shows the average VOC removal efficiency tested for 0.1 ppm and 1 ppm of challenge concentrations. PCO-A1 has the highest removal efficiency for all tested VOCs. O3-A generally has a higher efficiency than PCO-A, except for iso-butanol in both concentrations. Both NTP units show low efficiency. While PCO-A1 shows greater than 80% efficiency for styrene and iso-butanol at 0.1 ppm, NTP units have less than 12% efficiency. The removal efficiency of styrene and iso-butanol is generally higher than for the other VOCs as these compounds have higher rate constants for their reaction with hydroxyl radicals, as presented in Table 5-2. Ozonation unit O3-A test results show that the styrene removal efficiency is the highest for both 0.1 ppm and 1 ppm cases. This can be explained by the fact that styrene has a higher rate constant for the reaction with ozone compared to the other tested VOCs. For PCO-A1 and PCO-A, the removal efficiency at 1 ppm is around half of the one at 0.1 ppm; however, O3-A shows more decrease in efficiency. The n-octane removal efficiency of PCO-A and O3-A is mostly lower than the one for other VOCs at both challenge concentrations; however, for PCO-A1 it is the 3rd highest among the tested VOCs. PCO-A1 combines PCO mechanism and ozonation, and the combined effect is clearly synergistic for n-octane removal. Other synergistic effects are observed for 1ppm cases of iso-butanol and n-hexane.

Figure 5-15 presents the by-product generation rates quantified by HPLC analysis. Formaldehyde, acetaldehyde and acetone were generated for all the tested VOCs. For aromatic compounds, only these three by-products were detected by HPLC analysis. For iso-butanol, crotonaldehyde and MEK were also detected. Alkanes have generated crotonaldehyde, propionaldehyde and MEK as well. For iso-butanol, MEK is the leading by-product, followed by acetone and formaldehyde. For all tested aromatic compounds, formaldehyde is the main by-product. Formaldehyde is dominant for styrene, especially at 1 ppm. The by-product generation rates are higher at the higher challenge concentration.

In general, PCO-A1 produces most by-products because its removal efficiency is the highest. The removal efficiency of PCO-A is lower than the one of O3-A; however, it generates more by-products, except for styrene at both challenge concentrations and for 1 ppm of n-hexane. Due to the negligible removal efficiency of NTP, minor by-product generation was observed.

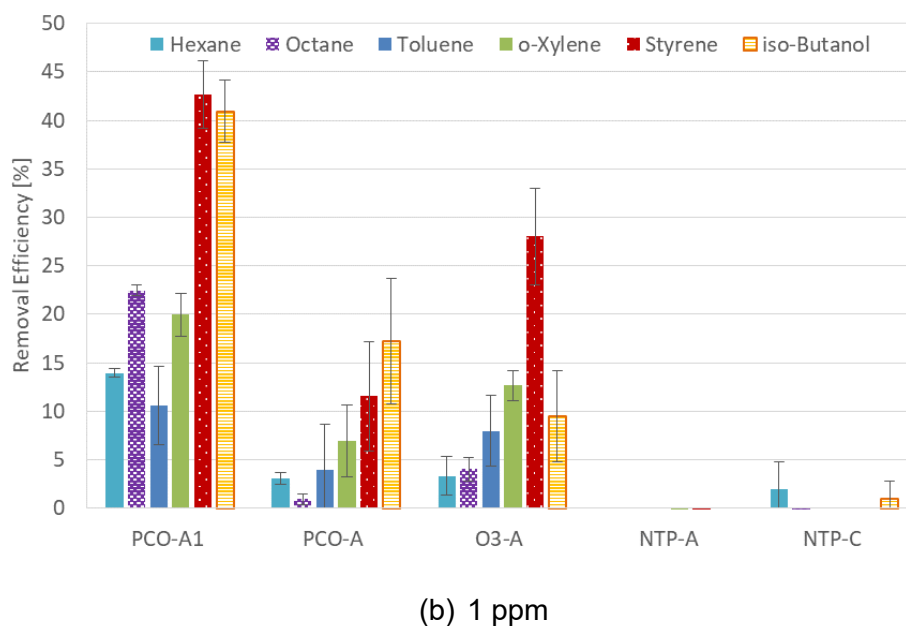
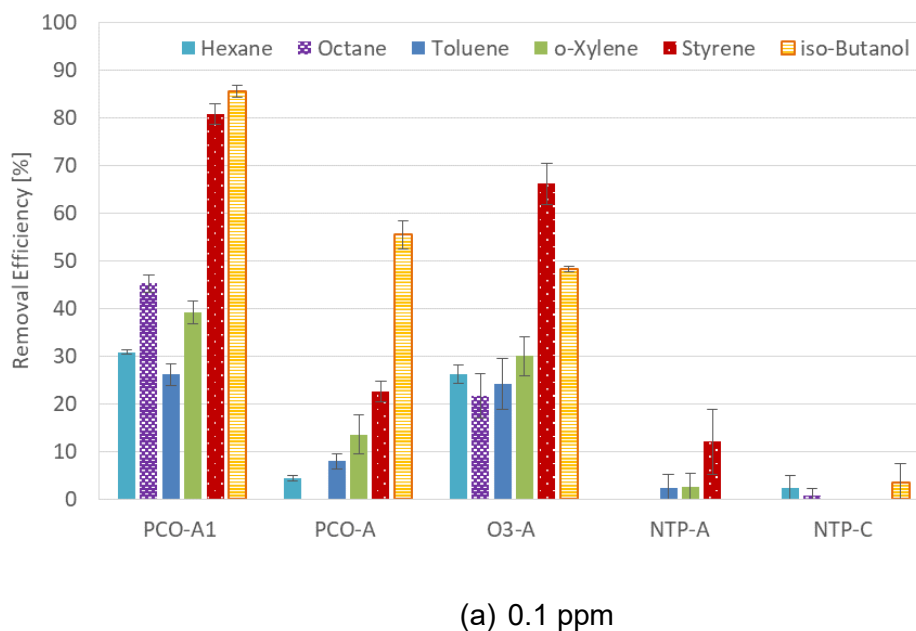
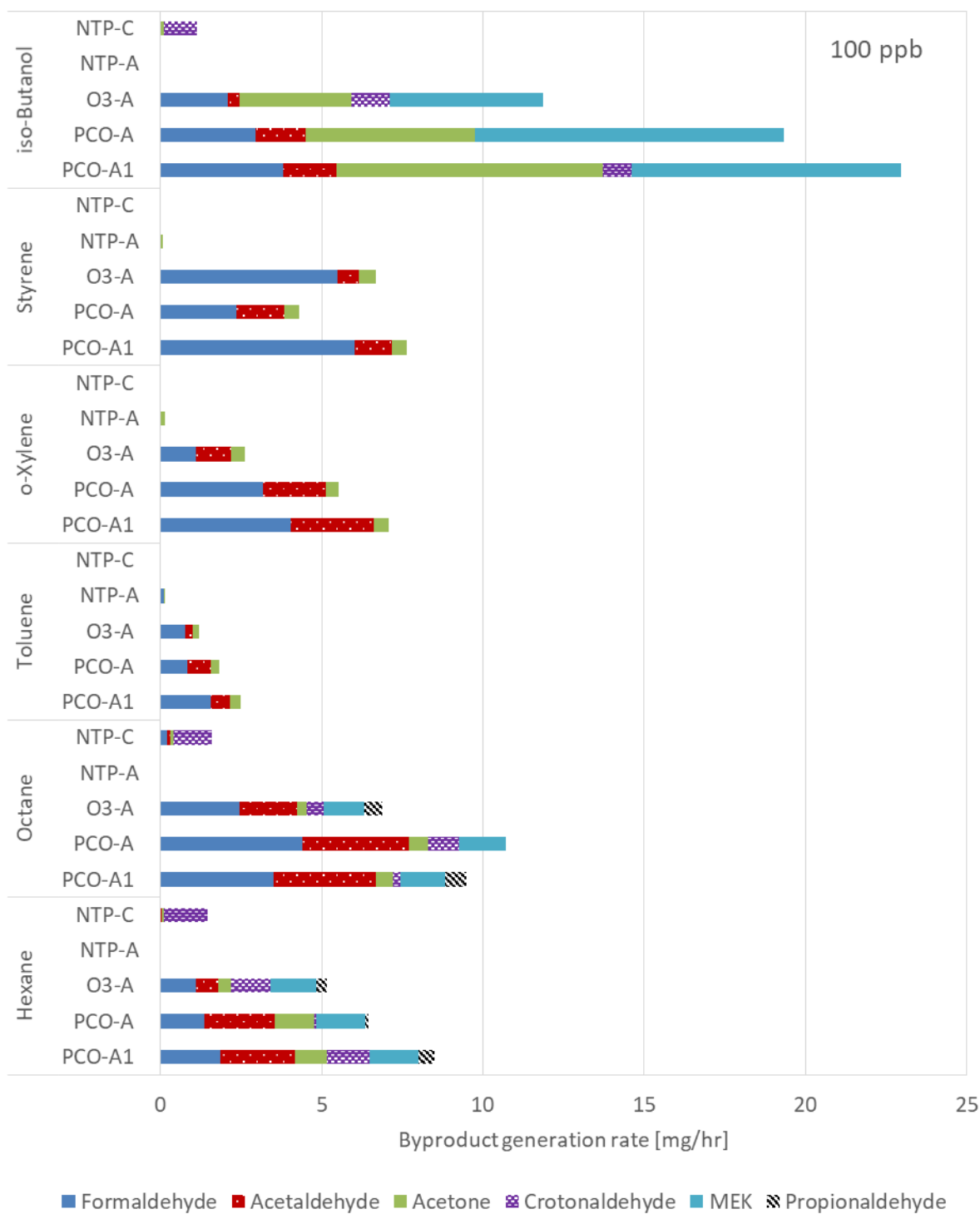
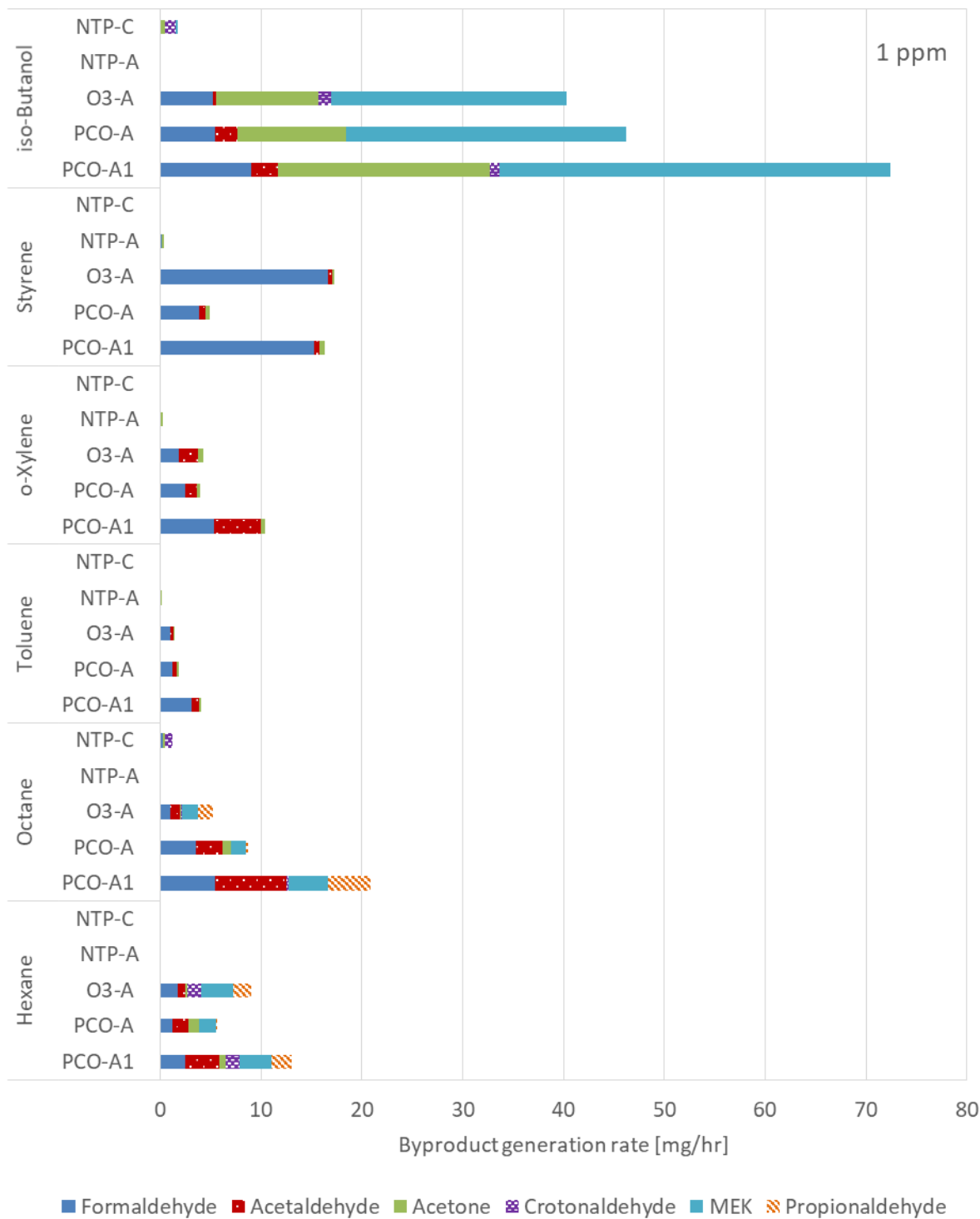


Figure 5-14. Removal efficiency of different VOCs.

Detecting by-products through ATD-GC/MS analysis can be tricky when the challenge VOC has to be sampled and analyzed by the same methods. When the challenge concentration is high and the conversion efficiency is low, the sampling volume has to be reduced not to overload the thermal desorption tubes and/or higher split ratio has to be applied in the thermal desorber method. This ends up raising the detection limits. For the aromatic compounds, only benzaldehyde was identified as a by-product in GC/MS analysis results, and for iso-butanol, iso-butanol, methacrolein, and 2,3-butanedione were identified.



(a) 0.1 ppm



(b) 1 ppm

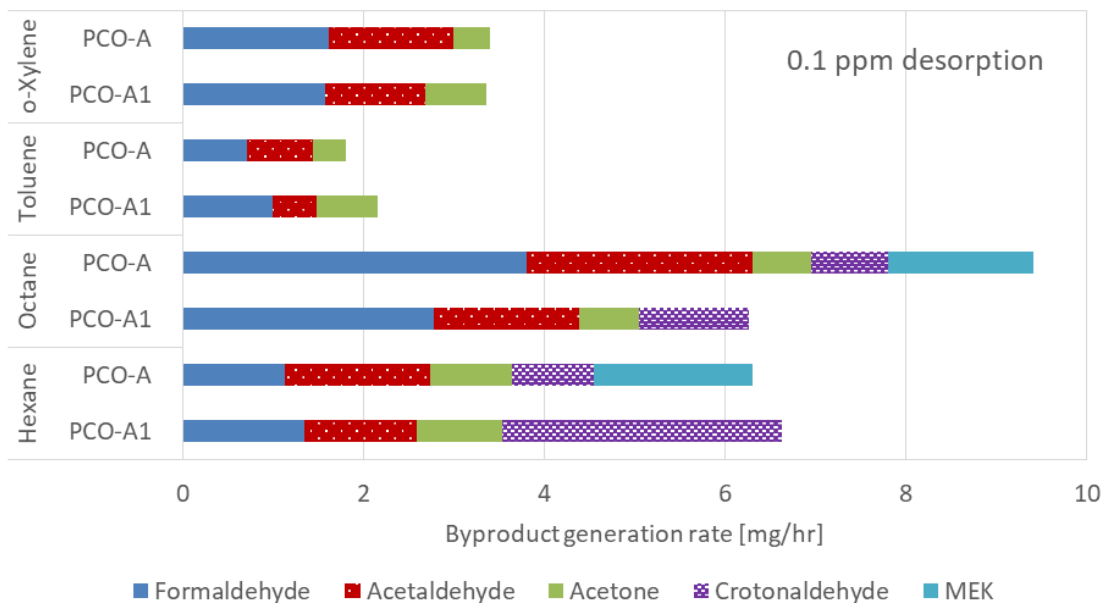
Figure 5-15. By-product generation rates of different VOCs.

The generation of residues on PCO surfaces and their oxidation by-products after stopping the introduction of challenge VOC was investigated. A “desorption test” named after a similar procedure adopted in adsorption-based air cleaning media testing, was conducted for one hour while the UV lamps remained turned on. Desorption test was not conducted for O3-A and NTP units. Figure 5-16 presents desorption test results that were conducted after 0.1 ppm and 1 ppm of challenge VOC testing. While the desorption test was carried out for all studied VOCs after 1ppm testing, it was conducted only for n-hexane, n-octane, toluene, and o-xylene after 0.1 ppm testing. Since PCO was activated by UV lamps during the desorption test, the prior challenge VOC was not detected or the downstream concentration was lower than the upstream trace level concentration. From HPLC analysis, measurable by-products were generated even after VOC introduction was stopped. Similar to the by-product generation profiles during VOC testing, alkanes produced more by-products compared to aromatic compounds, and the generation rates are only slightly reduced. However, desorption test results after iso-butanol testing show much lower generation rates compared to those of the challenge testing. Since TiO₂ catalysts are polar in nature, the adsorption of polar compounds is greater (Shayegan, Haghghat, Lee, Bahloul, & Huard, 2018; Zhong, Lee, & Haghghat, 2012). Since iso-butanol is polar, more generation of by-products during desorption testing was expected due to more adsorption on PCO surfaces. The high reactivity of iso-butanol by PCO may have counteracted, resulting in low emissions.

