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การเก็บตัวอย่างแบบพาสซีพสำหรับการตรวจคุณภาพอากาศ

Passive Sampling for Air Quality Monitoring

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บทคัดย่อ

การเก็บตัวอย่างแบบพาสซีพเป็นเครื่องมือที่มีประสิทธิภาพในการใช้งานด้านการวิเคราะห์ตัวอย่างทางสิ่งแวดล้อม โดยเฉพาะอย่างยิ่งการติดตามตรวจสอบคุณภาพอากาศ และเนื่องจากวิธีการเก็บตัวอย่างแบบนี้ถูกประดิษฐ์คิดค้นมานานกว่า 3 ทศวรรษ ทำให้ในปัจจุบันวิธีการนี้ถูกใช้งานอย่างแพร่หลายทั่วโลกสำหรับการเก็บตัวอย่างมลสารในอากาศ ไม่ว่าจะเป็นการใช้งานส่วนบุคคลที่เกี่ยวข้องกับการสัมผัสมลสารในสถานที่ทำงาน ตลอดจนถึงปัญหาระดับโลกที่เกี่ยวข้องกับการเปลี่ยนแปลงสภาพภูมิอากาศ วิธีการนี้สามารถประยุกต์ใช้กับสารได้หลายประเภท เช่น โลหะหนัก สารประกอบอินทรีย์และอนินทรีย์ เป็นต้น อุปกรณ์เก็บตัวอย่างแบบพาสซีพแบ่งได้เป็น 2 ชนิด ได้แก่ ชนิดแพร่ (diffusion-type) และชนิดซึมผ่าน (permeation-type) ซึ่งมีการออกแบบรูปร่างและลักษณะของอุปกรณ์ที่แตกต่างกันได้หลายรูปแบบ เช่น แบบแนวรัศมี (radial) แบบหลอด (tube) แบบเข็มเหน็บ (badge) และแบบปลอกกระสุน (cartridge) เป็นต้น ผู้ใช้งานจึงจำเป็นต้องเลือกใช้ให้เหมาะสมกับงานของตนเอง การทำงานของอุปกรณ์เก็บตัวอย่างชนิดนี้ จะอาศัยหลักการในเรื่องความแตกต่างระหว่างความเข้มข้นของมลสารในสิ่งแวดล้อมและอุปกรณ์เก็บตัวอย่าง ทำให้มลสารสามารถแพร่จากสิ่งแวดล้อมเข้าสู่อุปกรณ์เก็บตัวอย่างได้ ดังนั้นปัจจัยทางด้านสภาพอากาศหลายปัจจัย เช่น ความเร็วลม ความชื้นสัมพัทธ์และอุณหภูมิ จึงสามารถส่งผลต่อประสิทธิภาพการเก็บตัวอย่างและความน่าเชื่อถือของข้อมูลได้ ซึ่งปัจจัยเหล่านี้เป็นสิ่งที่ผู้ใช้งานต้องคำนึงถึง ในบทความนี้จะกล่าวถึงการประยุกต์ใช้อุปกรณ์เก็บตัวอย่างแบบพาสซีพในการติดตามตรวจสอบคุณภาพอากาศ โดยสรุปเนื้อหาออกเป็น 3 ส่วนตามประเภทของมลสารที่สามารถเก็บได้โดยใช้อุปกรณ์เก็บตัวอย่างชนิดนี้ ได้แก่ โลหะหนัก สารประกอบอนินทรีย์และอินทรีย์ นอกจากนี้ ปัจจัยทางสิ่งแวดล้อมต่างๆยังจะถูกกล่าวถึงในบทความนี้ด้วย

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ABSTRACT

Passive sampling is a useful tool for environmental analysis as well as in the field of air quality monitoring. As its invention more than three decade ago, it is now widespread using for air pollutants monitoring around the world with various area ranging from private workplace exposure to global issues of climate change. It was developed and applied for various types of analytes of interest *e.g.* heavy metal, inorganic compounds and organic compounds. Since it consists of two types *i.e.* diffusion- and permeation-types with varieties of geometry and configurations such as radial, tube, badge and cartridge, the user has to select an appropriate one for their applications. Based on the difference in the pollutant concentration, they diffuse from the environment to collecting media in the device. Because of this, many meteorological factors *e.g.* wind speed, relative humidity, temperature could influence to collection efficiency and reliability. Thus, the users have to take account for these parameters, when passive sampler is employed. In this reviews, the applications of passive sampler for air quality monitoring were summarized by dividing into three categories according to their chemical properties *i.e.* heavy metal, inorganic and organic compounds. Environmental parameters have also been discussed.

