CHAPTER 1

Introduction

Tropospheric ozone (O_3) is a secondary pollutant that highly reactive oxidant gas and unstable gas. It is the main component of photochemical smog that tends to steadily deteriorating and occur more often during the dry season. As at low concentration levels they have effects on human health that breathing ozone can trigger a variety of health problems, including chest pain, coughing, throat irritation and congestion. Especially, it can reduce lung function and inflame the linings of the lungs. In addition, ozone also affects ecosystem and sensitive vegetation. Normally, ozone level can be measured by an automatic device, which are expensive, complex and require special maintenance. Therefore, this study will focus on development of an efficient, simple and cost effective of an active ozone sampling device for tropospheric ozone monitoring.

Active sampling method is the use of a pump and an air flow meter to pull the air through collecting filter in the device under control conditions. There for, it is provides high precision and accuracy of the analyte concentrations and less dependence of meteorological conditions. Moreover, it is suitable for short-term sampling for assess to acute human health effect according to short term air quality standards.

1.1 Tropospheric Ozone

Ozone (O_3) is an important trace gas that composed three oxygen atoms. It is found both in the stratosphere and the troposphere (Figure 1.1). Most ozone in the stratosphere (90%) is protecting the earth from the sun's harmful rays while ozone in the troposphere is toxic pollutant that is a major constituent of smog, can effects on human health and ecosystem

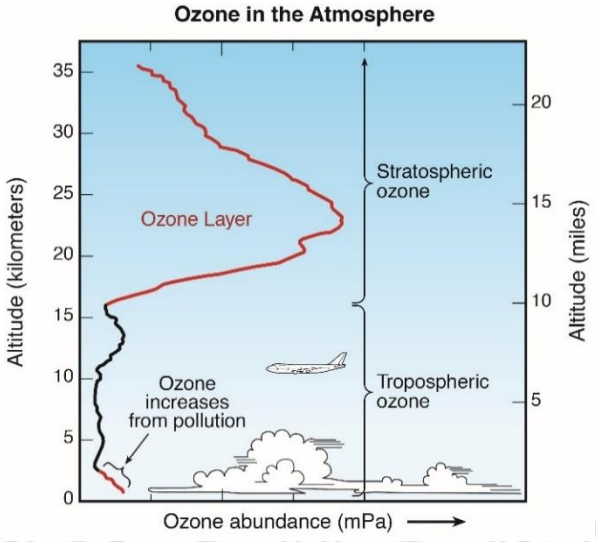

Figure 1.1 Ozone in the stratosphere and the troposphere

(https://encrypted-tbn2.gstatic.com/images?q=tbn:ANd9GcSfjxS08fCEfJtI833Ku_ktMo403uKj0vYEOHHKZRgZ7mSvi0juxcqGO)

Ozone in the troposphere is a colorless, reactive oxidant gas that is a major constituent of atmospheric smog. It is formed through a photochemical reaction of nitrogen oxides (NO_x = NO + NO_2) and volatile organic compounds (VOC_s) under solar radiation (Sadanaga *et al*., 2008).

Ozone concentrations are depended on the concentrations and the ratio of NO_x and VOC_s in each area, the response to changes on solar radiation in diurnal patterns and seasonal variations occur (Pollution Prevention and Abatement Handbook, WORLD BANK GROUP. July 1998). In generally, ozone concentrations are higher in afternoon. Mean concentrations are highest during in dry season, especially in summer.

1.1.1 The formation of ozone

Ozone in the stratosphere is produced by photochemical reactions of oxygen molecular (O_2) with ultraviolet sunlight (light wavelength < 240 nm).

$$O_2 + \text{ultraviolet sunlight} \rightarrow O^{\cdot} + O^{\cdot}$$

$$O^{\cdot} + O_2 \rightarrow O_3$$

Some stratospheric ozone is transported down into the troposphere and can influence ozone amounts at Earth's surface.

Ozone in the troposphere is a secondary pollutant, which is not emitted directly into the air, but it is produced through a photochemical reaction of precursor pollutants: nitrogen oxides (NO_x = NO + NO_2) and volatile organic compounds (VOCs)

as represented by non-methane hydrocarbons (NMHCs) under intense solar radiation are show in Figure 1.2 (Sadanaga *et al*., 2008).