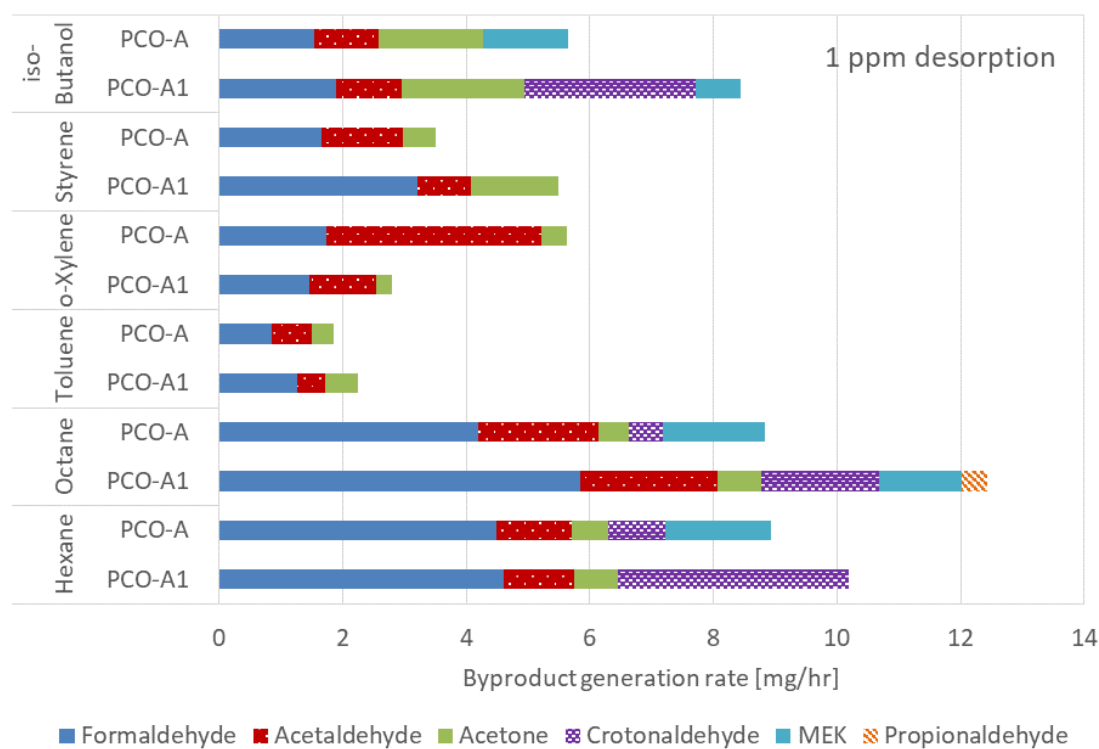
The average ozone generation expressed the difference between downstream and upstream concentrations which was 748 ± 45 ppb for PCO-A1 and 669 ± 30 ppb for O3-A for all tested VOCs except for styrene. During styrene tests, ozone generation was 765 ± 262 ppb for PCO-A1 and 592 ± 323 ppb for O3-A. When styrene was used as a challenging compound, it has greatly affected ozone monitoring using UV absorption technology. ASTM standard D 5156 – 02 (ASTM International, 2016) *Standard Test Methods for Continuous Measurement of Ozone in Ambient, Workplace, and Indoor Atmospheres (Ultraviolet Absorption)* summarizes some reported interfering species as shown in Table 5-3. Inconsistent effects of styrene interference were reported in Table 5-3: one showed 13% overestimation of ozone reading, while another showed 80% underestimation. Since ozone is one of the main harmful by-products, which must be measured for the evaluation of the overall performance of oxidation-based technologies, it would be better to avoid using those species interfering with ozone measurement as challenge compounds.

Table 5-3. Compounds interfering with ozone monitoring using UV absorption (modified from ASTM International, 2016)

Interfering compound	Response (% of concentration)
Ozone	100
Styrene	113 (20)
2,5-dimethylstyrene	147
Benzaldehyde	<1 (5)
2-methyl-4 nitrophenol	139
2-nitrotoluene	78
naphthalene	116
2,4-dimethylphenol	18



(a) After 0.1 ppm testing



(b) After 1 ppm testing

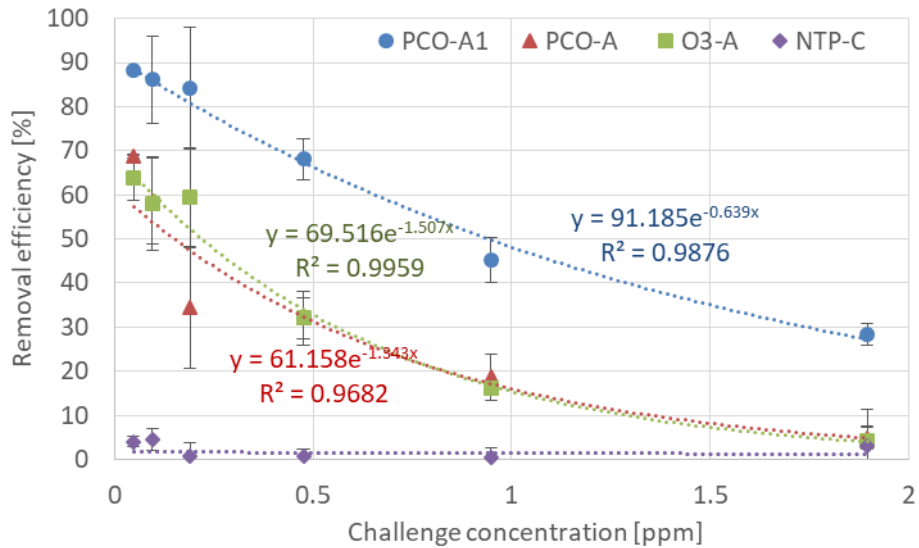
Figure 5-16. By-product generation rates during desorption test.

The effects of challenge VOC concentrations were investigated further for iso-butanol, toluene, and o-xylene in the range between 0.05 ppm and 2 ppm. Figure 5-17 presents the removal efficiency of different air cleaning units as a function of challenge concentrations. All tests were conducted in similar airflow and temperature conditions, but RH was different. Iso-butanol was tested for two different humidity levels – 44% RH and 25% RH as shown in Fig. 5-17 (a) and (b), respectively. Toluene shown in Fig. 5-17 (c) was tested at 49% RH, and o-xylene was tested at 23% RH (Fig. 5-17 (d)). Due to the low efficiency of NTP, it was not tested for aromatics. The removal efficiency of all tested oxidation-based air cleaning units generally decreases as the challenge concentration increases.

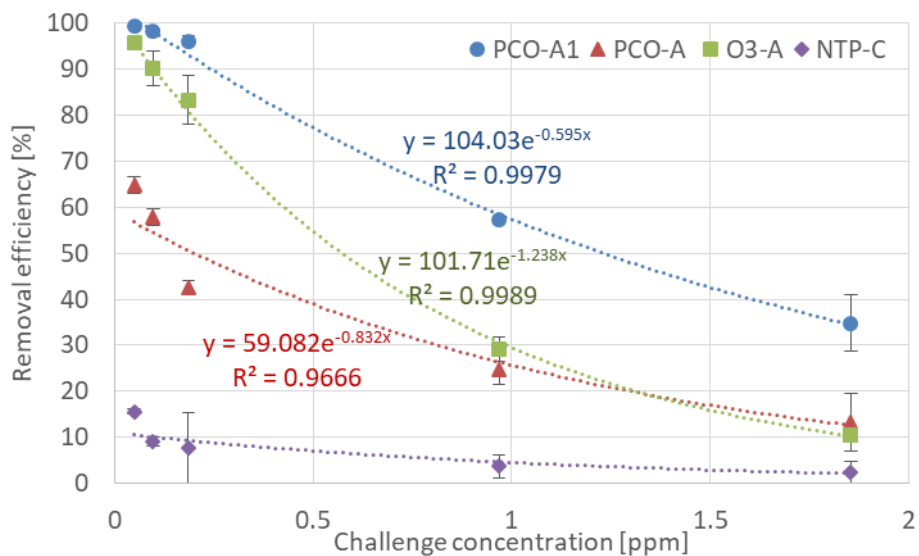
For iso-butanol, the decrease of efficiency tends to follow exponential decay profiles. Especially air cleaning systems involving ozone (i.e., PCO-A1 and O3-A) show excellent fits. At higher humidity conditions, PCO-A and O3-A show mainly similar iso-butanol removal efficiency in the tested concentration range; however, at low humidity O3-A shows a much higher efficiency at low ppb range. The ozone generation of O3-A was 723 ± 32 ppb for testing at 44% RH, and 752 ± 32 ppb at 25% RH. It has been reported that the formation of ozone in the presence of humidity is suppressed, as the energetic electrons are extinguished by water molecules (Raju, Reddy, Karupiah, Reddy, & Subrahmanyam, 2013). The presence of water can promote the formation of hydroxyl radicals, increasing the potential for VOC conversion. Considering the ozone levels generated by O3-A, the humidity condition of 25% RH would provide sufficient water molecules required for OH formation; therefore, increasing humidity has not instigated the increased efficiency. Bahri, Haghghat, Rohani, and Kazemian (2017b) reported that increasing the relative humidity level could have a negative effect on the removal efficiency due to decreasing electron density and quenching of the reactive species in the reactor. Compared to PCO-A1 and O3-A, PCO-A shows a rapid decrease in iso-butanol removal efficiency with the increase of concentration within ppb ranges. Photocatalysts have limited active sites and the competition among the challenge VOC molecules as well as water vapor and other molecules becomes fierce at higher challenge concentrations and/or humidity conditions. This indicates that raising challenge concentration in order to accelerate air cleaner testing, which is a commonly applied approach in the evaluation of adsorption-based technologies, is not suitable for oxidation-based air cleaning technologies. NTP-C shows low iso-butanol removal efficiency (i.e., less than 5%) for testing at 44% RH. At 25% RH, the performance is slightly better at the ppb range.

Toluene test results conducted at 49% RH (Fig. 5-17 (c)) show a gradual decrease in removal efficiency with an increasing challenge concentration. In contrast, more rapid decreases in o-xylene removal efficiency were observed in Fig. 5-17 (d). This may be explained by the fact that o-xylene removal efficiency is higher than for toluene removal at the same RH level, as shown in Fig. 5-14. Note that o-xylene testing was conducted at a more favorable condition of low humidity level. Therefore, the change in o-xylene removal efficiency due to the change in concentration may have become more discernible. PCO-A shows a lower performance compared to O3-A in toluene testing. In contrast, o-xylene test results show that PCO-A and O3-A have similar removal efficiency in the considered concentration range. While TiO_2 is a polar compound, toluene and o-xylene are non-polar compounds. Water vapor adsorbed on photocatalyst can bond with TiO_2 through hydrogen bonding; however, non-polar compounds have much weaker dipole-induced dipole attraction (Obee & Hay, 1997). This can cause more adverse effects of the humidity level on the removal of non-polar compounds by PCO.

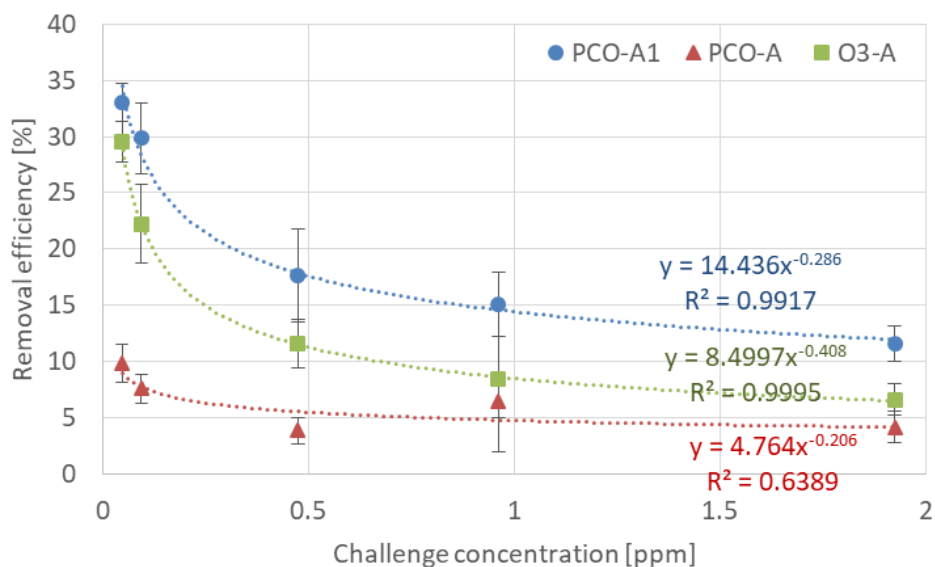
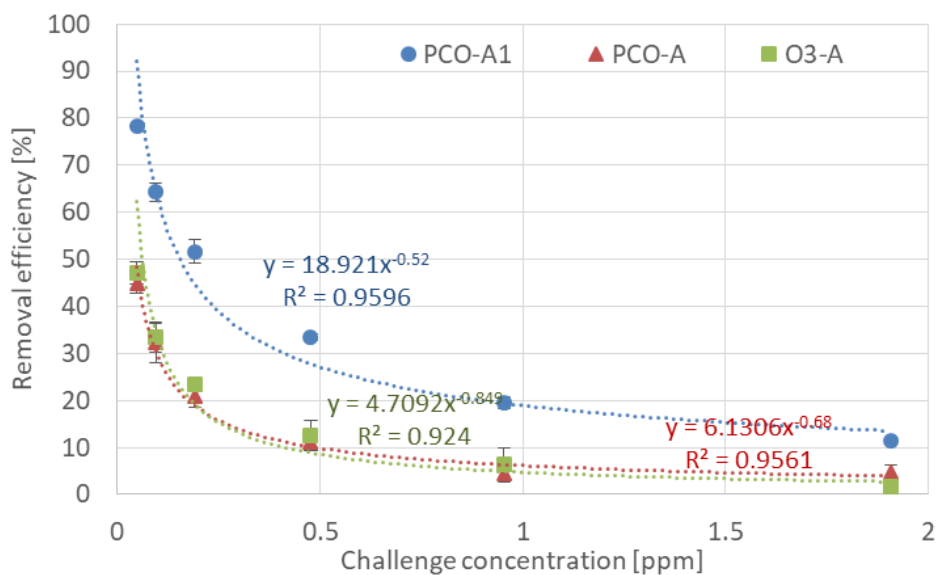
By-product generation rates were measured for every concentration in iso-butanol testing at 44% RH condition, and the results are presented in Figure 5-18. The by-products generated by PCO-A1, PCO-A, and O3-A increase as the iso-butanol challenge concentration increases, and there are few changes in the composition of by-products. Due to the low performances of NTP-C, low by-product generation rates are observed.



(a) iso-butanol at $178 \pm 4 \text{ m}^3/\text{hr}$, $20.7 \pm 0.2 \text{ }^\circ\text{C}$ and $44 \pm 2 \text{ \% RH}$



(b) iso-butanol at $174 \pm 11 \text{ m}^3/\text{hr}$, $20.5 \pm 0.2 \text{ }^\circ\text{C}$ and $25 \pm 2 \text{ \% RH}$

(c) toluene at $177 \pm 3 \text{ m}^3/\text{hr}$, $20.7 \pm 0.1 \text{ }^\circ\text{C}$ and $49 \pm 1 \text{ \% RH}$ (d) xylene at $180 \pm 5 \text{ m}^3/\text{hr}$, $20.9 \pm 0.1 \text{ }^\circ\text{C}$ and $23 \pm 1 \text{ \% RH}$ **Figure 5-17. Effects of challenge concentrations on removal efficiency.**

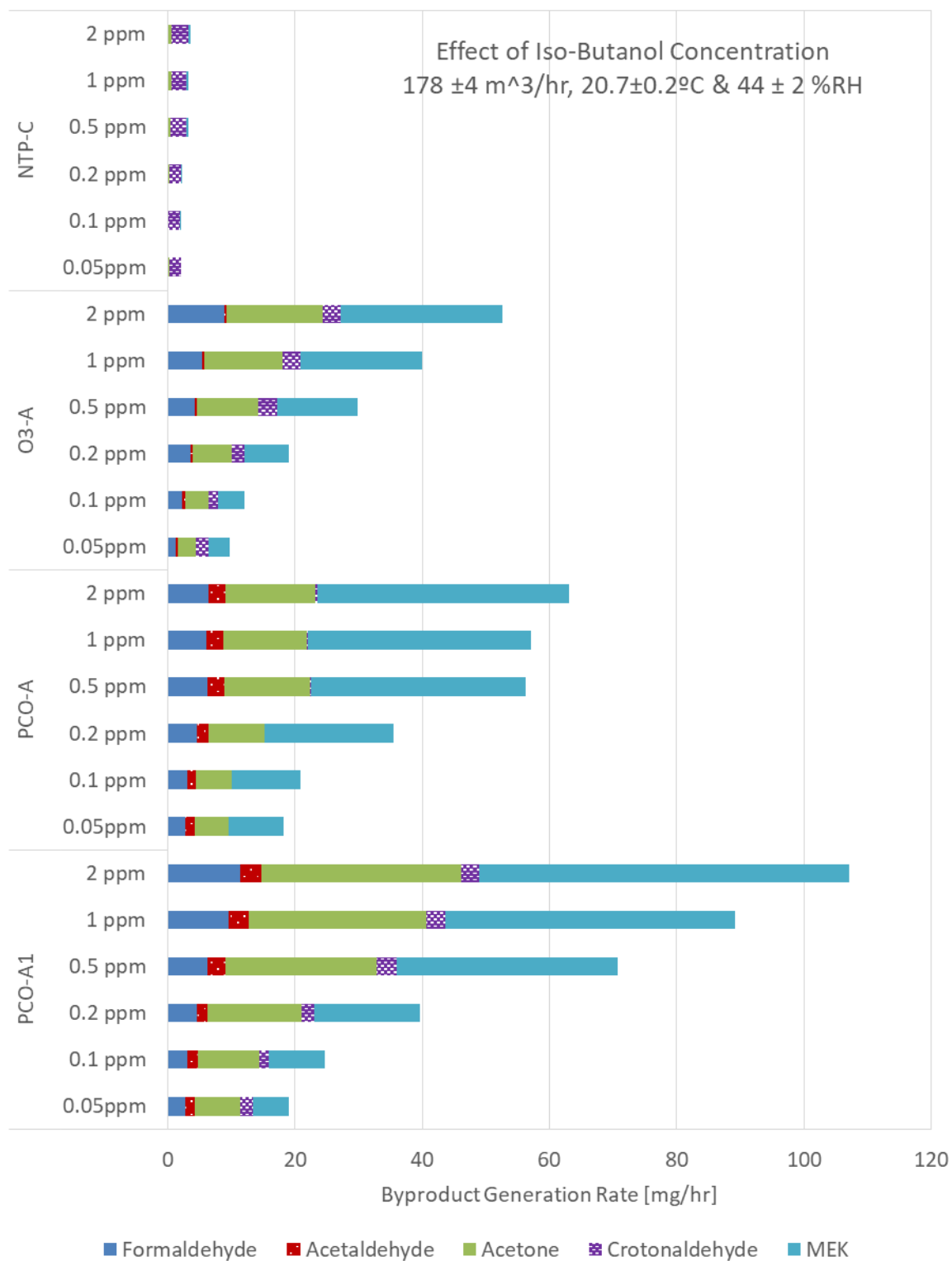


Figure 5-18. Effects of concentration on by-product generation: iso-butanol.

5.5 Effects of humidity level

As presented in Chapter 2, the humidity level can affect the performances of oxidation-based air cleaning technologies as water is necessary for the creation of hydroxyl radicals for VOC oxidation, yet excessive water can create unfavorable reaction conditions. As the humidity level in a building can affect the thermal comfort of the occupants, potential for mold growth and other indoor air quality-related issues, as well as activities and processes taking place in the building, there are recommended ranges for humidity. For example, the recommended relative humidity level in office buildings is 20% to 30% RH in winter, and 50% to 60% RH in summer (ASHRAE, 2015a). Since the 4-duct test rig uses filtered laboratory air as the carrier air and was not equipped with any active humidity control system, the tests conducted in different seasons have different humidity conditions in the ranges found in normal building operations. It should be noted that the test results reported here were obtained through testing in different seasons. The humidity level ranged between 20% and 60% RH.