คำสำคัญ: การเก็บตัวอย่างแบบพาสซีพ การตรวจคุณภาพอากาศ
Keywords: Passive sampling, Air quality monitoring

Introduction

Hazardous pollutants contaminated environment is very important problem around the world since this would affect the human health by both direct and indirect way. Particularly for air pollution which is a great public health concern since human could be easily exposed them via normal breathing and/or skin. This made the monitoring of hazardous pollutant in air is an ongoing challenging research among environmental scientists and related fields for both investigation of air quality and method development for air monitoring.

The success of air monitoring depends on two key roles *i.e.* sampling and analysis methods. The most reliable method for air monitoring is being carried out by the continuous instrumental monitoring stations which make both sampling and analysis could be performed continuously resulted in less of contamination and loss of sample. However, these are very expensive and mostly limited to urban sites (Cox, 2003). Therefore the common way is firstly sampling the air sample from the site, then carrying to the laboratory for analysis.

There are two methods to sampling the air *i.e.* active and passive sampling (Klánová et al., 2006; Kot-Wasik et al., 2007; He and Balasubramanian, 2010). Active sampling is a conventional method which is done by pumping air samples though the sampling media. This makes appropriate pollutants contaminated in the air are adsorbed on the sampling media which then could be carried to the laboratory and desorbed before analysis. However, this sampling technique is costly (Kot-Wasik et al., 2007; He and Balasubramanian, 2010) since active pump, flow meter for measuring the flow rate and volume of the air, and sampling media *e.g.* sorbent are required. The maintenance and power supply for active pump are also needed. It also could not allow collecting air sample in remote and high risk areas (Thammakhet et al., 2004; Thammakhet et al., 2006; He and Balasubramanian, 2010).

For passive air sampling, pollutants contaminated in the target air freely diffused to adsorb on the sampling media due to a difference in chemical potential of pollutants between two media (Górecki and Namiesnik, 2002). This makes no requirement of air pump resulting in no need of power supply and any maintenance. Thus, this sampling technique is more cost effective than active sampling. It is also simpled and can be used in high risk and/or remote areas. Therefore, current reports of air sampling around the world trended to use this alternative passive sampling such as monitoring of sulphur dioxide, nitrogen dioxide, ozone and ammonia in some areas of Asia, Africa, and South America (Carmichael et al., 2003), volatile organic compounds concentration in Japan (Kume et al., 2008), ozone in North Central Pennsylvania (Yuska et al., 2003), South Western Europe (Sanz et al., 2007), suphur dioxide in China (Chao, 2001; Zou et al., 2007), and so on.

Therefore, this article summarized the use of passive sampling for air monitoring. Its applications were divided into 3 categories depending on types of the pollutants *i.e.* heavy metals, inorganic and organic compounds.

Passive Sampling

Passive sampling was defined as the sampling technique that analyte molecules freely flow from sampled media to collecting media due to the difference in their concentrations between two media followed Fick’s first law (Górecki and Namiesnik, 2002; Thammakhet et al., 2006). There are two types of collecting media called passive sampler, commonly used in environmental analysis *i.e.* diffusion-type and permeation-type. Both types of samplers usually consist of a barrier and a sorbent. For diffusion-type sampler, a static layer of surrounding medium was commonly used as a barrier while polymer membrane was used for permeation-type sampler. The net transport across the barrier should be mainly occurred due to analyte molecular diffusion following Fick's law, while avoided from the convective transport (Seethapathy et al., 2008).

A sorbent that acts as the zero sink, *i.e.* concentration of analytes on the sorbent surface is zero, can be selected in various types available for air monitoring *e.g.* solvent, chemical reagent, polymer resin, porous adsorbent. Good sorbent should maximize collection of the interested analytes while minimize the collection of the potential interferences by other reactive gases in the environment, and inert from environmental factor such as moisture. The user was recommended to carefully choose the suitable both receiving material (sorbent), type, and configuration (geometry) of passive sampler to be specified with interested analytes and the matrix since they affect to the sampling efficiency.