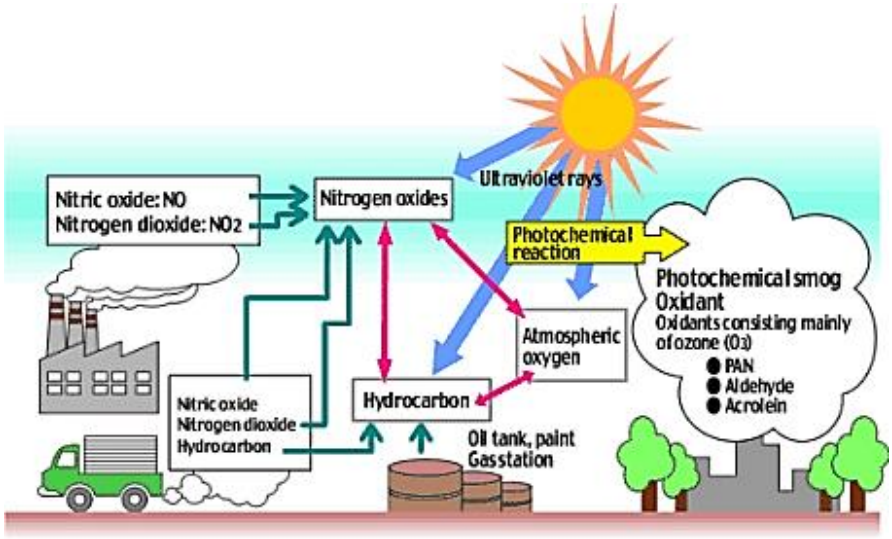

Figure 1.2 The formation of ozone

(http://t0.gstatic.com/images?q=tbn:ANd9GcQxEOOTv4XtYhQPl3dPPG-tx_jDZdixQKCzapK9dt0Qd-KvvGV6)

Ozone is produced by the reaction of an oxygen molecule (O_2) with an oxygen atom, which originates from the photolysis of nitrogen dioxide (NO_2)

$$NO + O^{\cdot} \rightarrow NO_2$$

$$NO_2 + h\nu\ (420\ nm) \rightarrow NO + O^{\cdot}$$

$$O^{\cdot} + O_2 \rightarrow O_3$$

Net reaction: $\underline{NO_2 + O_2 \rightarrow NO + O_3}$

The reaction of the hydroxyl radical (OH) of VOCs in the atmosphere with nitric oxide (NO) (Im *et al*., 2013). Ozone is also emitted from germicide lamps, copy machine, printers, welding and other industrial process.

$$NO + ROO^{\cdot} \rightarrow NO_2 + RO^{\cdot}$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

Where $ROO^{\cdot}$ is hydro- and alkyl-peroxy radicals and $RO^{\cdot}$ is the related oxy radicals

1.1.2 Effects of ozone

1.1.2.1 Health effects of exposure to ozone

Breathing ozone can trigger a variety of health problems including chest pain, coughing, throat irritation, and congestion. It can worsen bronchitis, emphysema, and asthma. Moreover, ozone also can reduce lung function and inflame the linings of the lungs (Table 1.1). Even relatively low levels of ozone can cause health effects. Children, people with lung disease, older adults, and people who are active outdoors, including outdoor workers, may be particularly sensitive to ozone (Table 1.2).

According to air quality standard of Thailand, ambient ozone should not exceed 200 µg/m^3 or 100 ppbv (1 hour) and 140 µg/m^3 or 70 ppbv (8 hour). The value was higher than the standards announced by other organizations/countries such as EU (Eupean union) (120 µg/m^3 for 8 hour), WHO (World Health Organization) (100 µg/m^3 for 8 hour).