Figure 5-19 presents toluene removal efficiency tested under three different humidity levels: $35 \pm 3\%$, $49 \pm 1\%$ and $58 \pm 1\%$ RH. The other test conditions are $176 \pm 4 \text{ m}^3/\text{hr}$ of airflow (or $0.53 \pm 0.01 \text{ m/s}$ air velocity) and $21 \pm 0.1^\circ\text{C}$. The effects of the humidity level are influenced by the challenge concentration. At 0.1 ppm of toluene, PCO-A1 and PCO-A performances are better at 35% RH compared to higher humidity levels; however, at 1 ppm, their performance peak is at 49% RH. Toluene removal efficiency of O3-A is lower at 35% RH and slightly increases at higher humidity levels; however, the absolute differences in removal efficiency are less than 4%. Due to the poor performances of NTP-A, it was impossible to observe the effects of humidity levels.

A wider range of RH was applied in o-xylene testing: 1) low at $21 \pm 2\%$ RH for 0.1 ppm testing and at $25 \pm 1\%$ RH for 1 ppm; 2) medium at $37 \pm 1\%$ RH; and 3) high at $60 \pm 1\%$ RH. The other test conditions are $179 \pm 4 \text{ m}^3/\text{hr}$ of airflow (or $0.54 \pm 0.01 \text{ m/s}$ air velocity) and $21 \pm 0.1^\circ\text{C}$. As shown in Figure 5-20, the effects of the humidity level are more appreciable in o-xylene. The removal efficiency of PCO-A1 and PCO-A decreases with increasing humidity at 0.1 ppm; however, the test results of 37% RH show the best performance at 1 ppm though the change with humidity is not significant. O3-A is less affected by humidity changes – the maximum difference in removal efficiency is 6.2%.

The test results of toluene and o-xylene indicate that PCO system performances are more affected by the humidity level. Contradictory effects of RH have been reported in the literature on PCO and these data were reanalyzed to compare with our results (Ao & Lee, 2003; Ao, Lee, Mak, & Chana, 2003; Einaga, Futamura, & Ibusuki, 1999; Jeong et al., 2005; Mo et al., 2013). To isolate the effects of RH from the influence of other parameters like reactor design and test conditions, the removal efficiency of different RH levels was normalized by the maximum reported removal efficiency under a specific RH condition given in each study. Since more studies are available for aromatic compounds, studies on toluene, benzene, and xylenes, were considered. As shown in Figure 5-21, two distinct trends were observed for non-polar aromatic compounds.

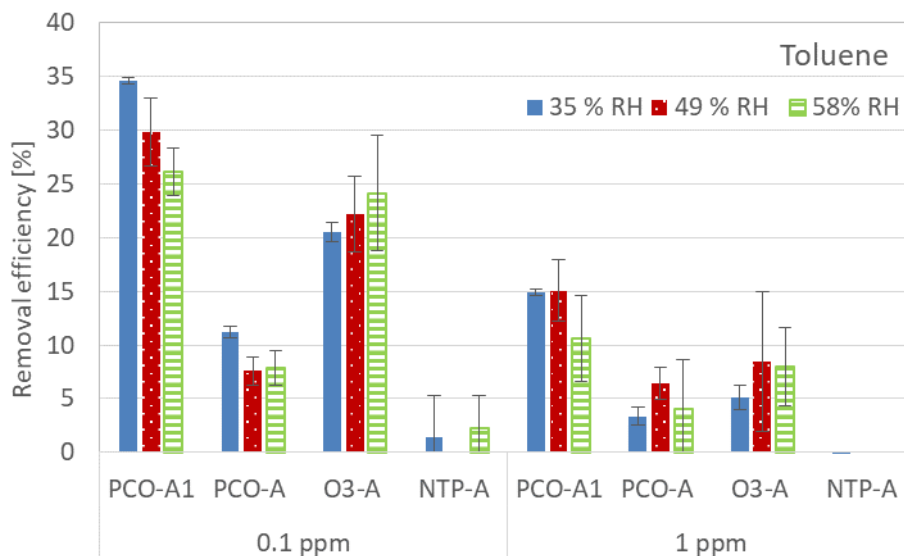


Figure 5-19. Effect of humidity levels on toluene removal efficiency.

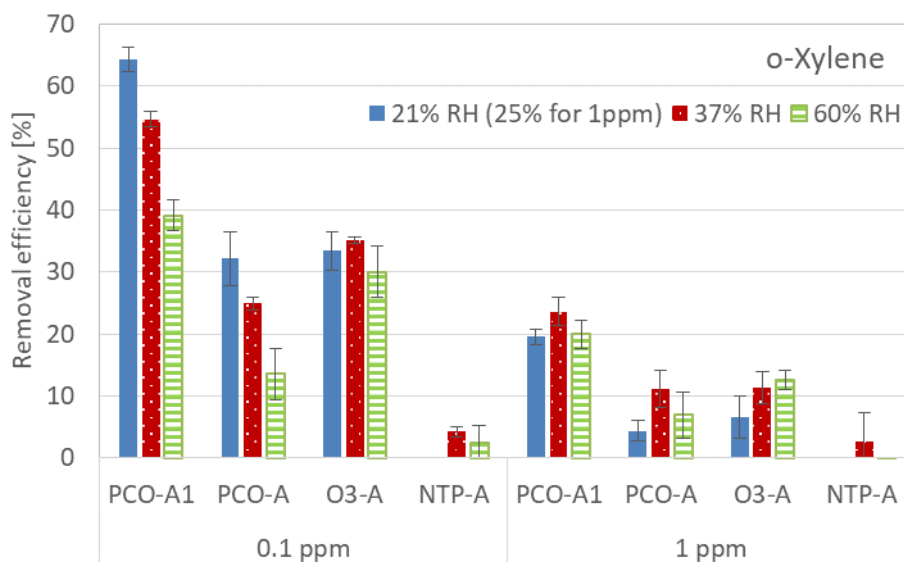
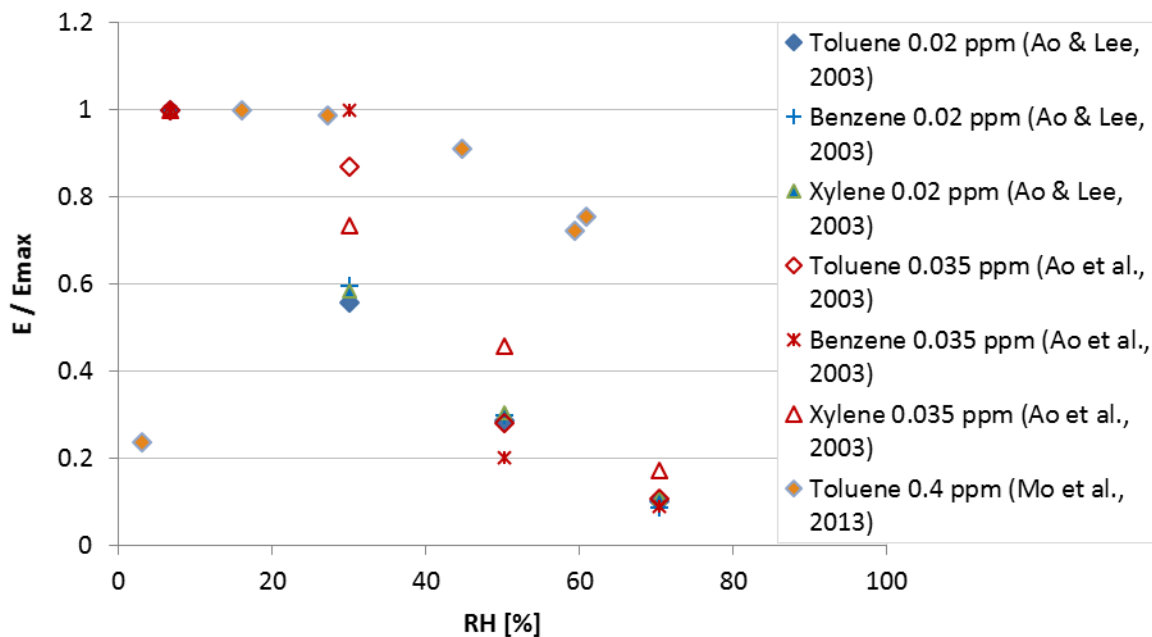
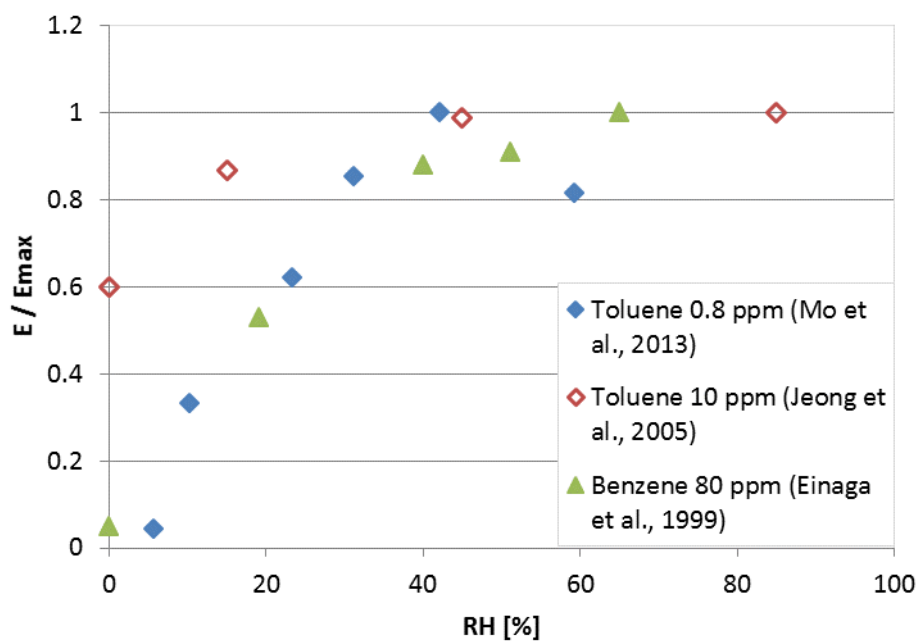


Figure 5-20. Effect of humidity levels on o-xylene removal efficiency.

When the challenge concentration is low, the highest efficiency is observed in low RH (usually 5-25% RH) and increasing RH resulted in decreased efficiency. At higher concentrations, efficiency tends to increase with RH increase. There are also other studies that show negligible effects of RH under low challenge concentrations because of the high removal efficiency of the tested PCO (Jo & Park, 2004; Mo et al., 2013). The toluene oxidation efficiency reported by Mo et al. (2013) shows that the optimal RH for a given concentration generally increases as the challenge toluene concentration increases.



(a) low challenge concentrations



(b) high challenge concentrations

Figure 5-21. Effect of relative humidity on removal efficiency normalized by the maximum efficiency (data compiled from the literature).

The effects of humidity levels on iso-butanol observed in the 4-duct rig are presented in Figure 5-22. The considered RH are $25 \pm 2\%$, $45 \pm 3\%$ for 0.1 ppm or $42 \pm 2\%$ for 1 ppm, and $59 \pm 1\%$ RH. The average test conditions are $178 \pm 7 \text{ m}^3/\text{hr}$ of air flow rate (or $0.53 \pm 0.02 \text{ m/s}$) and $21 \pm 0.2^\circ\text{C}$. The RH effects are different from the cases of aromatic compounds. The iso-butanol removal efficiency of PCO-A1 decreased more between 25% RH and 45% RH, compared to the change between 45% RH and 59% RH. In contrast, less effect of RH was observed for PCO-A. While O3-A showed minor changes in efficiency for aromatic compounds, humidity clearly adversely affects iso-butanol removal efficiency of O3-A. NTP-C showed decreasing efficiency by increasing humidity, but the change is non-significant. Higher RH can be favorable for hydroxyl radical formation, but at the same time, it can prevent contaminants from adsorbing onto the catalyst surface.

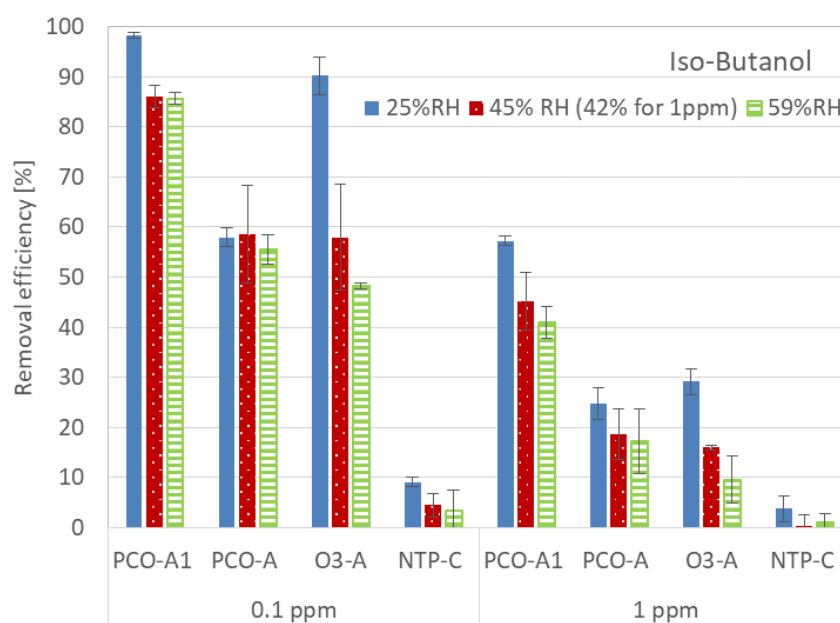
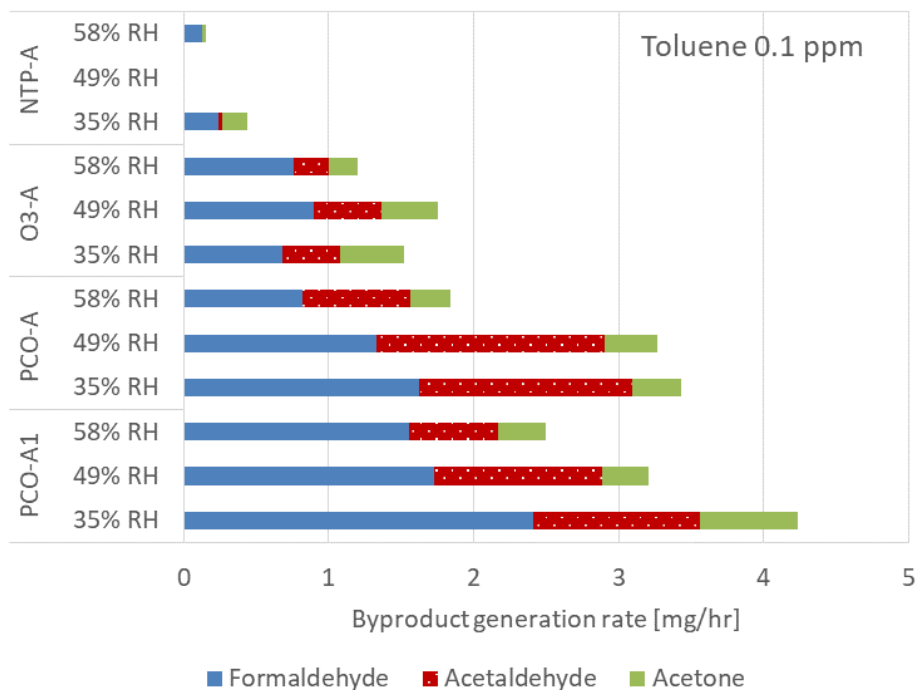


Figure 5-22. Effect of humidity levels on iso-butanol removal efficiency.

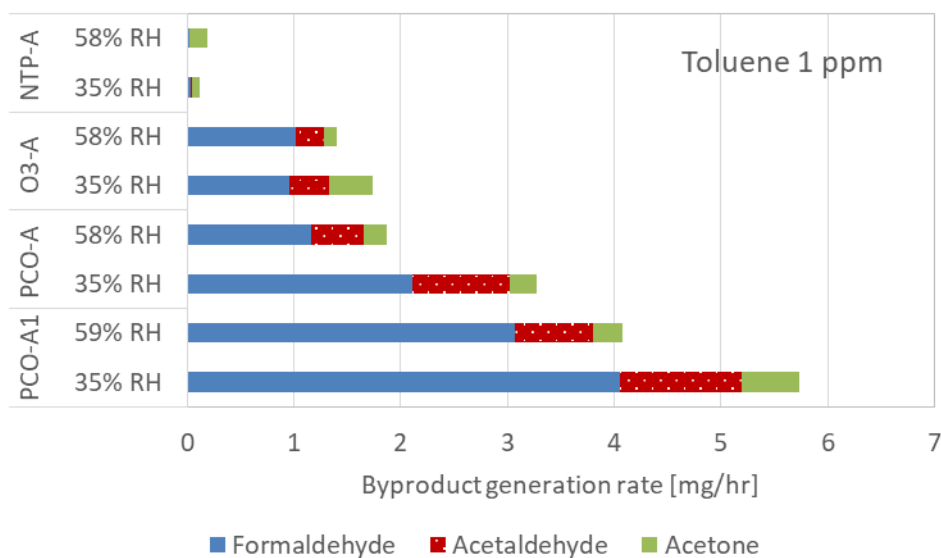
The by-products generated from toluene and iso-butanol testing are presented in Figures 5-23 and 5-24. The by-product generation rates for toluene tend to follow the removal efficiency patterns, showing generally higher by-product generation rates at lower RH. However, iso-butanol test results show different profiles. In 0.1 ppm of iso-butanol testing, 25% RH condition resulted in much lower by-product generation rates for PCO-A1 and PCO-A thanks to high removal efficiency. The by-product generation rates of 1ppm of iso-butanol tests are hard to be correlated with the efficiency data.

Standards for air cleaner testing normally require to be carried out at 50% RH condition and under elevated concentrations to accelerate the test. The different effects of RH under different challenge concentrations and the challenge VOC type can be an important aspect to consider in the development of proper PCO test standard. In general, more changes in the performances of oxidation-based air cleaning systems were observed in low to medium humidity ranges. Testing oxidation-based air cleaning technologies under real operation conditions would be ideal but complicated to execute. This study results indicate that the performances of oxidation-based air

cleaning systems are generally more sensitive to humidity under 40% RH. Therefore, low humidity conditions are better to be avoided as the standard test condition.