When the sampler was used for sampling, the sorbent allowed exposing to the sampled air. The analytes thus was starting to be adsorbed on the sorbent. The amount of analyte collected on the sampler (adsorbed on the sorbent) can be presented as in Figure 1. Analyte molecules continuously flow to the collecting media until either reaching equilibrium or was terminated by user. In case that the equilibrium is achieved, the concentration of the analytes would not change with time. Thus, this concentration could be determined based on the ratio of analyte distribution between two mediums (Górecki and Namiesnik, 2002). However, the equilibrium time of each analyte for different sampler depends on many factors such as configuration of sampler which varied from seconds to months. Therefore, it is not proper to determine the exact equilibrium time and time-weighted average (TWA) concentrations of pollutants in the real environment (Ouyang and Pawliszyn, 2007).

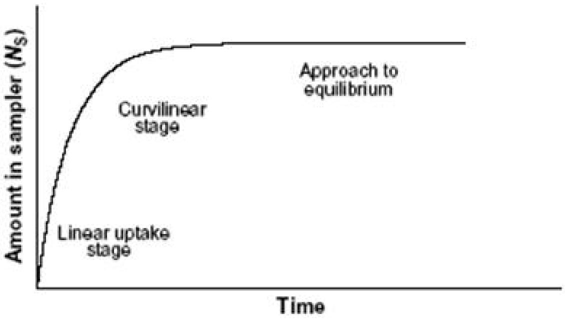

Figure 1. Uptake rate of passive sample (Bartkow et al., 2005) (reproduced with permission)

When the sampling was terminated by the user, the amount of collected analytes depends on both their concentrations in sampled media and exposed time. The user usually calibrated the device in the linear uptake stage (in Figure 1) and either pre-determined the sampling rate in the laboratory or predicted with the empirical equation prior to use in the field. Using the relationship between sampling rate and analytes concentration, TWA concentrations of the analytes can be easily determined.

For diffusion-type sampler, the application of Fick's law is expressed as in equation (1):

$$(\frac{M}{t}) = D\frac{A}{L_d}(C_0 - C) \qquad (1)$$

where *M* is mass of analyte collected by the sampler in time *t*; *D* is diffusion coefficient (rate) of the analyte; *A* is the cross-section area of the diffusion barrier; L_d is the diffusion path length; *C* is concentration of the analyte near the diffusion path- sorbent interface; C_0 is concentration of the analyte in the vicinity of the diffusion barrier inlet.

The diffusion-type samplers can be broadly classified into tube, radial, badge, and cartridge-type sampler (Krupa and Legge, 2000) (Figure 2) which have substantially different uptake rates, thus suitable for different applications. Badge- and radial-type provided higher uptake rates because of the shorter diffusion path length and larger surface area, thus suitable for short-term (daily mean) monitoring such as personal or occupational exposure (Kot-Wasik et al. 2007). While tube-type samplers which typically have longer axial diffusion path length and smaller cross-sectional diffusion area, thus generally provided lower uptake rates which suitable for long-term (monthly mean) monitoring (Kot-Wasik et al. 2007).