Table 1.1 Summary of ozone health effects expected at various exposure level (ppm)

Level (ppm)	Human health symptoms
10.00	Severe pulmonary edema; possible acute bronchiolitis; decreased blood pressure; rapid weak pulse
1.00	Coughing; extreme fatigue; lack of co-ordination; increased air way resistance; decreased forced expiratory volume
0.50	Chest constriction; impaired CO diffusions capacity; decrease in lung function without exercise
0.30	Headache; chest discomfort sufficient to prevent completion of exercise; decrease in lung function in exercising subjects
0.25	Increase in incidence and severity of asthma attacks; moderate eye irritation
0.15	For sensitive individuals, reduction in pulmonary lung function; chest discomfort; irritation of the respiratory tract, coughing and wheezing

Source: Utah State Department for the Environment, 2000

Table 1.2 Air Quality Index (AQI) and Health Concerns

AQI Value	Descriptors	Health Effects
0-50	Good	No health impacts are expected when air quality is in this range.
51-100*	Moderate	Unusually sensitive people should consider limiting prolonged outdoor exertion
101-150	Unhealthy for Sensitive Groups	The following groups should limit prolonged outdoor exertion: • People with lung disease, such as asthma • Children and older adults • People who are active outdoors
151-200	Unhealthy	The following groups should avoid prolonged outdoor exertion: • People with lung disease, such as asthma • Children and older adults • People who are active outdoors Everyone else should limit prolonged outdoor exertion.
201-300	Very Unhealthy	The following groups should avoid all outdoor exertion: • People with lung disease, such as asthma • Children and older adults • People who are active outdoors Everyone else should limit outdoor exertion

Source: US. Environmental Protection Agency, 2009

1.1.2.2 Ecosystem Effects

Ozone can interfere ability of plants to produce and store food, including reduced tree growth and visible injury to leaves. In particular, ozone harms sensitive vegetation, including trees and plants during the growing season. Moreover, continued ozone exposure over time can lead to increased susceptibility of sensitive plant species to disease, damage from insects, effects of other pollutants, competition, and harm from severe weather (Figure 1.3). These effects can also have impacts on ecosystems, including loss of species diversity and changes to habitat quality and water and nutrient cycles.

Figure 1.3 Discoloration on leaves due to ozone
(http://media1.shmoop.com/images/chemistry/chembook_environchem_graphik_4h.png)
(http://a.static.trunity.net/files/119001_119100/119063/180px-Ozonedamagekl.jpg)

1.2 Ozone and meteorology

Meteorology plays an important role in the formation, dispersion, transport, and dilution of air pollutants (Ooka *et al*., 2011). The variations in local meteorological conditions such as radiation, temperature, wind speed, relative humidity and precipitation have a great influence on surface ozone concentrations and its precursors (Elminir, 2005; Tu *et al*., 2007). Meteorological factors can influence the ozone formation as below;

1.2.1 Radiation: the formation of tropospheric ozone depends on the solar radiation. It is required to initiate the ozone-forming photochemical reactions. Solar radiation stimulates the VOC_s and NO_x chemicals to recombine to ozone formation. Solar radiation is associated with the cloud, which the amount of cloud cover contributes to ozone formation. However, if there are few or no clouds, or only high

transparent clouds, solar radiation is more able to penetrate to ground level and lead to the photochemistry that generates ozone to occur.

1.2.2 Temperature: temperature an important role in the chemical reactions that occur in the atmosphere to form photochemical smog from other pollutants. Higher temperatures enhance the ozone formation chemistry and increase the evaporative emissions of volatile organic compounds.

1.2.3 Winds: wind direction and speed determines transport (Ghim *et al*., 2001) and accumulation of primary pollutants (VOCs and NOx), which the subsequent ozone formation. Higher wind speeds tend to dilute or disperse emissions. However, it can still transport ozone from other locations or blow photochemical smog away replacing it with fresh air.

1.2.4 Relative humidity: Relative humidity is an indicator of atmospheric moisture. Water vapor plays a role in photochemical reactions and in the production of wet aerosols. Water molecules are small and highly polar, it can bind strongly to many substances. If attached to particles suspended in the air they can significantly increase the amount of light scattered by the particles. Therefore, relative humidity is influence on the concentrations of ozone and its precursors. Increasing of relative humidity leads to a decrease in average concentrations of ozone (Li *et al*., 2007; Tu *et al*., 2007).

1.2.5 Precipitation: rainfall can washed out the ozone atmosphere. However, low levels of precipitation can contribute to ozone formation, including scattered showers do not produce enough precipitation to completely eliminate ozone.

1.2.6 Pressure: The pressure of the air affects whether pollution levels build up. During high pressure systems, the air is usually still which allows pollution levels to build up but during low pressure systems the weather is often wet and windy, causing pollutants to be dispersed or washed out of the atmosphere by rain (Hüseyin *et al*., 2005).