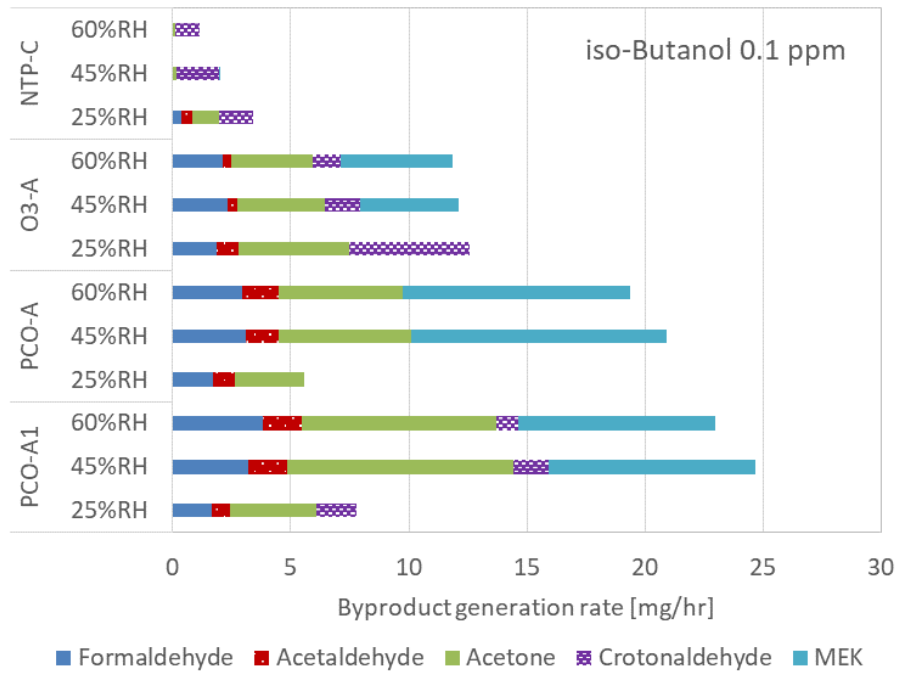


(a) toluene 0.1 ppm

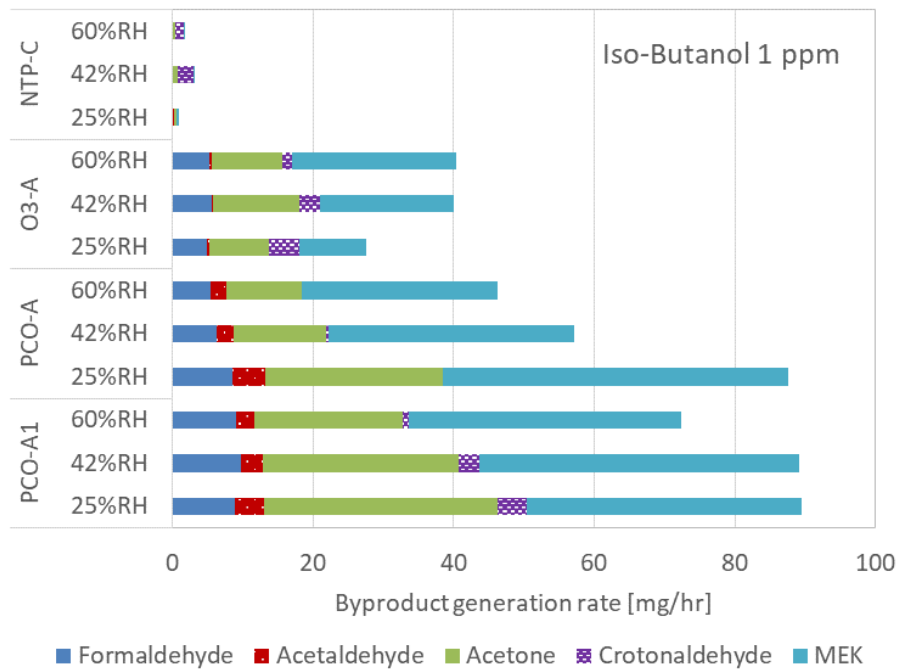


(b) toluene 1 ppm

Figure 5-23. Effects of humidity levels on by-product generation rates: toluene.



(a) iso-butanol 0.1 ppm



(b) iso-butanol 1 ppm

Figure 5-24. Effects of humidity levels on by-product generation rates: iso-butanol.

Throughout VOC removal testing, measurable effects of photocatalyst deactivation or soiling effects of UV lamps or plasma have not been observed. This may be due to generally low VOC conversion efficiency of commercial air cleaning units, clean filtered air supply in the test duct, and/or due to short test duration followed by desorption test period, which can act as a catalyst regeneration or system conditioning/cleaning. A field study on PCO systems by Hay et al. (2010) has shown that the main cause of PCO deactivation is because of the oxidation of silicon-containing compounds generated by the use of consumer products, building materials like sealants (Chemweno, Cernohlavek, & Jacoby, 2008; Hay et al., 2010; Lamaa et al., 2014). This effect is beyond the scope of this study, so long-term performances or deactivation of PCO were not considered. A decrease in UV output was observed by UV radiometer readings; however, to conduct the parametric study in controlled conditions, UV lamps were regularly replaced.

5.6 Ozone removal by PCO systems

Ozone is a toxic air pollutant and the application of ozone removing air-cleaning systems especially in air handling units is recommended to reduce exposure to indoor ozone and ozone reaction products. The use of ozone removal air cleaning devices with at least 40% efficiency is prescribed in the Ventilation Rate Procedure (VRP) in ASHRAE Standard 62.1-2016, when the ambient ozone level exceeds the design limit. Several studies have demonstrated the potential of ultraviolet photocatalytic oxidation (UV-PCO) in ozone removal (Cho, Hwang, Sano, Takeuchi, & Matsuzawa, 2004; He, Zhang, Yang, & Yang, 2006; Lin & Lin, 2008; Lu et al., 2014; Mills, Lee, & Lepre, 2003; Ohtani, Zhang, Nishimoto, & Kaglya, 1992). However, there is still a lack of information on the ozone removal performance of commercial UV-PCO systems. Though the main focus of this study is VOC removal, an additional experimental study was conducted to investigate ozone removal performance of three different commercial PCO (i.e., PCO-A, PCO-D and PCO-E) and one in-house PCO (PCO-F) under the same UVC light conditions. The effects of the number of PCO layers, challenge ozone concentration, relative humidity level, and air velocity on the ozone removal efficiency were also investigated.

Single-pass dynamic tests were carried out. The test procedure is as follows: first, the airflow of each test duct is set, and the background ozone levels were measured for at least 10 minutes. Then VUV lamps were turned on to introduce ozone into the test duct. Upstream and downstream ozone levels in three tested ducts were monitored for at least 15 minutes then UVC lamps in UV-PCO systems were turned on. The tests were carried out for at least 2 hours and the ozone levels were continuously monitored. During the whole test period, airflow rate, temperature, and relative humidity were observed. The tests were conducted at room temperature (i.e., 21 ± 1 °C) with different relative humidity levels (i.e., 30% - 60% RH) and air velocity (i.e., 0.122 - 1.04 m/s).

Prior to the main UV-PCO testing, ozone removal by photolysis of four UVC lamps and by adsorption on 3-layers of PCO-A were tested simultaneously. A total of six tests were conducted in various conditions of humidity, air velocity, and challenge ozone concentration. The efficiency of ozone decomposition through photolysis by 4 UVC lamps for the six tests varied between 1.6 and 6.4% with an average of 3.7%. Ozone removal efficiency by adsorption on PCO-A ranged from 3.6 to 8.1% with an average of 4.9%.

5.6.1 Ozone removal performances of different PCO systems

Three commercial PCO were installed in a 2-layer PCO setup in each duct and tested simultaneously at 0.554 ± 0.033 m/s of air velocity, $50 \pm 2\%$ RH and at two different ozone levels (i.e., 96 ppb and 143 ppb). The average ozone removal efficiency of all three commercial PCO was below 9%, as shown in Figure 5-25. These results are much lower than the minimum 40% of ozone removal efficiency required ASHRAE Standard 62.1-2016. The results are lower than Kadribegovic, Ekberg, Gillian, and Shi (2011)'s reported value of 15% single-pass ozone removal efficiency of a commercial UV-PCO system; however, their UV-PCO system was comprised of three PCO chambers. The overall ozone removal effectiveness in increasing order is PCO-E < PCO-D < PCO-A. Additional tests using PCO-A were carried out to investigate the factors affecting the ozone removal performance, which are presented in the following sections.

PCO-F, which was prepared in-house using activated carbon felt substrate, was installed identically in a 2-layer setup in two ducts, and simultaneously tested with and without UVC irradiation at 0.538 ± 0.02 m/s of air velocity, $56 \pm 2\%$ RH, and 184 ppb of challenge ozone concentration. Figure 5-26 presents the ozone removal efficiency profiles as a function of time for both cases of UVC on and off. Both profiles show more than 95% initial efficiency which slowly decreases with time. Under UVC irradiation conditions, the rate of decrease is lower than dark condition. After 2 hours, the difference in efficiency is more than 17%. Unlike the commercial PCO, PCO-F shows a much higher efficiency. Lu et al. (2014) also showed that TiO_2 coated on activated honeycomb carbon showed much higher ozone removal performance than TiO_2 coated on fiberglass cloth.

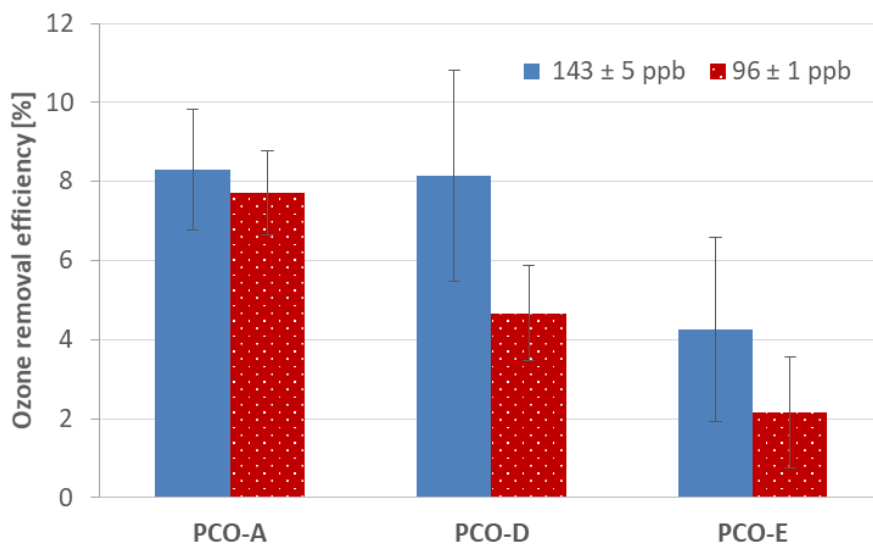


Figure 5-25. Ozone removal efficiency of commercial PCO in a 2-layer setup.

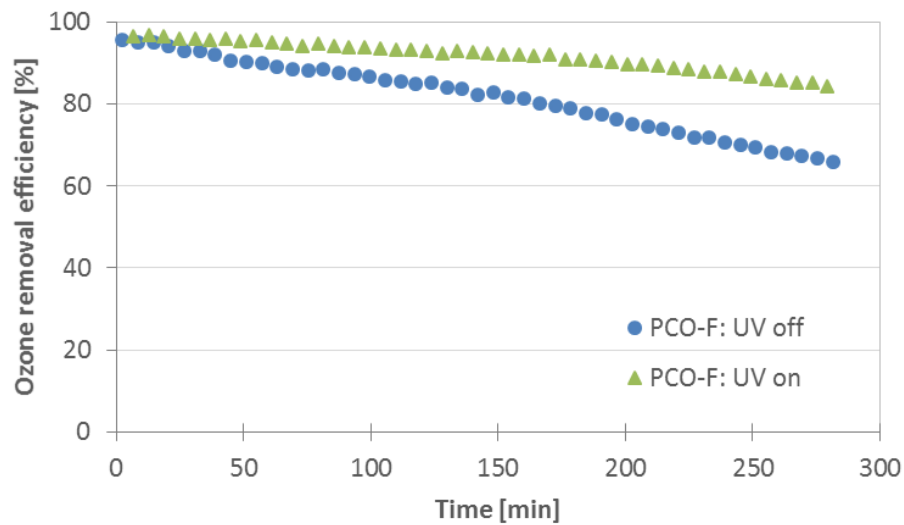


Figure 5-26. Ozone removal efficiency of PCO-F in a 2-layer setup.

5.6.2 Effect of the number of PCO layers

Seven tests were conducted under various conditions whereas 1, 2 and 3-layer setups of PCO-A were tested in parallel. Figure 5-27 presents the minimum, the maximum, and the average values of E_{2h} for each setup. As the number of PCO layers increases, the removal efficiency tends to increase. While the average efficiency of the 2-layer setup is more than double that of the 1-layer setup, increasing the number of PCO layers to three only increases the efficiency by 1%.

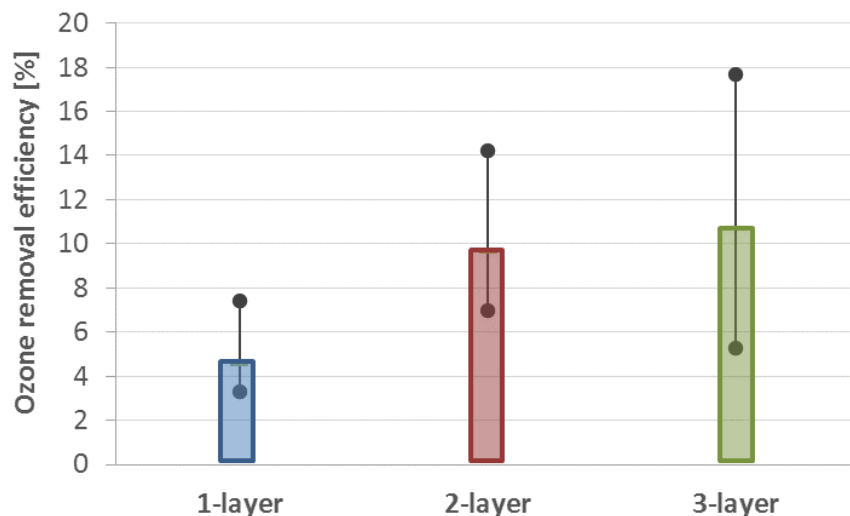


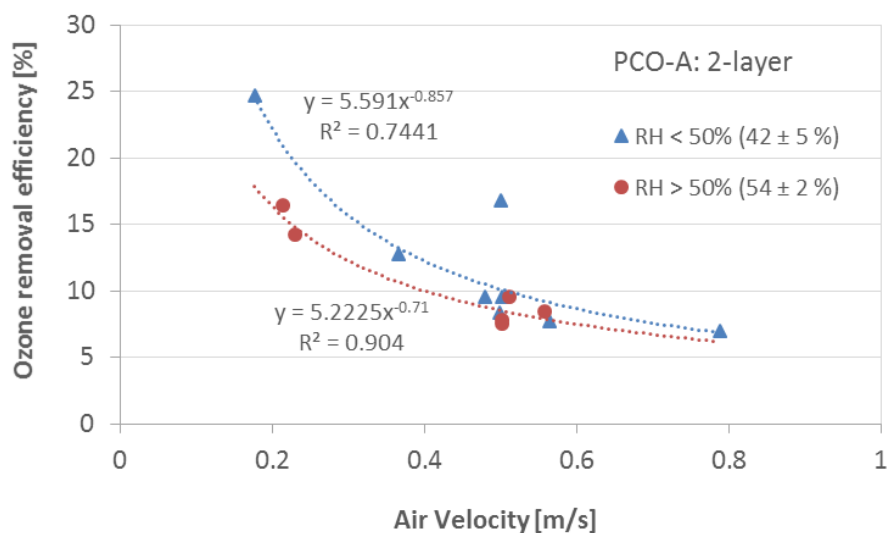
Figure 5-27. Effect of the number of PCO-A layers on ozone removal efficiency.

5.6.3 Effect of UV-PCO operational conditions

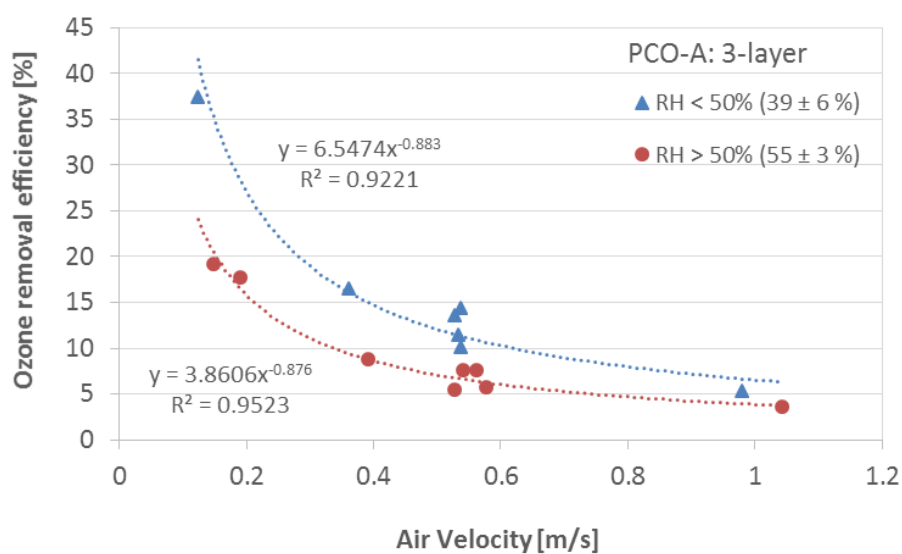
The influence of UV-PCO operational conditions like ozone concentration, air velocity, and relative humidity was tested using PCO-A in 2-layer and 3-layer setups. No clear effect of ozone challenge concentrations in the range of 85 ppb and 200 ppb was observed. Figure 5-28 shows the effects of air velocity on ozone removal efficiency under different humidity conditions. The efficiency decreases as air velocity increases, and the profile shows power law trend. When RH is greater than 50%, the efficiency tends to be lower. Cho et al. (2004) showed that ozone removal efficiency decreases rapidly for UV-PCO using pure TiO_2 at greater than about 45% RH, whilst platinum doped TiO_2 is unaffected. Pure TiO_2 is hydrophilic in nature and the adsorbed water can promote electron/hole recombination resulting in decreased PCO performance: in contrast, noble metal doping on TiO_2 may reduce the hydrophilicity and diminish the recombination (Cho et al., 2004). This indicates that pure TiO_2 is used in PCO-A, which agrees with EDS elemental analysis results.

From the ozone removal testing of UV-PCO systems, the following was found: UV-PCO systems using commercial catalysts showed poor ozone removal performance, which was much lower than the minimal 40% efficiency set by ASHRAE Standard 62.1-2016. In contrast, UV-PCO with in-house catalyst using fibrous activated carbon substrate showed 95% of 2-hour average efficiency. The significant difference in ozone removal performance can be originated from the difference in the adsorption capacity of substrates. However, as Ohtani et al. (1992) demonstrated, the crystal structure of TiO_2 itself can affect the performance. This needs to be investigated further.

A parametric study was conducted using the most efficient commercial PCO. Increasing the number of PCO layers increases the removal efficiency, but increasing from 2 layers to 3 layers resulted in minor improvements. No clear relationship between the challenge ozone concentration and the ozone removal efficiency was observed in this study. Increasing the air velocity lowers the removal efficiency, and it follows the power law trend. The tests conducted under greater than 50% of relative humidity showed lower ozone removal efficiency.



(a) 2-layer PCO-A



(b) 3-layer PCO-A

Figure 5-28. Effect of air velocity and humidity level on ozone removal efficiency.

6. RECOMMENDED FULL-SCALE TEST PROTOCOL AND RESULTS

The preliminary experimental methods for the evaluation of oxidation-based air cleaning systems developed and applied in 4-duct testing, underwent extensive testing and continuously improved. Based on the knowledge gained through the process and the parametric study outcomes, together with the consideration of existing air cleaner test standards presented in Chapter 1, a full-scale test protocol has been developed. This chapter presents the full-scale test protocol and the experiments which were conducted with it.