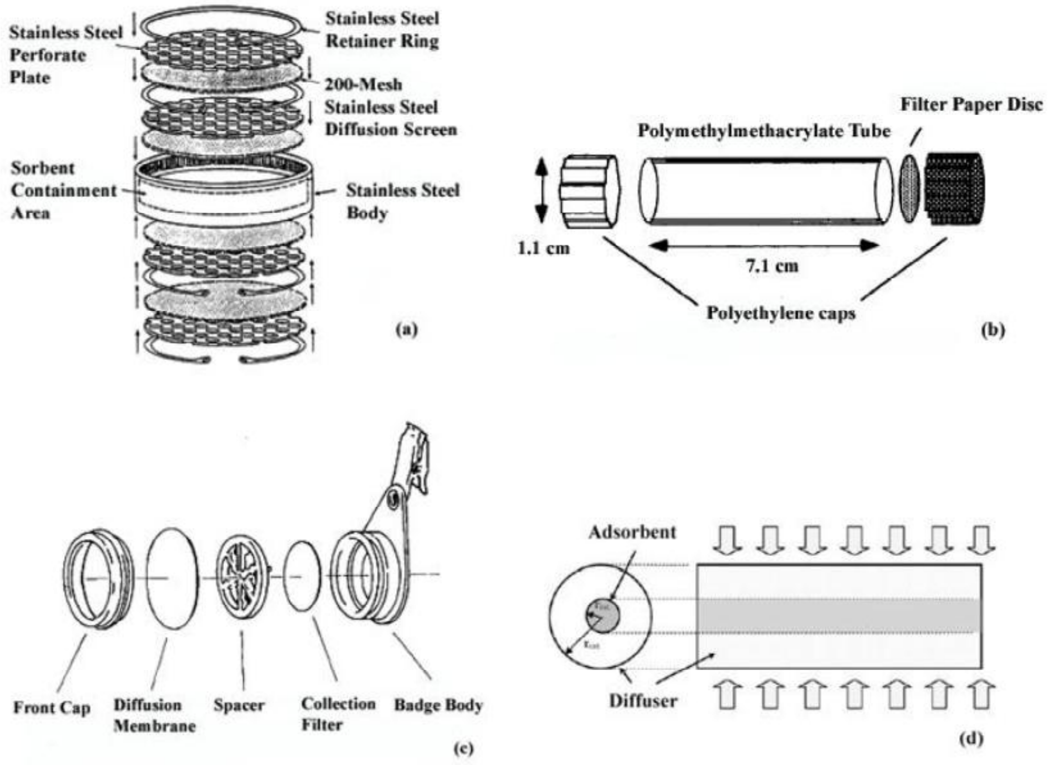

Figure 2. Examples of the passive sampler designed in the form of (a) Cartridge-type (Krupa and Legge, 2000) (b) Tube-type (Gibson et al., 1997) (c) Badge-type (Zhou and Smith, 1997) (d) Radial-type (Bruno et al., 2005) (reproduced with permission)

For permeation-type Fick's law was applied as:

$$(\frac{M}{t}) = D\frac{A}{L_m}(C_{ma} - C_{ms}) \qquad (2)$$

where *M* is mass of analyte collected by the sampler in time *t*; *D* is diffusion coefficient of the analyte in membrane; *A* is surface area of membrane; L_m is the membrane thickness; C_{ma} is concentration of the analyte on the surface of membrane exposed to air which equal to KC_0 (*K* is partition coefficient of analyte between the air and the membrane; C_0 is concentration of the analyte in air); C_{ms} is concentration of the analyte on the membrane surface in contact with the sorbent.

Calibration constant (*k*) of two samplers are different *i.e.* $k = \frac{L_d}{AD}$ for diffusion-type and $k = \frac{L_m}{AKD}$ for permeation-type. Thus, the average concentration of the analyte in the air over a certain period of time (time-weighted average; TWA) could be easily calculated as:

$$C_0 = \frac{kM}{t} \qquad (3)$$

Theory for mass transfer coefficient and rate constant has been described elsewhere for both diffusion- and permeation-type (Bartkow et al., 2004; Bartkow et al., 2005; Van drooge et al., 2005; Levy et al., 2009).

In order to successfully use passive sampler for air monitoring, the user should take account for a number of factors including sample matrix, the chemical and physico-chemical properties, form and concentration of analyte in sampled media, type of monitoring required (semi- quantitative or quantitative measurement), sampling duration required, and especially for the variability of environmental parameters around the sampler.

Environmental parameters would affect to the reliability of passive sampling. These would directly impact on actual uptake of sample and make it deviate from Fick's first law based on the assumption of the steady-state occurred. The amount of analytes hold on the sorbent is varied with environmental factors *e.g.* temperature, moisture, wind velocity etc. Therefore, the passive sampler needed to be evaluated its performance *i.e.* analytical recovery, sampling capacity and uptake rate, reverse diffusion, storage stability, effect of the temperature, biofouling and fluid flow across the sampler, accuracy and precision, shelf life and the effect of humidity (Seethapathy et al., 2008). Since many environmental factors would affect the passive sampling, the US National Institute of Safety and Health (NIOSH) set the accepted accuracy of ±25% and a bias of ±10% for air monitoring using passive sampler (Cassinelli et al., 1987; Myers et al., 2005; Thammakhet et al., 2006; Seethapathy et al., 2008). The parallel comparison with active sampling is also recommended to validate the passive sampling performance.