1.3 Introduction of active sampling method

An active sampling procedure, air is drawn through an absorbing or adsorbing medium by a pump in order to trap the gas phase material (Figure 1.4). It is important

that the sampler has an accurate, calibrated means to determine the total volume of the gaseous sampler and the rate at which the gas is being sampled. This is most easily accomplished by the use of calibrated mass flow controllers.

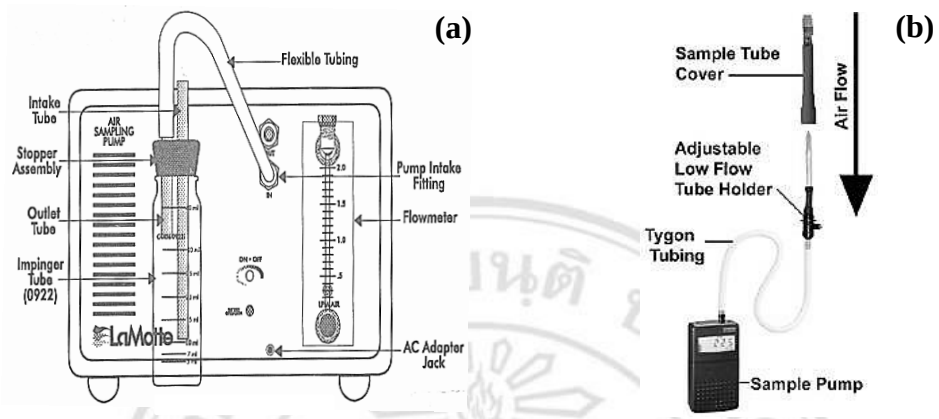

Figure 1.4 Active sampling method; (a) absorption bottles and (b) adsorbent tubes
(http://www.skcinc.com/catalog/images/product_images2/225-361%20Impinger_ Pump.JPG)
(http://www.skcinc.com/catalog/images/product_images/tubetraincallouts.jpg)

1.3.1 Types of active sampling methods

There are many active air sampling methods available. Each method utilizes different ways to collect gaseous samples and each sampling method has its own particular inherent, so each method has its own strengths and weaknesses. The basic mechanism, gaseous samples were adsorbed on the surface of various substances, which have large surface areas and are specifically designed to collect the gaseous chemical species desired. They may react chemically with some chemical adsorbed on the surface of the collection device or on particles in the collector. Gases may be collected in bags or canisters or trapped in bubblers or filter. Each of these methods will be described briefly below.

1.3.1.1 Adsorbent tubes

The adsorbent tubes can be filled with different kinds of adsorbents, depending of which components of interest. When used as a passive sampler, there is no need for any extra equipment. To decrease the minimum sampling period or to improve the detection limit, the tube can be connected to a pump.

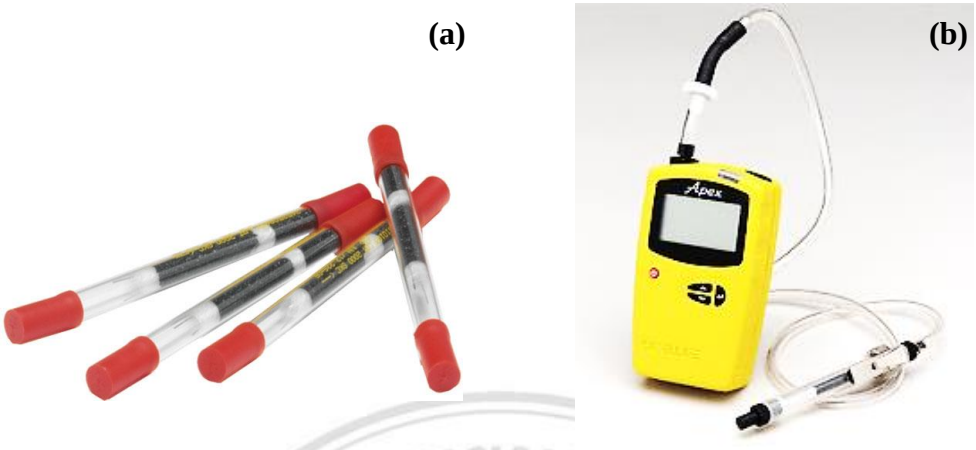

Figure 1.5 (a) adsorbent tubes and (b) adsorbent tubes connect connected to a pump
(http://3.imimg.com/data3/BB/SG/MY-6841817/air-monitoring-250x250.jpg)
(http://airsamplingsolutions.com/wp-content/uploads/2014/05/Charcoal_Tubes.jpg)

1.3.1.2 Absorption bottles

The most commonly used active device for gaseous sampling has been the bubbler with an absorption solution, often together with a filtration system. A chemical solution is used to stabilize the pollutant for subsequent analysis with minimum interference by other pollutants. The flow is set with a restrictor and measured with a mass flow meter.