6.1 Recommended full-scale test protocol

Purpose

The purpose of this laboratory test protocol is to assess the performances of commercial or pilot in-duct air cleaning systems using oxidation-based technologies as the sole mechanism or as a part of combined mechanisms for VOC removal.

Scope

- This protocol prescribes a full-scale dynamic single-pass test method to evaluate in-duct air cleaning equipment installed in air handling units.
- This protocol applies to air cleaning equipment using oxidation-based VOC removal technologies, which generate active oxidizing agents like radicals, ozone, and ions generally through the utilization of electric or electronic devices. Oxidation-based VOC removal technologies include photocatalysts, plasma (thermal or non-thermal plasma) generators, ionizers, plasma catalysts, and ozone generators.
- The test protocol adopts the evaluation in two-tier challenge concentrations: One is considering indoor air quality applications, which are relevant to commercial, public, educational, and other buildings or spaces covered by ASHRAE Standard 62.1-2016. The other is for light industrial workplaces experiencing sub-ppm VOC levels. This standard may be applied to other workplaces with higher VOC levels; however, it may require a modification of the protocol including but not limited to challenge VOC concentrations, air sampling and analysis methods.
- Air cleaning performances are evaluated in terms of removal efficiency, Clean Air Delivery Rate (CADR), and toxic by-product generation rate, aiming at the application of test data in ventilation system design such as ASHRAE Standard 62.1-2016 indoor air quality procedure.
- The by-products generated after complete oxidation of VOC like carbon dioxide, carbon monoxide, and water molecules are not considered in this protocol due to their abundance and concentration variations in the air.
- Decreased output of oxidizing agents by the air cleaning systems and/or the soiling effects generally found after long-term use are not considered in this test protocol.

Applicable documents

This protocol was developed based on the following available standards:

- ANSI/ASHRAE Standard 145.2-2016 Laboratory Test Method for Assessing the Performance of Gas-Phase Air Cleaning Systems: Air Cleaning Devices, the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE, 2016b);
- Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes, Method TO-17, U.S. Environmental Protection Agency, EPA/625/R-96/010b (EPA, 1999a);
- Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Determination Of Volatile Organic Compounds (VOCs) In Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS), Method TO-15, U.S. Environmental Protection Agency, EPA 625/R-96-010b (EPA, 1997);
- Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC), Method TO-11A, U.S. Environmental Protection Agency, EPA/625/R-96/010b (EPA, 1999b);
- Volatile Organic Compounds (Screening): Method 2549, Issue 1, NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, National Institute for Occupational Safety and Health (NIOSH, 1996);
- ASTM Standard D5156-02-2016: Standard Test Methods for Continuous Measurement of Ozone in Ambient, Workplace, and Indoor Atmospheres (Ultraviolet Absorption), ASTM International, West Conshohocken, PA (ASTM International, 2016).

Test apparatus and apparatus qualification testing

The test protocol shall apply the full-scale test duct specified in ASHRAE Standard 145.2-2016 or an equivalent setup. The requisites for the test apparatus, equipment and qualification test methods, and criteria prescribed in ASHRAE Standard 145.2-2016 shall be followed as they are intended to attain repeatability within $\pm 10\%$ of the measured value for air cleaning of gas-phase air contaminants including VOCs. However, ASHRAE Standard 145.2-2016 is designed for the measurement of single compound removal performance without considering any by-product, which cannot be applied for oxidation-based air cleaning technologies.

Air sampling and analysis methods selected in this protocol shall be appropriate for identifying and quantifying challenge VOC and its oxidation by-products. The method detection limit shall be less than 5% of the challenge concentration.

Active air sampling using multi-sorbent tubes appropriate for the challenge VOC and its by-product, followed by thermal desorption combined with capillary gas chromatography and mass spectrometry (TD-GC/MS) complying EPA TO-17 method or other sampling and analysis methods that deliver equivalent analysis results (e.g., EPA TO-15 method), is recommended. When the list of oxidation intermediate/by-products is already established, other GC detectors like the flame ionization detector (FID), the electron capture detector (ECD), or the photoionization detector (PID) can be applied.

Considering low performances of some oxidation-based air cleaning systems, the accuracy of the gas monitoring method is recommended to be enhanced by taking the following precautions:

- Ozone can be produced at high concentration by oxidation-based air cleaning technologies. The influence of ozone on air sampling and artifact generation shall be evaluated and reported.
- It is recommended to monitor the sampling flow rate during the entire sampling duration.
- It is recommended to use an automated gas-phase standard internal option in the thermal desorber to introduce the internal standard onto the sorbent tube before primary (tube) desorption for TD-GC/MS analysis system integrity.
- Dry purge of sample tubes prior to primary thermal desorption of tube is normally applied to control the interference of water in the sample. Since intermediates and by-products of VOC oxidation process generally have higher water solubility, loss of these compounds during dry purge shall be evaluated.

Ozone, formaldehyde, and acetaldehyde are major toxic by-products that can be generated in abundance by oxidation-based air cleaning technologies. The ozone analyzer shall have a minimum accuracy of 2 ppb or 2% of reading. VOC interference in ozone monitoring shall be examined to be an acceptable level (i.e., less than 5% of reading). If not, another sensor technology shall be applied.

Formaldehyde, acetaldehyde, and other aldehydes and ketones shall be sampled using 2,4-dinitrophenylhydrazine (DNPH) containing cartridges coupled with potassium iodide (KI) ozone scrubber, followed by High Performance Liquid Chromatography (HPLC) analysis using UV/Vis detector as per EPA TO-11a. To ensure the sufficient collection of analytes, it is recommended to collect at least 90 liters of air samples.

The detection limits of the challenge VOC and its organic by-products shall be less than 1 ppbv. Among by-products, ozone, formaldehyde, and acetaldehyde shall be measured and reported. The other by-products measured above the detection limit should be reported.

Test conditions

The test conditions are as follows:

- Temperature: 23 ± 2 °C
- RH: $45 \pm 5\%$
- Airflow: design airflow specified in the product specification $\pm 5\%$, if unspecified at 1700 ± 85 m³/hr

Challenge VOC and concentrations

The exemplary challenge VOC for providing comparative performance data of different oxidation-based air cleaning devices is iso-butanol. In ASHRAE Standard 145.2-2016, toluene is the required test gas in VOC category. To offer a potential comparison with other air cleaning technologies like adsorbent media, toluene is selected for exemplary challenge VOC. Toluene testing shall be applied especially for an oxidation-based air cleaning system combined with

adsorbent media. Another VOC can be selected for testing; however, ozone interference in the sampling shall be evaluated.

Two-tier challenge concentrations shall be applied:

- 1) 0.1 ± 0.005 ppm for IAQ applications
- 2) 1 ± 0.05 ppm for light industrial applications

The above test conditions shall be maintained constant throughout the whole test period.

Test procedure and data analysis

Prior to the testing, air cleaning devices shall be contained in the original packaging and stored in a clean storage room without any strong air pollution sources or VOC. The test procedure is as follows:

- 1) **Installation and preconditioning:** Install the air cleaning device to be tested in the test section. If a PCO unit is tested, UV lamp(s) or other design light source should be turned on to precondition the PCO for 1 hour, then, the lamp shall be turned off.
- 2) **Start-up:** Turn on the data acquisition system, then turn on the fan and adjust the flow rate. Monitor the temperature and the humidity level. If necessary, turn on the humidifier and wait until the required temperature and humidity conditions are achieved.
- 3) **Background monitoring:** Start direct reading from the challenge gas analyzer connected to the upstream sampling port and from the ozone monitor connected to the downstream sampling port, and measure the background concentrations for a minimum of 30 min.
- 4) **Preparation for VOC injection:** Adjust the compressed air flow rate through VOC injection port to be sufficient to evaporate the injected VOC. For the exemplary VOCs, 30 l/min of airflow is sufficient. Challenge VOC is filled in the gas-tight syringe and installed in the automatic syringe pump.
- 5) **Low concentration VOC injection start:** When the experimental conditions become stable, start the injection of the challenge VOC at a lower injection rate and continue the monitoring of the direct-reading VOC analyzer to ensure the stability of challenge VOC concentration.
- 6) **Activation of test air cleaning systems:** After 10 minutes of VOC injection, turn on the test oxidation-based air cleaning device.
- 7) **Air sampling in low concentration test:** Wait for UV output to become stable for about 5 minutes, and then start air sampling. Upstream and downstream samples shall be taken simultaneously. Minimum triple sets of air samples for challenge VOC shall be taken with an even sampling interval. Take one set of DNPH sampling for by-product measurements due to the requirement of a long sampling duration. At least 25% of duplicate samples shall be taken. The low concentration test should be carried out for a minimum of 2 hours.
- 8) **Regeneration period and desorption sampling:** Stop the VOC injection for the low concentration test for one hour to prepare for the high concentration test; this period should provide the opportunity to regenerate PCOs for the high concentration test. When UV-PCO systems are using porous substrates (i.e., the specific surface area of the substrate is

greater than 50 m²/g), take air samples to measure any generation of challenge VOC and other by-products desorbed from the photocatalyst.

- 9) **High concentration VOC injection start:** Start the VOC injection for the high concentration testing. Check the upstream VOC readings of the direct-reading VOC analyzer until the target challenge VOC concentration is reached.
- 10) **Air sampling in high concentration test:** Once the target VOC is reached, start air sampling in the same manner as for the low concentration test.
- 11) **Desorption sampling:** To measure the challenge of VOC or other reaction intermediates released from PCO, conduct the air sampling for 1 hour after stopping the VOC injection.
- 12) **Switch-off test air cleaning systems:** Turn off the test air cleaning systems and observe the direct-reading VOC analyzer and the ozone monitor while they are returning to the background levels.
- 13) **Finish-up:** Transfer the collected data and shut down all the test systems and equipment. Seal and store the air samples.

The performance of an oxidation-based air cleaning device shall be evaluated in terms of challenge VOC removal efficiency, clean air delivery rate (CADR), and by-product generation rate, as defined in Chapter 3.

6.2 Full-scale test results and discussion

For applying the developed full-scale test protocol, 14 different commercial in-duct air cleaning systems using oxidation-based air cleaning technologies were tested. The tested systems can be divided into 7 PCO systems, 3 systems using PCO combined with adsorption-based scrubbers, 2 ozone generators, and 2 non-thermal plasma units. The details of the tested systems are presented in Chapter 3. The ozone generation was 207 ± 4 ppb for PCO-1; 190 ± 3 ppb for PCO-2; 213 ± 4 ppb for PCO-3; and 439 ± 12 ppb for PCO-Af1. The other PCO systems did not generate ozone.

This is to examine the suitability of the developed full-scale test protocol, and to investigate the performances of commercial units in VOC removal tested in full-scale setup. The tests were conducted in the recommended conditions – for iso-butanol and toluene at 0.1 ppm and 1 ppm with 1697 ± 9 m³/hr of the flow rate at 23.3 ± 0.6 °C and 45 ± 3% RH. For the given condition, the iso-butanol removal efficiency of both plasma units was less than 1%; therefore, plasma units were not studied further.

Figure 6-1 presents the iso-butanol removal efficiency of 7 different PCO units. PCO-Af1 has the highest removal efficiency for both challenge concentrations; since it has the highest ozone generation, there were more combined effects of photocatalysis and ozonation. Generally, PCO with ozone generating VUV lamps (PCO-1 to PCO-3 and PCO-Af1) have higher performances. However, photocatalyst type “A”, which showed the best photocatalytic performances among commercial PCOs tested in 4-duct testing, showed similar performances as PCO-3. While all other PCO units show a clear decrease in removal efficiency at 1 ppm, PCO-4 and PCO-4a showed little changes probably due to their low photocatalytic activity.

The manufacturer of PCO-2 normally installs a scrubbing system using v-shaped modules filled with granular activated carbon (GAC) in the downstream of PCO. The manufacturer of PCO-4 uses combination panel filters, which are comprised of fine granules of activated carbon and permanganate alumina sandwiched between fibrous filter media. Two different types of 2.5 cm thick panel filters were supplied, so these were tested with PCO-4 and denoted as PCO-4+Sc1 and PCO-4+Sc2. Figure 6-2 presents the performance of PCO alone and combined with scrubbers. GAC applied with PCO-2 significantly improved iso-butanol removal efficiency, up to more than 85%. Considering the amount of carbon used (i.e., a total about 0.1 m³), close to 100% efficiency was expected. When the scrubber modules were installed, only the sealing mechanisms provided by the manufacturer were applied without any additional gasket. This may have caused some bypass between the modules and the test section door, resulting in removal efficiency of about 85%. The panel filters applied with PCO-4 showed improvement in removal efficiency but the increase was not as significant as with GAC because the amounts of adsorbent media in panel filters were much smaller than that of GAC. PCO-4+Sc2 showed much better efficiency than PCO-4+Sc1. By visual inspection, two panel filters looked similar. Since no product information was provided by the manufacturer, the difference cannot be explained. As shown in Figure 6-3, the CADR calculated for the tested PCO systems varies significantly.

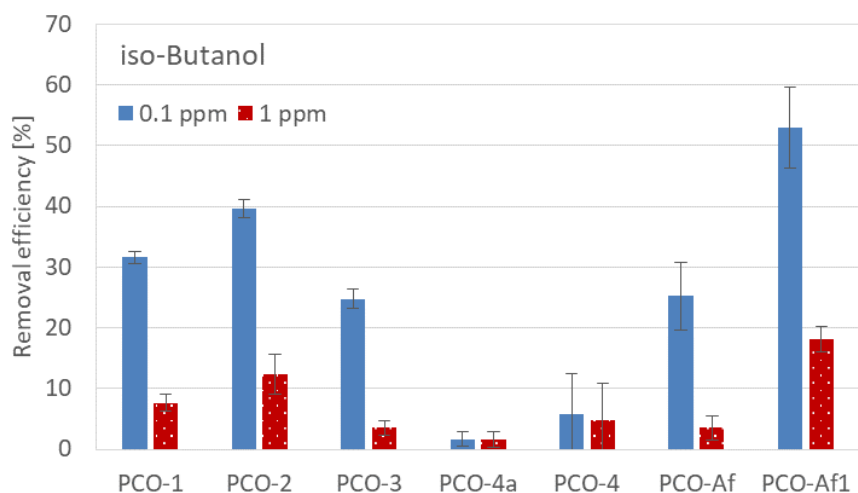


Figure 6-1. Iso-butanol removal efficiency of PCO systems.

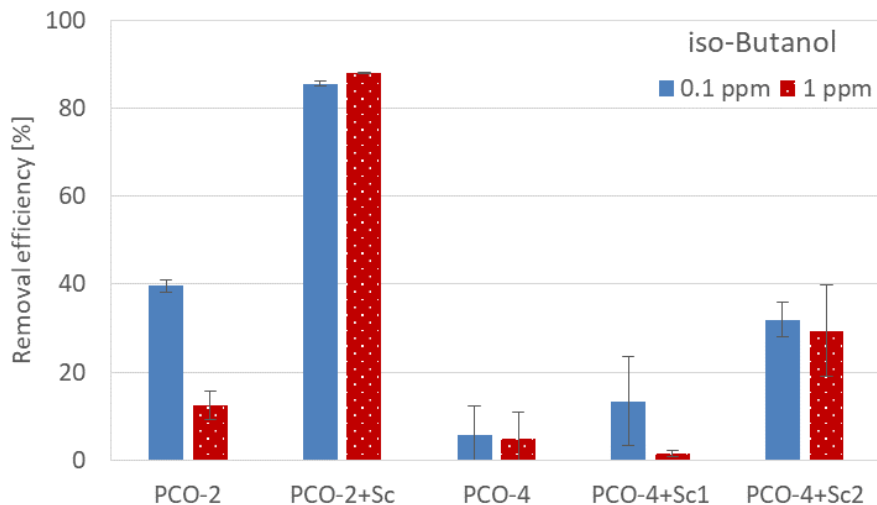


Figure 6-2. Effect of scrubbers on iso-butanol removal efficiency.

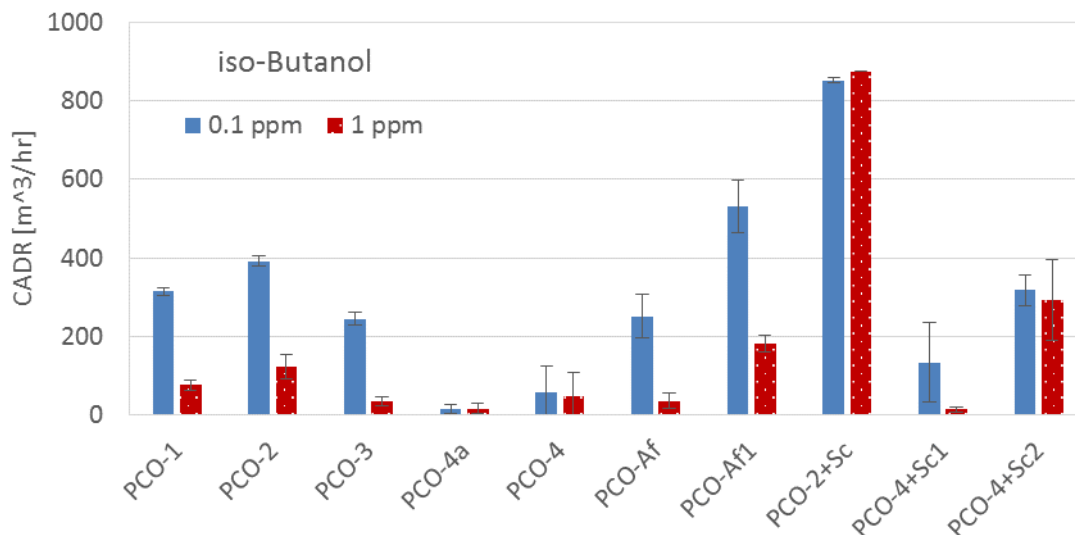


Figure 6-3. Clean Air Delivery Rate (CADR) of PCO systems: iso-butanol.

Figure 6-4 presents the by-products generated by the tested PCO systems and PCOs with scrubbers during iso-butanol testing. In all cases, by-product generation rates are higher at 1 ppm. Considering PCO-only systems, the by-products tend to be generated more when the removal efficiency is higher, except for PCO-Af. PCO-Af efficiency is similar to the one of PCO-C; however, twice or more by-products were generated by PCO-Af. Applying a GAC scrubber in PCO-2 has reduced the by-product generation rates as GAC removed them. Acetone and formaldehyde concentrations were even lower than the upstream concentrations, resulting in negative values in generation rates. The ozone generation was also reduced from 190 ± 3 ppb to 9 ± 2 ppb as GAC removed ozone as well. In contrast, both panel filters applied with PCO-4 have not shown much reduction in by-product generation rates. These results are unexpected because permanganate

alumina media are considered to be effective in removing light compounds that are difficult to be removed by activated carbons (ASHRAE, 2015a). Using permanganate media is a common practice in the air cleaning industry for the removal of light aldehydes and ketones, like the by-products found in this study. Since complete oxidation by PCO unit is not expected, air cleaning equipment manufacturers often select activated carbon and permanganate media blends to remove unconverted VOC along with by-products. The results obtained in this study show the need for further investigation on the effectiveness of this practice.