Applications for Air Monitoring

A number of researches reported the use of passive sampler for environmental analysis as well as many reviews involved with theory and application of passive samplers (Krupa and Legge, 2000; Górecki and Namiesnik, 2002; Cox, 2003; Kot-Wasik et al., 2007; Seethapathy et al., 2008). In this article, applications of passive sampling for air monitoring were focused. Applications were divided into three groups according to properties of interested analytes *i.e.* heavy metal, inorganic pollutants, and organic pollutants which were further divided into subgroups *i.e.* semi-volatile and volatile organic compounds.

Heavy Metal

Even though heavy metals usually contaminated in water and soil more than in air, the atmosphere is a major source of some heavy metals *e.g.* mercury distributed to the ecosystem (Lindberg and Stratton, 1998).

However, the use of passive sampling for heavy metal still limited. Recently, Lyman et al. (2010) reported the used of passive sampler for estimating gaseous oxidized mercury concentration. Cost effective passive sampler was designed as shown in Figure 3 consisted of an activated polysulfone cation-exchange membrane collection surface, a series of acrylic plates and a polycarbonate container as a protective housing. This cation-exchange membrane provided an extremely efficient uptake of gaseous oxidized mercury (Lyman et al., 2009). The passive sampler could be used regardless of temperature, humidity, or low concentration of gaseous elemental mercury, particulate-bound mercury, but sampling rate was affected by wind speed. However, the concentration of atmospheric gaseous oxidized mercury calculated from passive sampling data still correlated with those obtained from an automated analyzer (Lyman et al., 2010).

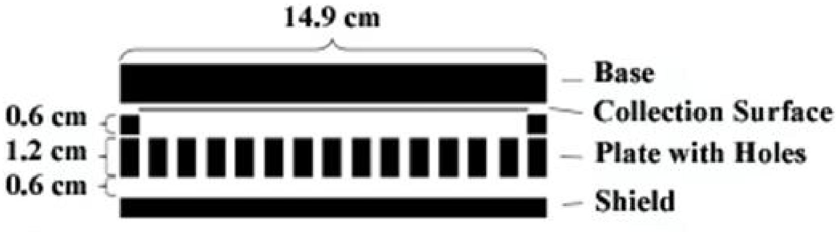

Figure 3. Two-dimension diagram of the gaseous oxidizing mercury passive sampler (Lyman et al., 2010) (reproduced with permission)

Inorganic Compounds

The use of passive sampler for monitoring various inorganic compounds in air were reported, *e.g.* ammonia (Roadman et al., 2003; Perrino and Catrambone, 2004; Wilson and Serre, 2007), carbon dioxide (Bertoni et al., 2004), nitrogen oxides (Stranger et al., 2008; DeForest Hauser et al., 2009; Vardoulakis et al., 2009), and sulphur dioxide (Cruz et al., 2004), ambient acid gases (Bytnerowicz et al., 2005; Gibson et al., 1997), and ozone (De Santis et al., 2003; Manes et al., 2003; Yuska et al., 2003; Plaisance et al., 2007; Sanz et al., 2007; Vardoulakis et al., 2009). These inorganic compounds came from different sources and belong to the different properties, leading to the different designs of passive sampler.

Gaseous ammonia

Gaseous ammonia was released from agricultural activities, in particular animal husbandry such as swine farm. The tube-type passive sampler containing with acidic adsorbent were used as sampling device (Roadman et al., 2003; Perrino and Catrambone, 2004; Wilson and Serre, 2007). Perrino and Catrambone (2004) found that glass body sampler provided the unsatisfactory results of underestimated ammonia concentration (30-40% difference from the reference concentrations) depending on the cleaning procedure. Pyrex glass denuders also showed the same results, while polyethylene bodies were shown to be free from this behavior. Thus, passive sampler with polyethylene body was recommended for ammonia monitoring. For the acidic adsorbent, paper filters impregnated with various types of acid *i.e.* oxalic, citric, phosphorous acid were compared. Of all acids, the oxalic acid provided the lowest ammonia concentration, because of its volatility. Citric acid provided the same results as phosphorus acid. However, with the lower standard deviation, the phosphorus acid was recommended (Perrino and Catrambone, 2004).