Figure 1.6 Absorption bottles
(http://www.skcinc.com/catalog/images/product_images2/225-36-1%20Impinger_Pump.JPG)

1.3.1.3 Impregnated filter sampling

A relatively simple alternative to the use of solutions for absorption and chemical reaction is to use chemically impregnated filters. These filters are

prepared by dipping filters into a solution of the selected chemical and drying them before sampling commences. This sampler consists of a glass bulb with an impregnated filter inside. The impregnated filter bulb is connected to a pump that draws a steady air flow through the filters (Figure 1.7), for example 4-stages filter pack used for atmospheric dry deposition monitoring (EANET, 2003) are show in Figure 1.8. After exposure, the filter and the pollutant of interest react with the chemical on the filter. The filter is sent to the laboratory for analysis. The detection limit is better than for the other methods but the method is more labor intensive and depends of extra sampling equipment such as a high precision electric pump.

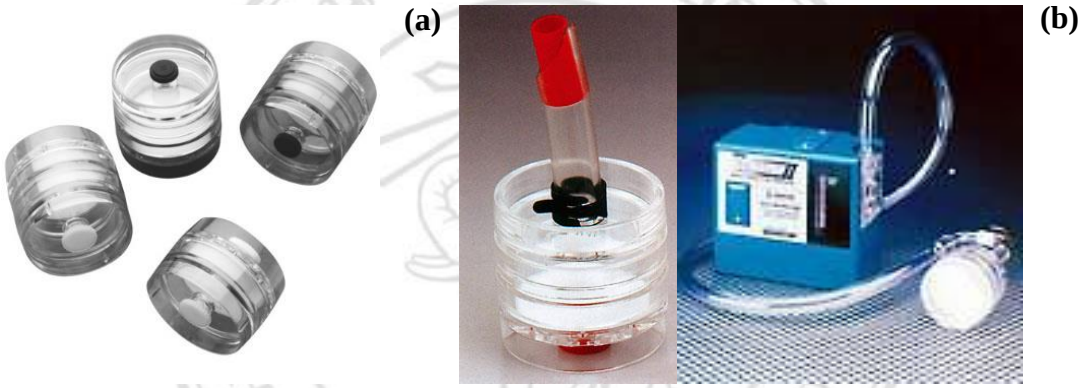

Figure 1.7 Impregnated filter sampling device; (a) glass bulb with an impregnated filter inside and (b) the impregnated filter bulb is connected to a pump
(http://www.skcinc.com/catalog/images/M-ISOCHEK.jpg), (http://www.zefon.com/store/images/T/t_204-01.jpg)

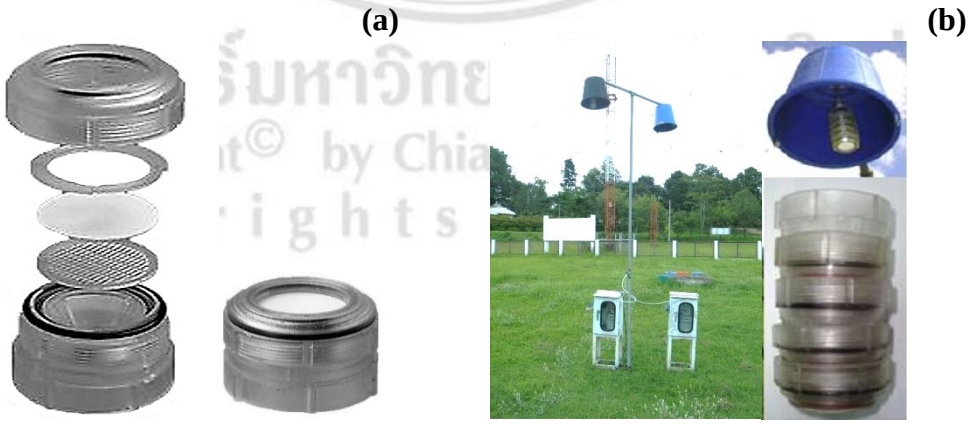

Figure 1.8 (a) configuration of filter pack and (b) 4-stages filter pack
(http://products.nilu.no/LinkClick.aspx?fileticket=xgVNNb6XIAc%3d&tabid=1931&mid=4112&lang uagee=en-GB), (Chantara *et al*., 2012)