Figure 6-5 shows the toluene removal efficiency of all PCO-related devices. The efficiency of the systems using PCO alone is less than 12%. This may indicate that iso-butanol testing should be conducted first and if the iso-butanol removal efficiency is less than 50%, there is no need for toluene testing for the purpose of comparative testing among different products. PCO-2+Sc shows slightly better efficiency for toluene compared to iso-butanol, since activated carbons are generally non-polar so non-polar compounds like toluene adsorb better. Like iso-butanol test results, PCO-4+Sc2 shows a better performance than PCO-4+Sc1.

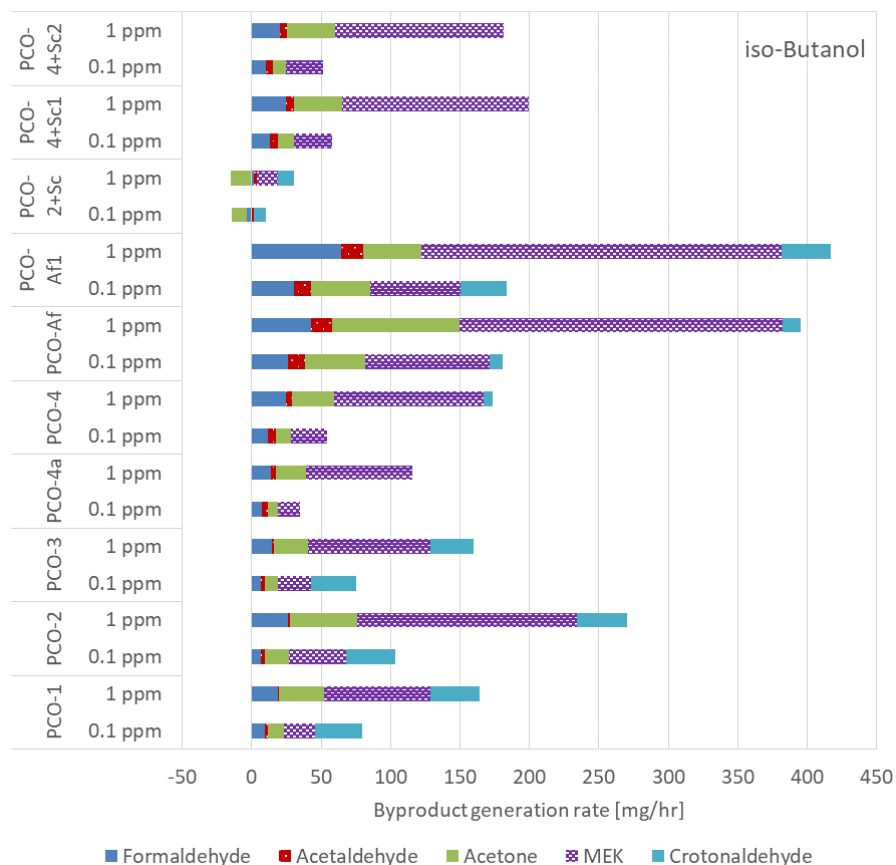


Figure 6-4. By-product generation rates of PCO systems: iso-butanol.

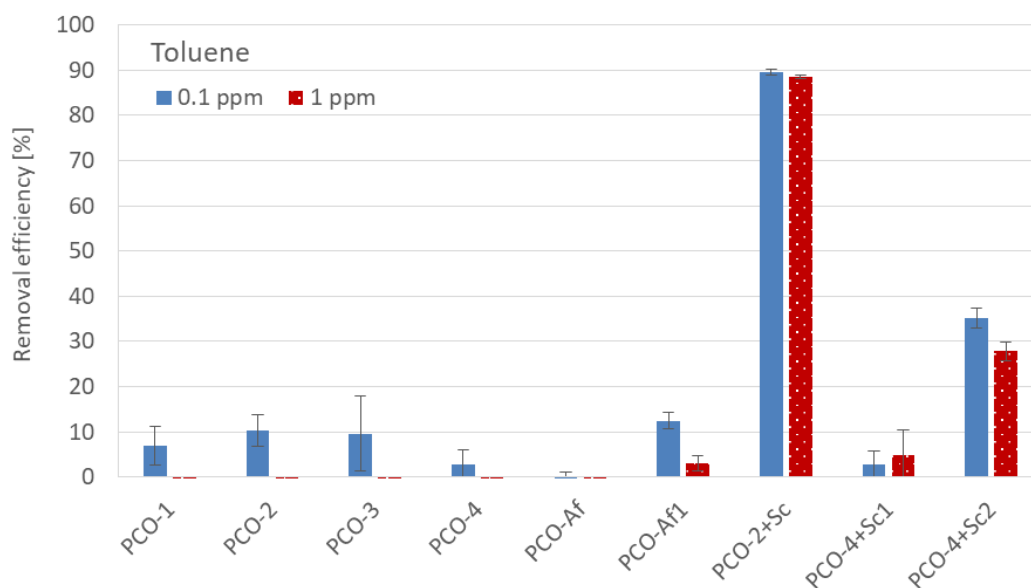


Figure 6-5. Toluene removal efficiency of PCO systems.

Due to low removal efficiency in toluene testing, the by-product generation rates are lower as shown in Figure 6-6. PCO-Af and PCO-Af1 tend to generate more formaldehyde compared to other systems, which is a concern. Also, PCO systems with ozone-generating VUV lamps generally generate more crotonaldehyde, which is rarely reported as a by-product of toluene oxidation. Farhanian and Haghghat (2014) have reported the generation of crotonaldehyde from UV-PCO testing of toluene; however, the possible reaction pathways have not been identified. GAC scrubber applied with PCO-2 decreases the by-product generation rates like iso-butanol test results. However, both panel filters applied with PCO-4 showed no removal performances for the by-products.

During the desorption test period, all tested PCO systems and PCO with scrubbers show no desorption of challenge VOC, except PCO-4+Sc2. As shown in Figure 6-7, iso-butanol was desorbed from PCO-4+Sc2 after 1 ppm challenge testing. Toluene is also desorbed; however, in a much smaller amount. This can be a concern when adsorbent media are applied with oxidation-based air cleaning technologies as a part of a complete air cleaning system. Figures 6-8 and 6-9 show the by-products generated during desorption periods. The generation of by-products is more significant in PCO systems with VUV lamps.

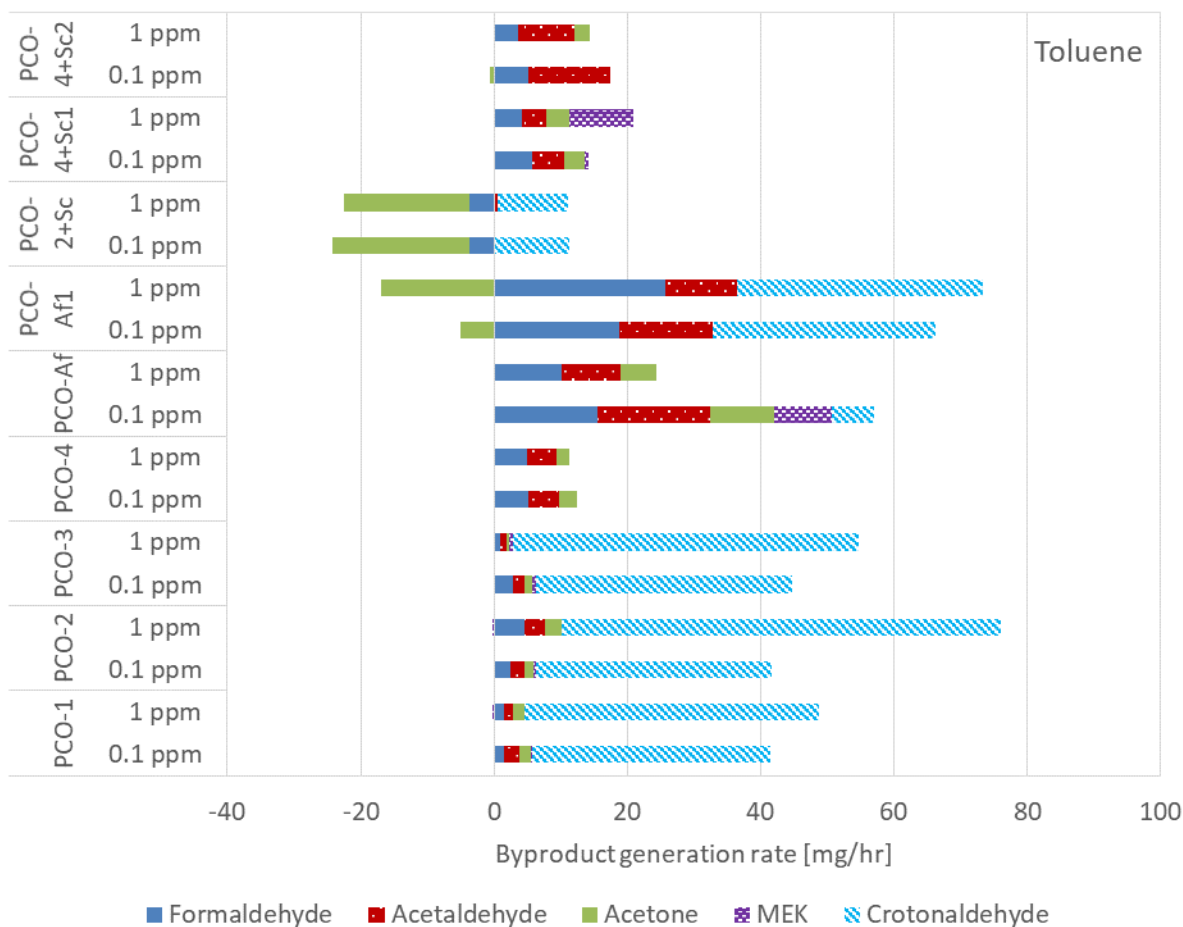


Figure 6-6. By-product generation rates of PCO systems: toluene.

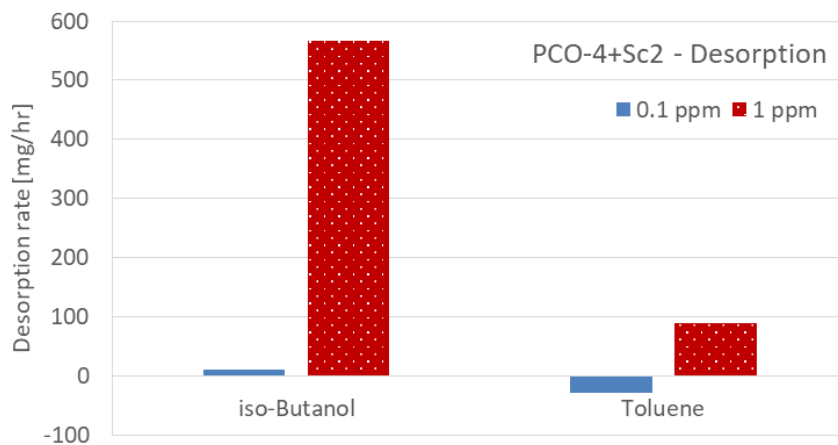


Figure 6-7. Desorption of challenge VOC by PCO-4+Sc2.

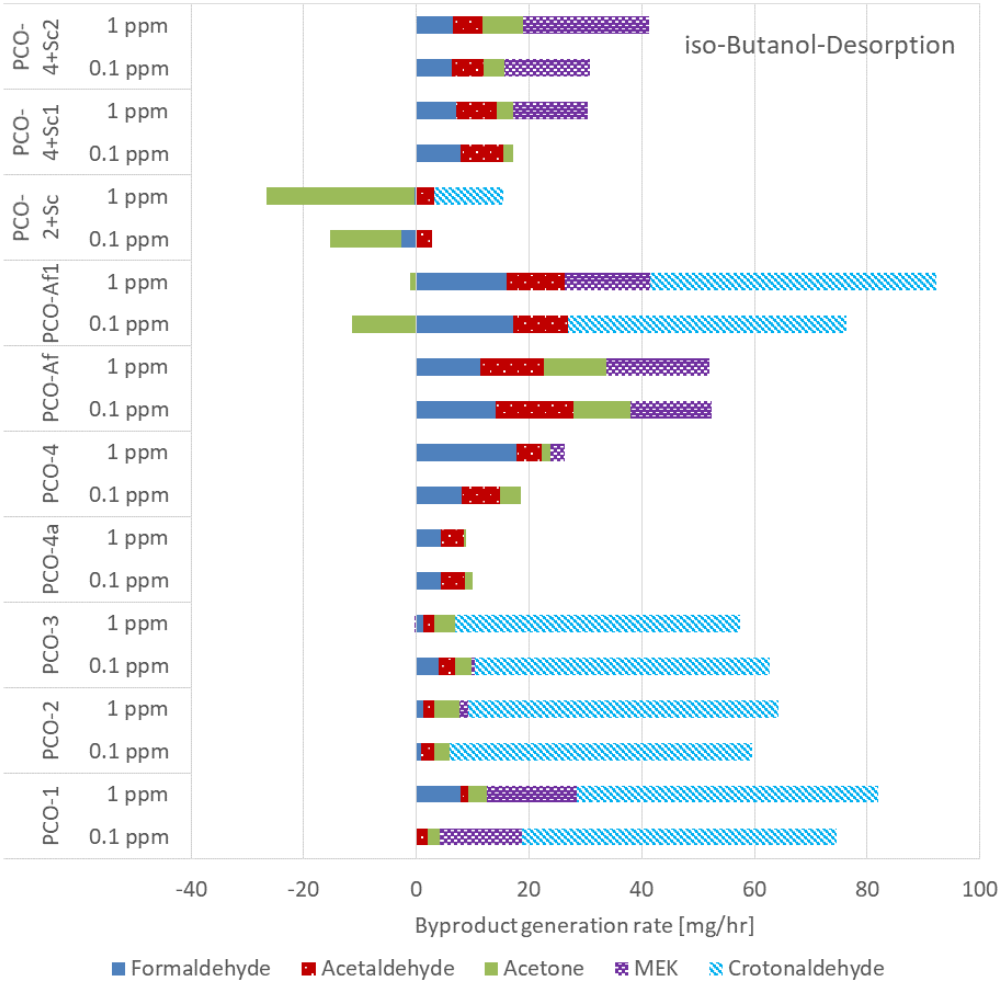


Figure 6-8. By-product generation rates during iso-butanol desorption testing.

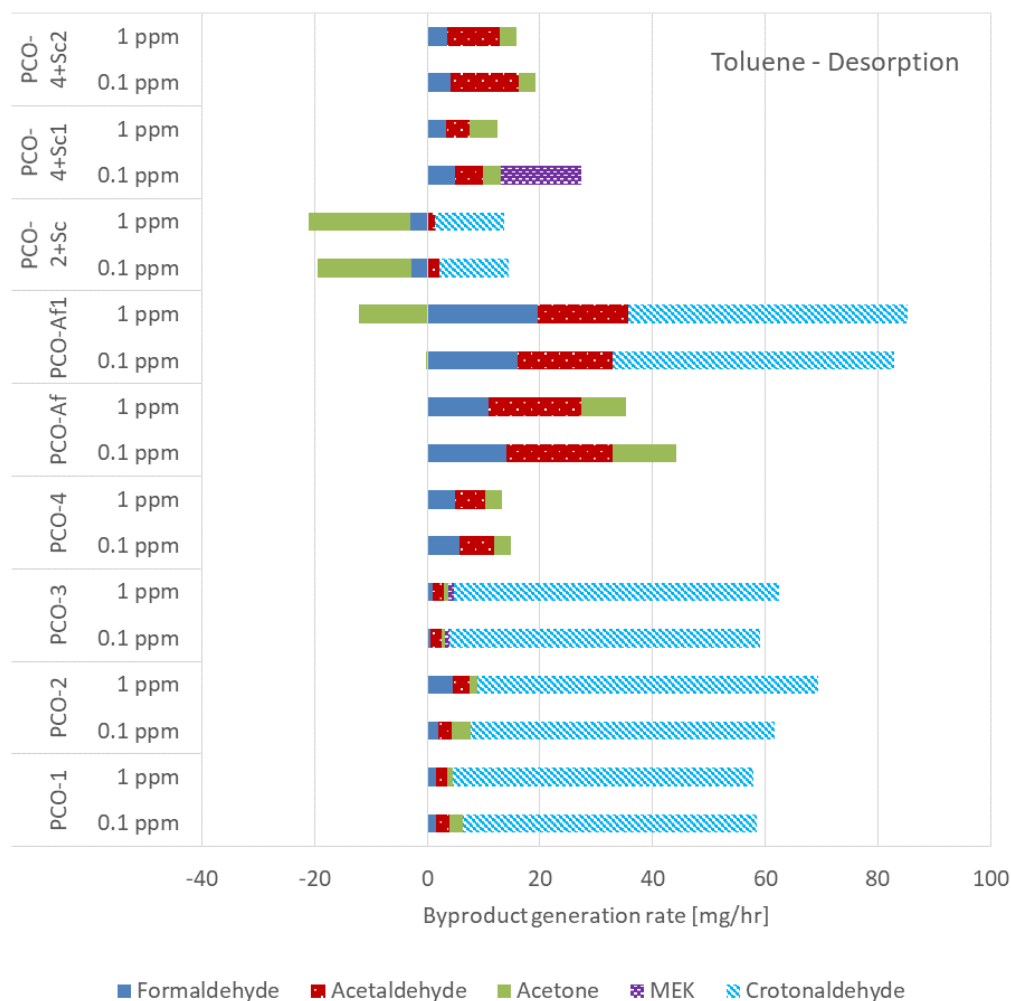


Figure 6-9. By-product generation rates during toluene desorption testing.

Two different ozone generating systems were tested: O3-1 comprised of 2 UVC lamps and 2 VUV lamps, and O3-2 has 4 VUV lamps. The ozone generation was 300 ± 9 ppb for O3-1 and 546 ± 13 ppb for O3-2. Compared to the differences in ozone generation levels, the differences in removal efficiency are small (i.e., less than 6%) as shown in Figure 6-10. Higher removal efficiency in iso-butanol testing resulted in more by-product generation (Figure 6-11).

The full-scale test results indicate that the proposed full-scale test protocol can capture different characteristics in the performances of different systems except for NTP units, which showed poor performances throughout the study. For the other systems, the proposed testing protocol can be sufficient enough to be applied as a ranking test. Also, the measured performances can be directly applied in the mass-balance analysis required in the ventilation design using IAQP of ASHRAE Standard 62.1-2016. Since a limited number of NTP units were tested in this study, more research is needed to understand NTP performances.