Acid vapor

Nitric acid vapor is a principle component of photochemical smog that produced highly in the day time, in opposite to nitrous acid vapor which was highly formed in the night. Both acid could be sampled using passive sampler as shown in Figure 4(a). They were adsorbed on the nylon filter which was reported as a perfect sink for nitric acid (Durham and Stockburger, 1986). However, there were 30% HNO_3 lost using this design due to the adsorption on particulate matter in the Teflon pre-filter or water condensing during cool and moist conditions (Bytnerowicz et al., 2005). For acetic and formic acid, the Palmes diffusion tube (Figure 2(b)) was used (Gibson et al., 1997). The filter paper disc was impregnated with 20 μl of a solution of 1 M potassium hydroxide and 10% (v/v) glycerine prior to expose to atmosphere. When acetic and formic acid freely diffused to the sampler, they were trapped on the paper filter as potassium acetate and potassium formate, respectively. The accumulated salts after that were washed by de-ionized water for further analysis.

Carbon, nitrogen and sulphur dioxides

Carbon dioxide (CO_2), oxides of nitrogen (NO and NO_2), and sulphur dioxide (SO_2) are traffic-related air pollutants which emitted from petrol- and diesel-engines vehicles (Rijnders et al., 2001) and have increasing impact on urban air quality (Stranger et al., 2008). Passive samplers were therefore reported for monitoring these oxides quantity in air.

For carbon dioxide which is actually regarded as a primary air pollutant due to its involvement in global greenhouse effect, the hydro-alcoholic $Ba(OH)_2$ solution was used as CO_2 adsorbent. The determination based on the determination of solute Ba^{2+} in barium hydroxide before and after adsorption of carbon dioxide (acid-base reaction), in which its carbonate salt precipitates. A passive sampler was set up (Figure 4(b)) for determination of CO_2 in indoor air. The results showed the constant uptake rate over six weeks exposure with good precision and reproducibility (Bertoni et al., 2004).

For oxide of nitrogen, various designs of passive samplers *e.g.* Palmes-type sampler (Palmes et al., 1976; Glasius et al., 1999; Stevenson et al., 2001), Ogawa commercial sampler (DeForest Hauser et al., 2009), Radiello® sampler (Stranger et al., 2008), badge-type sampler (De Santis et al., 2001) were reported. Despite the different design, most samplers based on the adsorption of NO_2 on filter coated with triethanolamine (TEA) (Figure 4(c)). TEA reacted with NO_2 to form a nitrosodiethanolamine (Panella et al., 2000). For total sampling of NO and NO_2, the oxidant filter was added by coating filter with 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (PTIO) or potassium chromate and chromium (V) (Brown, 2000; DeForest Hauser et al., 2009; Vardoulakis et al., 2009). These oxidants oxidized NO to NO_2 which then diffused further to react with TEA. However, potassium chromate and chromium (V) was reported to have ineffective conformation of NO to NO_2 at high ambient concentration during winter (Vardoulakis et al., 2009). Overestimation of NO_2 was commonly reported due to the reaction of NO and O_3 inside the tube and eddy diffusion caused by wind turbulence at the entrance of sampling tube that leaded to the shortening of diffusion path length (Heal and Cape, 1997; Ayers et al., 1998; Heal et al., 1999a; Heal et al., 1999b; Kirby et al., 2001). Sheltered sampler provided underestimation of NO_2 concentration by 9-10%, while unsheltered provided the overestimation by 8-9% with the same measurement (Bush et al., 2001). This would because wind turbulence increased the uptake rate (Campbell et al., 1994; Bush et al., 2001). While Glasius et al. (1999) found that unsheltered sampler provided the higher concentration of nitrogen dioxide than sheltered for 11% for wind speed around 3.5 $m\ s^{-1}$. In addition to wind velocity, relatively humidity and temperature was found to have smaller influences, around 3% /°C (Plaisance et al., 2004).