1.3.2 Comparison of active sampling method with other methods

Instruments for measurements of air quality can be classified into four types based on vary in complexity, price and performance levels are shown in Table 1.3.

Table 1.3 Instrumental air quality monitoring techniques

Method	Typical averaging time	Advantages	Disadvantages
passive	1-30 days	- very low cost - simple - no electric requirement - useful for screening and baseline studies in support of automatic monitoring for detailed assessments	- depended on the gas diffusion for collection - high interferences - affecting by meteorological conditions during the sampling - longer duration - inferior precision and accuracy to automatic methods - laboratory analysis required
active	24 hours	- low cost - easy and reliable to operate - historical data set in some cities	- integrated samples - some methods are labor intensive - filter conditioning may be required - laboratory analysis required
automatic	5 mins. – 1 hour	- proven high performance - continuous on-line measurement - low direct costs - on-line data collection possible	- complex and expensive - high skills required to maintain and operate - high recurrent costs
remote sensors	1 min	- provides path or range resolved data - useful for near sources and for vertical measurements - multi-component measurements	- difficult to support operate, calibrate and validate - not always comparable with fixed point sampling analyzers

Source: http://www.airqualityni.co.uk/air-quality/monitoring

1.4 Literature review on development of active ozone sampling device

Ozone is highly reactive and unstable toxic gas (Helalen et al., 2002), thus it is more interest to monitor their concentrations. However, it is limitation of high cost equipment. Many researchers tried to improve the methods for measuring ambient ozone to its simplicity, cost effectiveness and efficiency. The alternative method such as passive sampling and active sampling methods can be response to these reasons. Moreover, the selection of trapping reagents for ozone absorption is the one important factor for high efficiency of ozone collection.

According to the literature reviews, various trapping reagents have been developed in over the past ten years such as 1,2-di(4-pyridyl)-ethylene (Monn and Hangartner, 1990), indigo (Werner *et al*., 1989; Grosjean and Hisham, 1992; Cox and Malcolm, 1999), potassium iodide (Kanno and Yanagisawa, 1992; Yanagisawa, 1994), nitrite (Brauer and Brook, 1995; Helalen *et al*., 2002; Koutrakis *et al*., 1993; Koutrakis *et al*., 1994; Santis *et al*., 2003), 3-methyl-2-benzothiazolinone acetone azine with 2-phenylphenol (Hackney *et al*., 1994) and p-acetamidophenol (Ikeura and Mizoguchi, 1996). Amongst these reagents, only 1,2-di(4-pyridyl)-ethylene and nitrite found that they are suitable trapping reagents for ozone absorption because they are high sensitivity, relatively free of interference problems and specific reactions with ozone, and can used both in passive sampling and active sampling methods. Whereas other trapping reagents can be interfered from UV light and other atmospheric oxidants such as NO_x, SO_2 and peroxyacetyl nitrate (PAN) (Koutrakis *et al*., 1993; Helalen *et al*., 2002; Plaisance *et al*., 2007; Alejo *et al*., 2011; Zhou *et al*., 2012).

The using a nitrite-coated filter as ozone absorbent were used for the first time since 1993 by Koutrakis *et al*., which is based on the oxidation of nitrite (NO_2^-) by ozone to nitrate (NO_3^-) on the filter medium, $NO_2^- + O_3 \rightarrow NO_3^- + O_2$, and analyzed by ion chromatography in form NO_3^-. They developed a passive sampling device for ozone sampling by using a badge clip supporting a barrel-shaped body, which contains two glass fiber filters coated with a mix of sodium nitrite ($NaNO_2$), potassium carbonate (K_2CO_3), glycerol, methanol, and water. After exposed, the filters are extracted with ultrapure water and analyzed by ion chromatography. This device was tested both in the laboratory chamber and field (the U.S. EPA Environmental Monitoring and Assessment Program (EMAP) test site, located at Prince Edward, VA). The results showed that a

passive sampler affected by wind direction, which effect on the sampler collection rate of ozone.