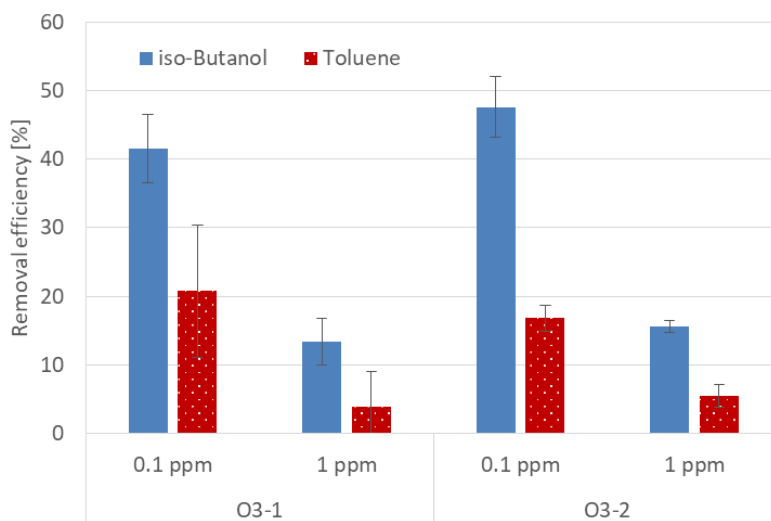


Figure 6-10. Performance of ozone generators.

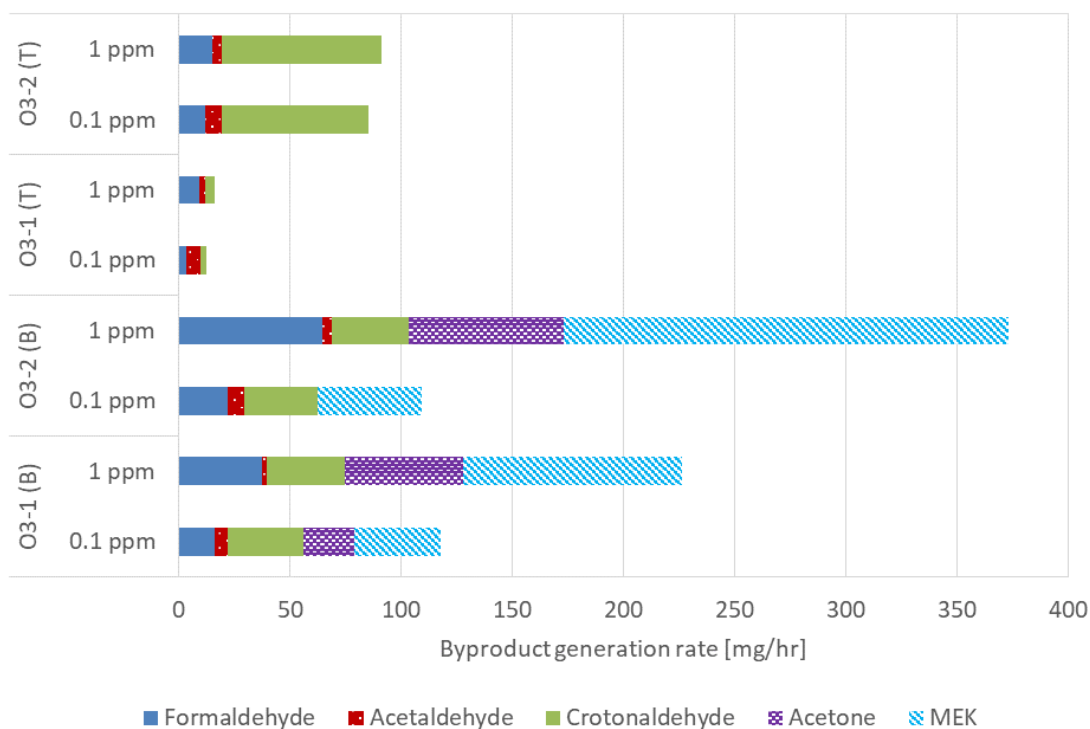


Figure 6-11. By-product generation rates of ozone generators: (B) iso-butanol and (T) toluene.

7. CONCLUSIONS AND RECOMMENDATIONS

Volatile organic compounds (VOCs) are a major gaseous contaminant group affecting the health of the workers operating not only in manufacturing or industrial setups, but also in non-industrial environments like offices, schools, retail, etc. Indoor VOC levels are generally higher than outdoors, and VOC is one of the identified causal factors for Sick Building Syndrome. Considering the fact that the majority of Quebec labor forces are in service sectors working in non-industrial settings, reducing VOC exposure in such environments is an important workers' health issue.

Various technologies have been applied for the removal of VOCs. There are conventional systems based on the adsorption process, i.e., activated carbon and/or potassium permanganate alumina pellets in trays or deep beds, particulate filters incorporating very thin beds of activated carbon or alumina pellets, and carbon cloth. These adsorption-based technologies have long been used in wide range of applications, so their performance and their efficiency under various conditions are well researched and understood. Standard test methods like ASHRAE Standards 145.1-2015 and 145.2-2016 are available for adsorption-based technologies.

There are other technologies applied in electronic air cleaning systems such as UV, UV with photocatalysts, non-thermal plasma, and ozone generators, which utilize oxidation mechanisms for the removal of VOCs. While the adsorption-based technologies transfer the air pollutants into adsorbents which need to be changed regularly, oxidation-based technologies can decompose the pollutants thus lessening the maintenance demands. This, along with generally lower flow resistance given by these systems, allows for a quick penetration of the market by air cleaning devices using oxidation-based technologies. However, there is no consensus on how to evaluate these air cleaning systems that are directly applied in air handling units (AHU).

This study focused on developing a reliable test protocol for in-duct oxidation-based air cleaning systems through a proper understanding of the overall performances of these systems. Simulating their applications in AHU, dynamic single-pass tests were conducted extensively in a four-parallel-duct test setup, which allows simultaneous evaluation of four different air purification systems under identical conditions.

In total, 18 different configurations of oxidation-based air cleaning units were tested in a 4-duct test rig. These include 12 different commercial PCO units, one in-house pilot PCO, 3 plasma and 2 ozonation units under 100% output (i.e., 430 ppb and 1300 ppb of ozone). Sixteen of them were tested for the removal of 0.1 ppm methyl ethyl ketone (MEK) and the single pass removal efficiency varied from 0 to 37%. Ozonation, PCO using ozone generating vacuum UV lamps tend to show a higher efficiency than PCO with non-ozone generating UVC lamps or plasma units. Formaldehyde, acetaldehyde, and acetone were the oxidation by-products detected in MEK testing. PCO-based systems tend to generate more by-products. Through acetone removal testing for PCO systems, it was found that acetone is not suitable as the challenge VOC in large-scale dynamic testing, because acetone can be generated as a by-product from other trace levels VOCs present in the carrier air.

Based on these test outcomes, we selected four units using different technologies: PCO-A for pure PCO technology, PCO-A1 for a combination of PCO and ozonation technologies, O3-A for ozonation, and NTP-A (or NTP-C) for plasma. From the parametric study conducted using the selected four systems, the following findings are worth mentioning:

- From toluene removal testing at different air velocities, increasing air velocity showed a decrease in removal efficiency, because increasing air velocity reduces the residence time required for oxidation reactions between air contaminants and oxidizing agents generated by the air cleaning systems. However, no clear trends were observed in by-product generation rates. It was also found that the performances of PCO-A1 and O3-A were more sensitive to air velocity changes, and pseudo-first order reaction can be applied.
- The selected units were tested for 6 different VOCs: n-hexane, n-octane, toluene, o-xylene, styrene, and iso-butanol. These were tested as single challenge gas, not as a mixture. The test results showed that the removal efficiency and the by-product generation patterns of an air cleaning unit differ substantially depending on the challenge VOC. Styrene and iso-butanol removal efficiency is higher in all devices, because of their higher rate constants when reacting with hydroxyl radical, which is the main oxidizing agent in the considered air cleaning technologies. Yet they showed clear distinctions in performance of different systems, which will be ideal to be a target challenge compound. However, styrene showed clear interference in ozone monitoring, so it was ruled out.
- The effects of challenge VOC concentrations were investigated further for iso-butanol, toluene, and o-xylene in the range between 0.05 and 2 ppm. The decrease in iso-butanol efficiency with increasing challenge concentration tends to show an exponential profile, while the change in the efficiency of aromatic compounds follows power laws. This indicates that significantly raising the challenge concentration in order to accelerate air cleaner testing, which is a commonly applied approach in the evaluation of adsorption-based technologies, is not suitable for oxidation-based air cleaning technologies.
- The effects of the humidity level were investigated in the range between 20 and 60% RH for iso-butanol, toluene, and o-xylene. Different effects were observed depending on the polarity of the challenge VOC. However, in general, the performances of oxidation-based air cleaning systems are more sensitive to humidity under 40% RH. Therefore, low humidity conditions are better to be avoided as the standard test condition.

In addition, some selected PCO systems were tested for ozone removal, and commercial PCO systems showed poor ozone removal efficiency.

Based on the knowledge gained from extensive testing of commercial systems in a 4-duct test rig, a recommended test protocol was developed by aiming at multifaceted performance evaluation beyond simple removal efficiency measurement. The test protocol adopts the evaluation in two-tier challenge concentrations: 1) Considering indoor air quality application, which is relevant to commercial, public, educational and other buildings or spaces covered by ASHRAE Standard 62.1-2016; 2) Considering light industrial workplaces experiencing sub-ppm VOC levels. It also considers by-product generation, and emission of challenging VOC residues and reaction intermediates after the challenging period is over. The developed test protocol for full-scale testing has been applied in 14 commercial in-duct air cleaning units under the

recommended test conditions: 7 PCO units, 3 units combining PCO and adsorption media, 2 plasma and 2 ozonation units. The test results indicate that the proposed testing protocol can capture different characteristics in the performance of different systems except for NTP units, which showed poor performances throughout the study.

Based on the findings of this study the followings are recommended:

- The test results have shown a wide variation in removal efficiency and in generation rates of harmful by-products. Therefore, oxidation-based air cleaning systems should not be applied without proper testing. As more air cleaners adopt oxidation-based technologies, there is an urgent need to develop a standard test method. The recommended test protocol can be a good starting point in standard development and can also be used as an interim test method.
- Ozone generation by some oxidation-based air cleaning devices can be a concern. Such a system should not be applied or the generated ozone shall be destructed below 50 ppb before the air is sent to occupied zones.
- Full-scale results indicated that adding adsorbent media for scrubbing unreacted contaminants and oxidation by-products can be a solution. However, the test results also showed that scrubber performance varies significantly. The common practice of using blended media comprised of activated carbon and permanganate alumina media in a thin bed needs more investigation. Overall, more research on the performances of adsorption-based scrubbers in removing mixtures of VOCs and their by-products is needed for the optimal design of air cleaning systems.
- NTP consistently showed very low performances in this study. Since only 4 NTP units were tested in this study, further investigation on commercial NTP devices is recommended.
- None of the oxidation-based air cleaning systems showed complete oxidation of VOCs. However, some PCO systems show some potential for improved air cleaning performances. More efforts are needed to develop an improved commercial PCO system.
- The proposed testing protocol is limited to the evaluation of the initial or short-term performance of oxidation-based air cleaning technologies. Long-term performances need to be investigated further from both laboratory and field testing so that a proper long-term evaluation method can be developed.
- The proposed testing protocol has been adapted to the single challenge gas testing. The effects of VOC mixtures and/or the presence of other inorganic gases have not been considered in this study. More experimental and theoretical studies are needed to investigate the mixture effects to be able to interpret the gauged air cleaner efficiency into the actual performances.

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ANNEXE A: CHARACTERIZATION OF PHOTOCATALYSTS

Five commercial photocatalysts (PCO-A to PCO-E) in different substrates and one in-house PCO (PCO-F) were used in four-duct test rig. Since PCO manufacturers have not revealed any detailed information about their products, characterization tests of the photocatalysts were conducted to understand them better. First, the PCO morphology was observed using a scanning electron microscope (SEM, Hitachi S-3400N SEM) equipped with an energy dispersive spectroscopy (EDS) system for elemental analysis.

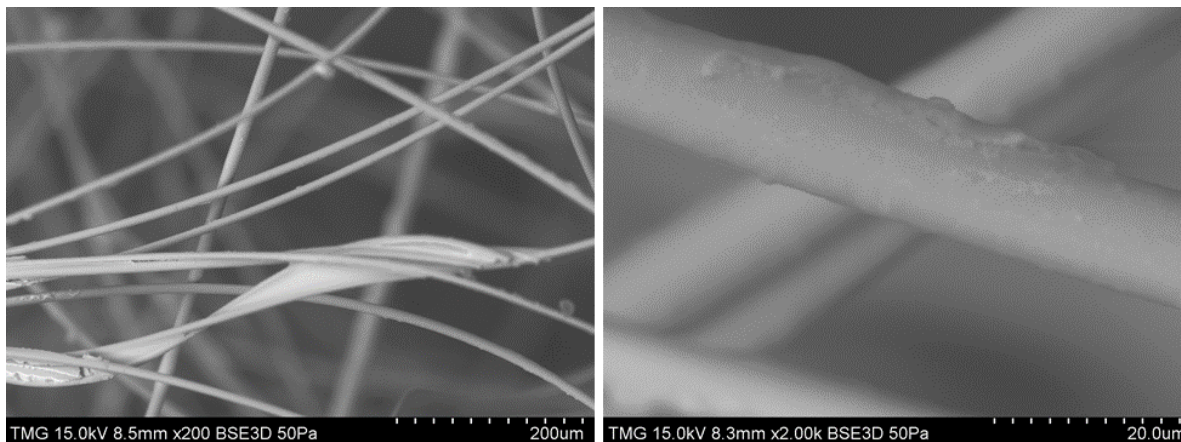
Figure A-1 presents the SEM images of five commercial PCOs, and Figure A-2 presents the SEM images of the in-house PCO and the uncoated fibrous activated carbon substrate. The elemental analysis results indicate that TiO₂ coatings are not uniform for all tested PCO. An irregular circular pattern, observed in SEM image of PCO-C (Figure A-1 (c)), is confirmed to be the pattern of TiO₂ coating as shown in the EDS analysis elemental maps of PCO-C in Figure A-3. The EDS elemental analysis was conducted in both areas with coatings and without coatings. Table A-1 presents EDS elemental analysis results. From this analysis, all the tested photocatalysts are TiO₂-based, and the substrates of the commercial PCO can be deduced as: 1) fiber glass pad for PCO-A, 2) aluminum mesh panels for PCO-B and PCO-C, 3) nickel foam for PCO-D, and 4) aluminum honeycomb panel for PCO-E. Since EDS generally have a poor limit of detection, it cannot provide reliable information on catalyst doping. TiO₂ content in the coated area is greatest in PCO-C followed by PCO-E > PCO-A > PCO-F > PCO-B > PCO-D.

The PCOs using fibrous substrates (i.e., PCO-A and PCO-F) tended to generate more TiO₂ powders during storage and handling compared to PCOs on metallic substrates, possibly due to the flexibility of substrates and/or the abundance of coatings on extended surfaces of fibrous substrates. The powders collected in the storage bag of PCO-A and the TiO₂ nano-powder used in preparation of PCO-F were analyzed by X-ray diffraction method (XRD, Philips PANalytical X'pert Pro X-ray diffractometer) with a copper K_α X-ray radiation at tension of 45 kV and current of 40 mA for the determination of crystalline phases. The XRD spectrum was acquired from 20° to 90° (2θ) with a 0.02° step size and 2 s of scan time per step. The analysis of the X-ray patterns was carried out using X'Pert HighScore Plus Rietveld analysis software in combination with Pearson's crystal database. Figure A-4 shows the XRD patterns, indicating 100% anatase phase TiO₂ for PCO-A; and 80.8% anatase/19.2% rutile phase TiO₂ for PCO-F. The crystallite sizes can be estimated from XRD results using Scherrer equation:

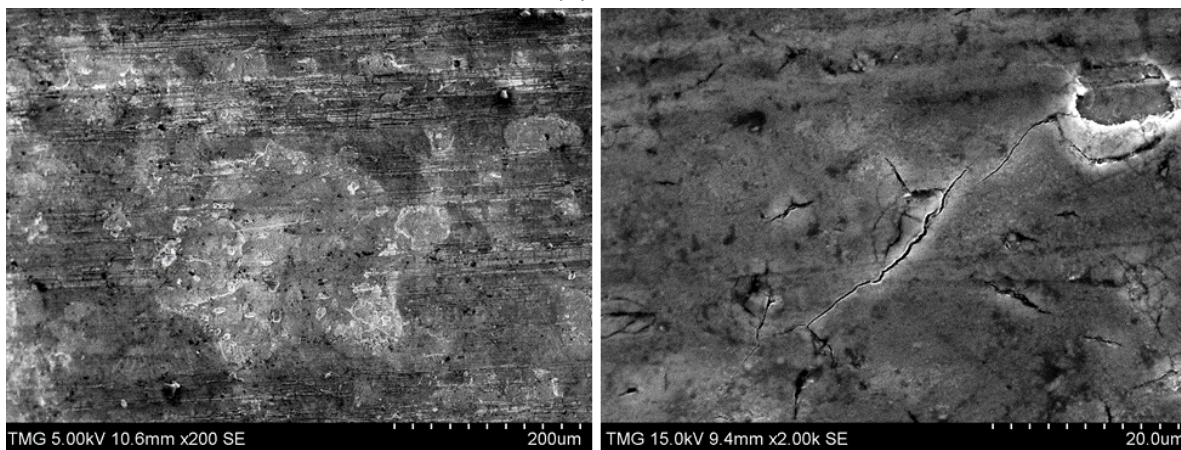
$$\tau = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (\text{A-1})$$

where, τ is the average crystallite size [nm]; K is the dimensionless shape factor; λ is the X-ray wavelength [nm]; β is the peak broadening at half-maximum peak height [rad]; and θ is Bragg angle [deg]. For unknown crystal shapes, the shape factor is generally assumed as 0.9, and λ of the applied XRD was 0.15418 nm. The calculated average crystallite size was 9.94 nm for 100% anatase-phase TiO₂ of PCO-A; and 19.4 nm and 29.2 nm for 80.8% anatase-phase and 19.2% rutile-phase TiO₂, respectively, of PCO-F. The average crystallite size of PCO-F can be obtained as 21.3 nm, which is in good agreement with < 25 nm of particle size information determined by TEM by the supplier. It is worth mentioning that pure TiO₂ was tested by XRD for carbon cloth

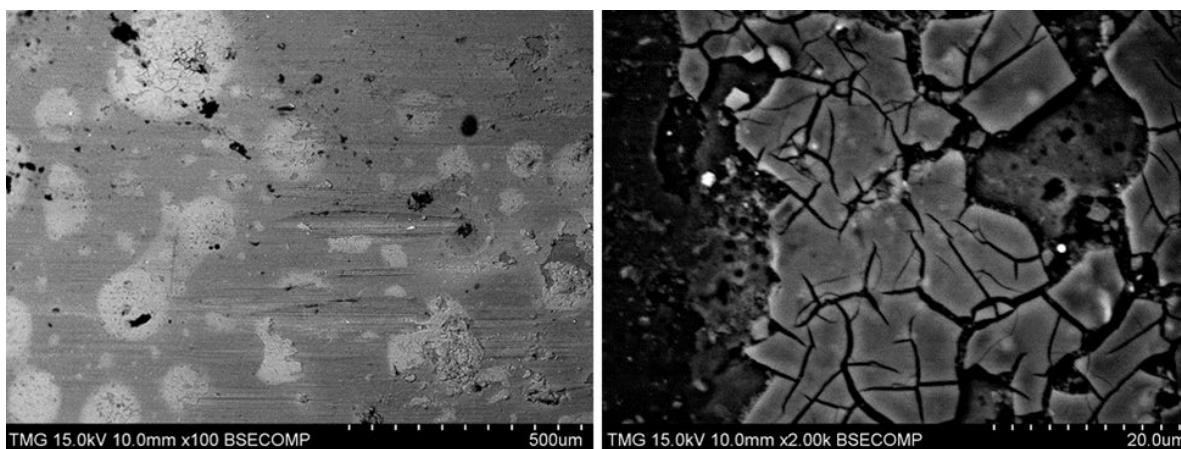
filters so it exhibits distinct sharp peaks, whereas XRD results of crystalline TiO_2 containing amorphous impurity (silica fibers) for fiberglass filters show large wide humps instead of high intensity narrower peaks.