Helalen *et al*., (2002) developed a passive sampling device with high sensitivity and less effect of wind velocity and humidity. The device is a plate type (The Yanagisawa type passive sampler), which contains four parts; (1) a badge case (outer and inner frame), (2) an absorbent filter, (3) diffusion filter, and (4) spacer. The device was tested both in the laboratory and field (at Tokushima University). In laboratory testing, they was tested the different filter-cleaning techniques, which have the lowest contaminant in the absorbent filter. Moreover, the different types of absorption filter (cellulose filter, glass fiber filter paper, and chromatography filter paper) were tested. These filters paper were coated with a mixing of 0.1% $NaNO_2$, 0.2% sodium carbonate (Na_2CO_3), and 1% ethylene glycol, and analyzed by using the same method with Koutrakis *et al*., (1993). In addition, the device was tested of the wind velocity and humidity effect on the passive sampler and response of the trapping reagent. The results showed that using of 2% H_2O_2 + water for filter-cleaning could reduce the contamination level in the absorbent filter. The glass fiber filter paper (GF/A) as absorbent filter gives the highest value of absorptivity. The absorption rate of ozone was unaffected by the wind velocity and the relative humidity. In the field tested, the passive sampler was good agreement when compared with ozone analyzer as standard method.

However, passive sampling depends on free flow of gases or natural gas diffusion to the sampling media. Therefore, it requires long exposure time, can easily be contaminated resulting in high interferences. Moreover, it can also be affected by meteorological conditions during the sampling. To overcome this problem, an active sampling was applied by using an air pump to control a flow rate and to pull air through collecting filters.

Geyh *et al*., 1997 developed an active sampling device by using a single tube diffusion denuder and connect to small personal pumps. The inner wall of the tube is coated with a nitrite-based reagent similar to that previously used in the passive ozone sampler (Koutrakis *et al*., 1993). The device was tested of the optimum flow and tube inner diameter (i.d.) with a target collection efficiency for ozone of at least 98%. Collection tubes with inner diameters ranging from 0.5 to 1.3 cm were tested at a flow of 120 cm^3/min (the maximum stable flow for the personal pump). The results showed

that reducing the flow to 65 cm^3/min, 10 cm tubes with an i.d. of 1.3 cm achieved the 98% target collection efficiency with ozone concentration at 55 ppbv and approximately 15% RH. After that, the device was tested both in laboratory and field. It founded that the active device gives the good results compare with UV photometer as reference method. Moreover, Geyh *et al*., 1999 applied this developed active sampling device for personal ozone monitoring. 40 children attending summer day-camp in Riverside, California wore the device for ~ 2.6 hrs on July 19 and 21, 1994 (ambient ozone concentrations were about 100 ppb and 140 ppb, respectively). The result showed that average ambient ozone from the active sampler 94.5 ± 8.2% and the device precision ± 3.7% when compare with UV photometric ozone monitors in this area.

Chang *et al*., 2001 developed an active sampling device, which improved of the previous passive sampling method. The active sampling device contain two nitrite-coated filters that was set on a polypropylene flow filters and close with polyethylene cap on the top. Air was sampled at a flow rate of 200 cm^3/min. After exposure, ozone were analyzed by using the same method with Koutrakis *et al*., (1993). The device was tested in laboratory of performance under different ozone concentration ~20, 40, 80 and 120 ppbv at 25 ºC and 70% RH, and tested in field during the summer of 1998 and the winter of 1999. The results showed that the conditions testing in laboratory agreed well at 25 ºC and 70% RH. The comparison of the active sampler in field with reference monitor given good results both in the summer 1998 and winter 1999. It has a collection efficiency ranging between 0.92 and 0.96 that did not vary with temperature or RH, and a precision for 1 hr measurements ranging between 4 and 6 ppb. The LOD were 9 ppbv/h for the chamber tests and ~16 ppb/h for the field comparison tests.

1.5 Research objectives

1) To develop an efficient, simple and cost effective active ozone sampling device.

2) To find out relationships between ambient ozone concentrations and meteorological parameters