(a) PCO-A



(b) PCO-B



(c) PCO-C

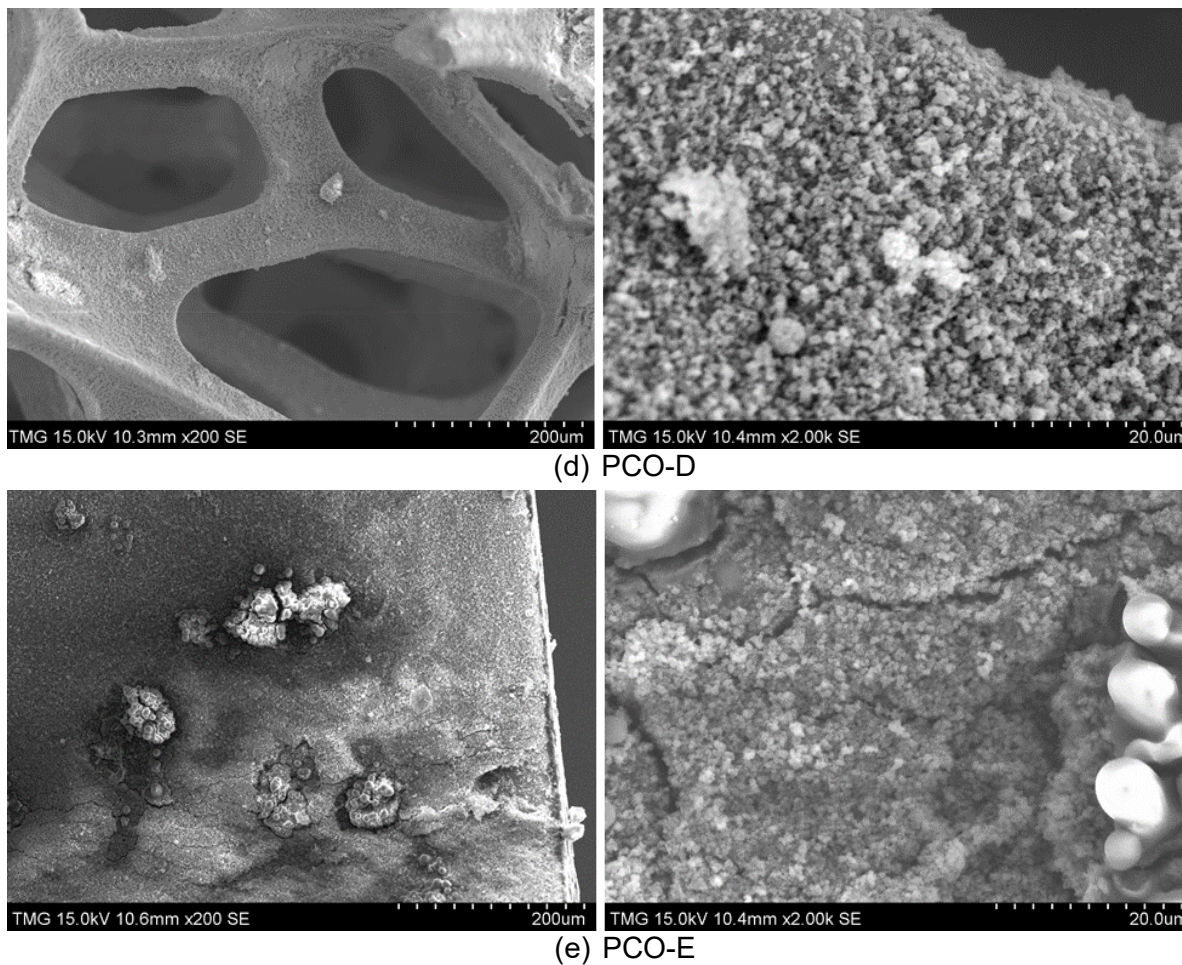
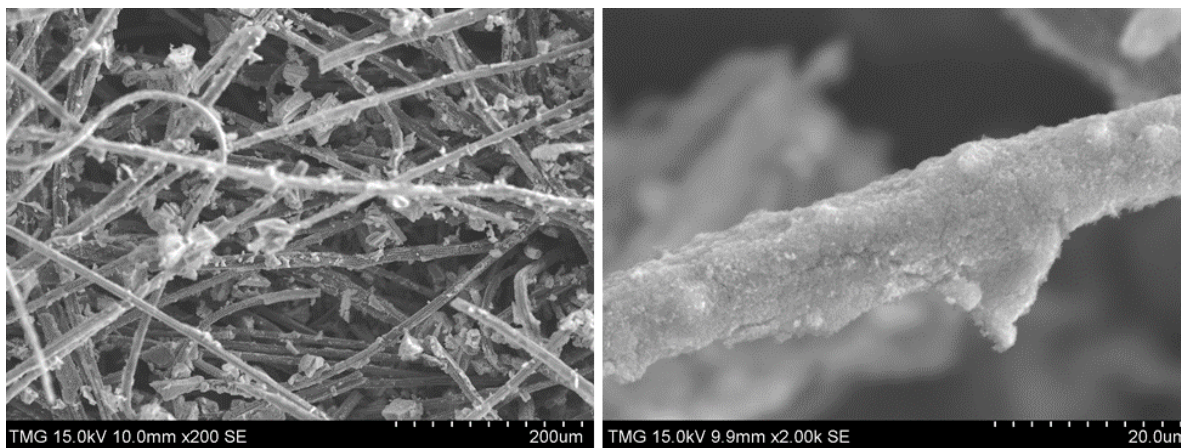
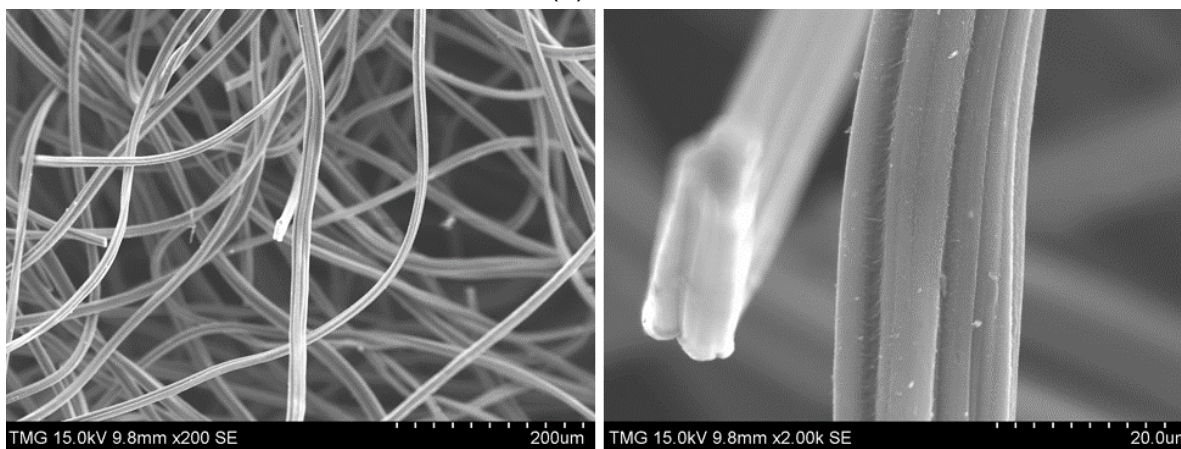


Figure A-1 SEM pictures of the tested commercial photocatalysts.

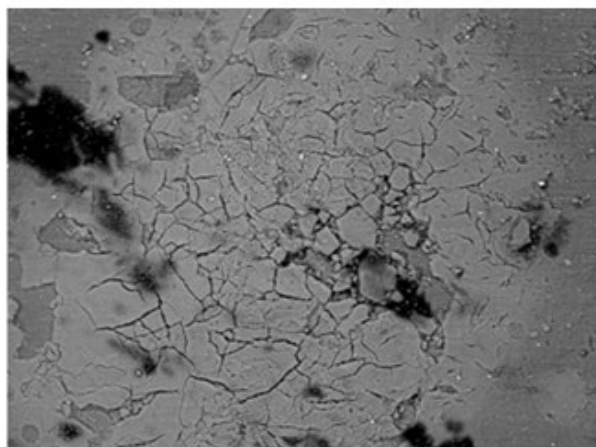


(a) PCO-F

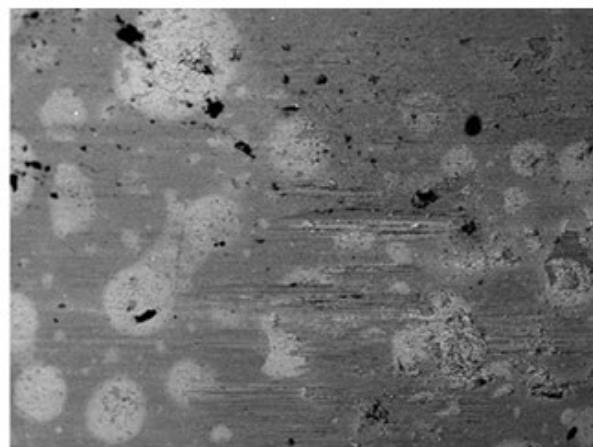


(b) Activated Carbon Fiber used as the substrate for PCO-F: before coating

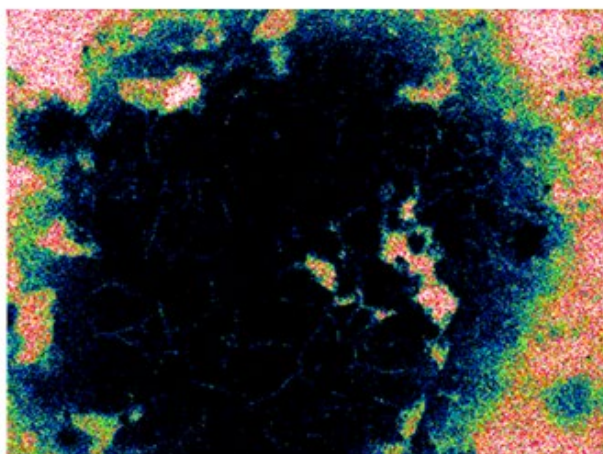
Figure A-2 SEM pictures of (a) PCO-F, (b) uncoated fibrous activated carbon substrate.



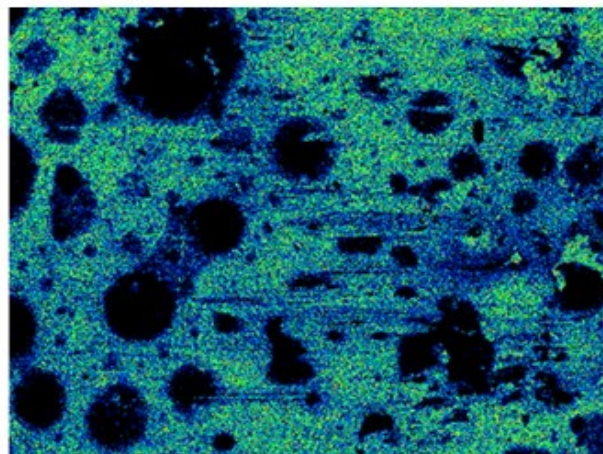
Electron Image 1



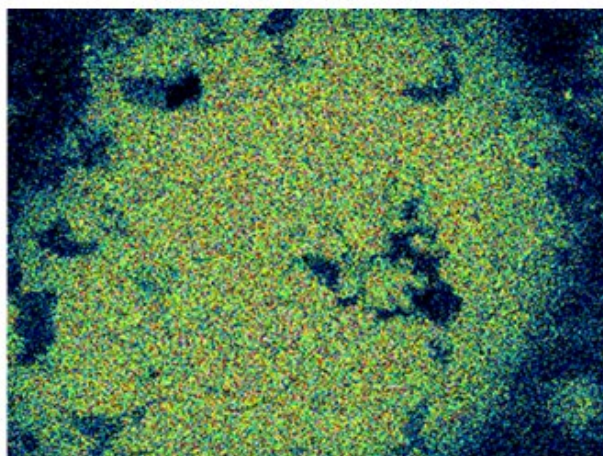
Electron Image 1



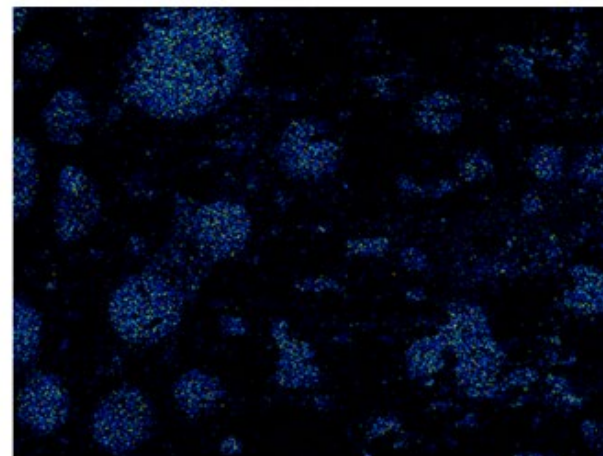
Al Ka1



Al Ka1



Ti Ka1



Ti Ka1

Figure A-3 Elemental mapping of PCO-C.

Tableau A-1 EDS elemental analysis results of some of the tested photocatalysts in atomic percent

Element	PCO-A		PCO-B		PCO-C		PCO-D		PCO-E		PCO-F	
	Coated area	Exposed area	Coated area	Exposed area	Coated area	Exposed area*	Coated area	Exposed area	Coated area	Exposed area	Coated area	Exposed area
C	-	1.90	21.7	10.1		NA	4.53	11.0	6.99	-	34.8	84.6
O	68.4	72.6	38.2	6.16	71.4	NA	66.0	29.1	59.2	9.38	52.2	13.9
Na	-	-				NA	5.87	3.87	0.76	-	0.29	0.26
Al	-	-	28.1	82.8	5.31	NA	-	-	9.50	85.6	-	-
Si	17.1	23.1	0.66	0.45	1.08	NA	-	-	-	-	-	-
Ca					0.42	NA						
P	-	-	-			NA	4.71	2.89	0.65	-	0.24	0.13
S	-	-	0.21			NA	0.95	-	-	-	-	-
Ti	14.5	2.45	10.9	0.49	21.3	NA	10.5	3.26	20.0	-	12.4	1.04
Fe			0.26	0.31		NA						
V	-	-	-			NA	-	-	2.87	-	-	-
Mn	-	-	0.17	0.42		NA	-	-	-	4.99	-	-
Ni	-	-				NA	7.45	49.9	-	-	-	-
Zn			0.13			NA						
Zr					0.51	NA						

* Exposed area: the surface observed to be without or less coating of photocatalyst, exposing more substrate

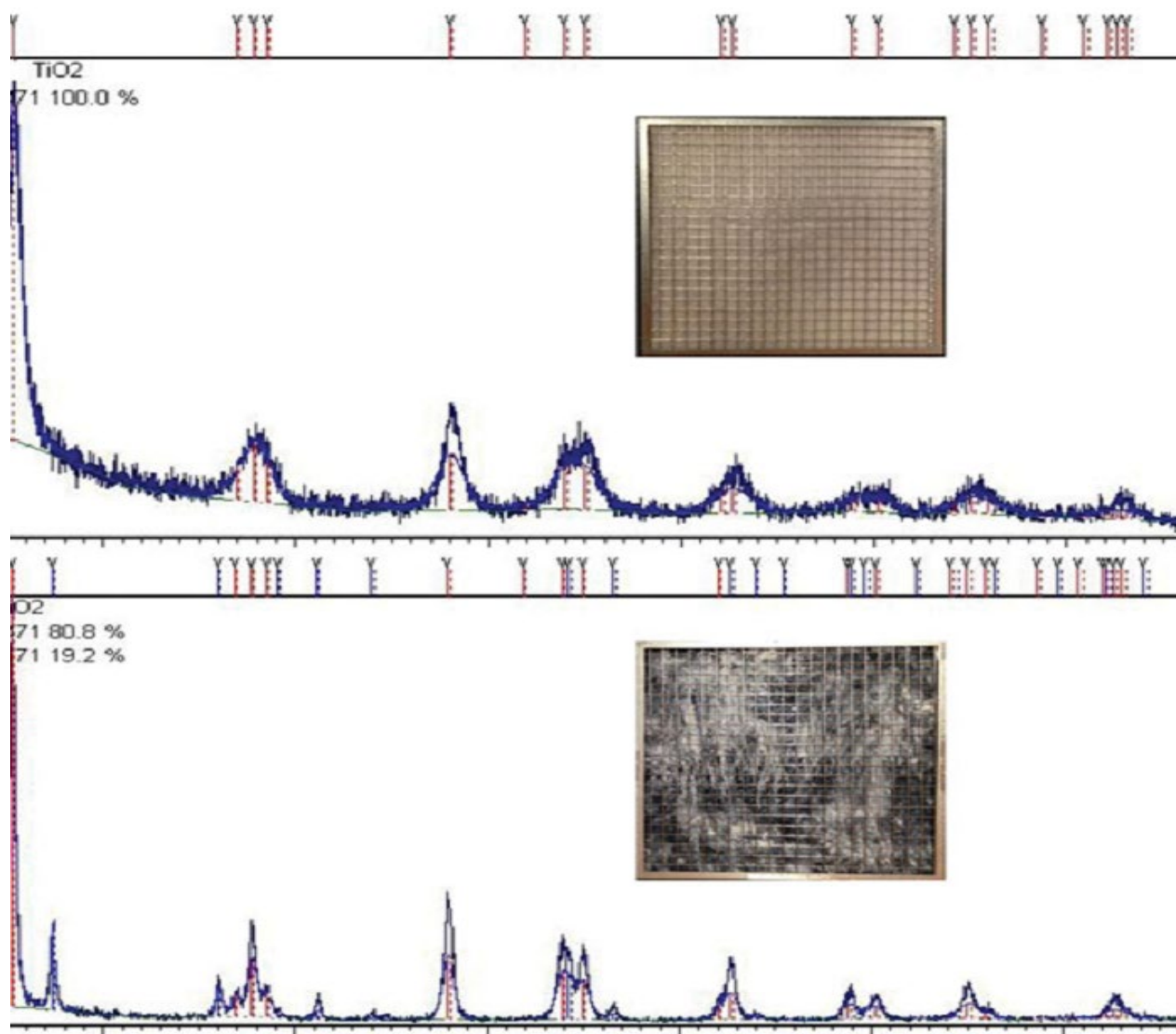


Figure A-4 XRD patterns of TiO₂ catalyst powders of PCO-A (top) and PCO-F (bottom).