Solution of TEA was an important for the adsorption of NO_2. Underestimation of NO_2 concentration reported using 50% TEA/water, while this effect did not show using 10% or 20% TEA/water (Kirby et al., 2000). It was thus suggested to prepare the solution with sufficient hydration for complete adsorption of NO_2 (Palmes and Johnson, 1987; Kirby et al., 2000). However, TEA may react with SO_2 leading to the reduction of adsorption efficiency of NO_2 due to the acidified adsorbent (Cox, 2003). This interference of SO_2 could be reduced by limiting exposure of sampler to 1 to 2 weeks. Other adsorbing reagents reported for NO_2 sampling were KI in conjunction with NaOH to maintain high surface alkalinity for long-term exposure (Ferm and Rodhe, 1997), and Na_2CO_3/ 1% glycerin solution (De Santis et al., 2001).

Causing a respiratory and cardiovascular disease, SO_2 is another pollutant measured by passive sampler. Na_2CO_3 , K_2CO_3, TEA, NaOH, or Na_2HgCl_4 impregnated filter was used as SO_2 adsorbent (Krochmal and Kalina, 1997a; Krochmal and Kalina, 1997b; Ferm and Svanberg, 1998; Cox, 2003; Cruz et al., 2004; Zou et al., 2007; Campos et al., 2010). After exposure, SO_2 trapped on filter *e.g.* Na_2CO_3 impregnated filter before extracted by either ultrasonic bath using H_2O_2 and determined as SO_4^{2-} or washed with de-ionized water and determined as SO_3^{2-} for TEA filter. The passive sampler provided an overall accuracy of 15% compared to active sampling under real conditions of industrial and urban areas (Cruz et al., 2004).

<u>Ozone</u>

Since ozone is a major greenhouse gas and a species involved in photochemical processes through the production of hydroxyl radicals (De Santis et al., 2003), measurement of ozone is very important. There has been a great interest to improve the diffusion-type passive sampler for O_3 measurement (Krupa and Legge, 2000; Helaleh et al., 2002; Manes et al., 2003; Plaisance et al., 2007; Sanz et al., 2007). Radial and badge-sampler was preferred rather than tube-type due to the lower pollutant residence time in badge reduced the potential NO scavenging of the ozone within the diffusion path (Cox, 2003; Plaisance et al., 2007). Various reagents were reported as ozone adsorbent *i.e.* 1,2-bis(4-pyridyl) ethylene (DPE) (Plaisance et al., 2007), nitrite (Koutrakis et al., 1993; Tang and Lau, 2000; De Santis et al., 2003; Yuska et al., 2003; Campos et al., 2010), indigo compounds (Cox and Malcolm, 1999), potassium iodine (Kanno and Yanagisawa, 1992), 3-methyl-2-benzothiazolinone acetone azine with 2-phenylphenol (Hackney et al., 1994) and *p*-acetamidophenol (Ikeura and Mizoguchi, 1996). However, most reagents, except DPE and nitrite, lack of specificity since they could react with other atmospheric oxidants such as NO_x and peroxyacetyl nitrate (PAN) (Helaleh et al., 2002; Plaisance et al., 2007).

For DPE which is light sensitive, the prepared filter cartridge was stored in a closed-tube in the dark and placed in dark color-sampler body (*e.g.* blue) during exposure (Figure 4(d)). DPE would react with freely diffused ozone to form ozonide intermediate, which upon hydrolysis yields pyridine-4-aldehyde (PA). Before analysis, 3-methyl-2-benzothiazolinone (MBTH) was added to react with PA resulting in azide molecule that would be determined by colorimetry (Plaisance et al., 2007). For nitrate coated filter, ozone would oxidize nitrite and produce nitrate ion which then could be determined by ion chromatography (De Santis et al., 2003).

Solid phase micro-extraction (SPME) is another approach used as ozone passive sampler (Lee and Tsai, 2008). The polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber was coated with ozone derivatizing agent *i.e.* o-2,3,4,5,6,-(pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) and DPE prior to use. This made ozone in air that freely diffused into the sampler reacted with DPE to form PA which then further reacted with PFBHA to be oximes derivatives. The derivatives were then direct thermally desorbed and determined by gas chromatography. The correlations between the results obtained from field sampling using this SPME sampler and direct-reading ozone monitor were found to be consistent with r = 0.9837.

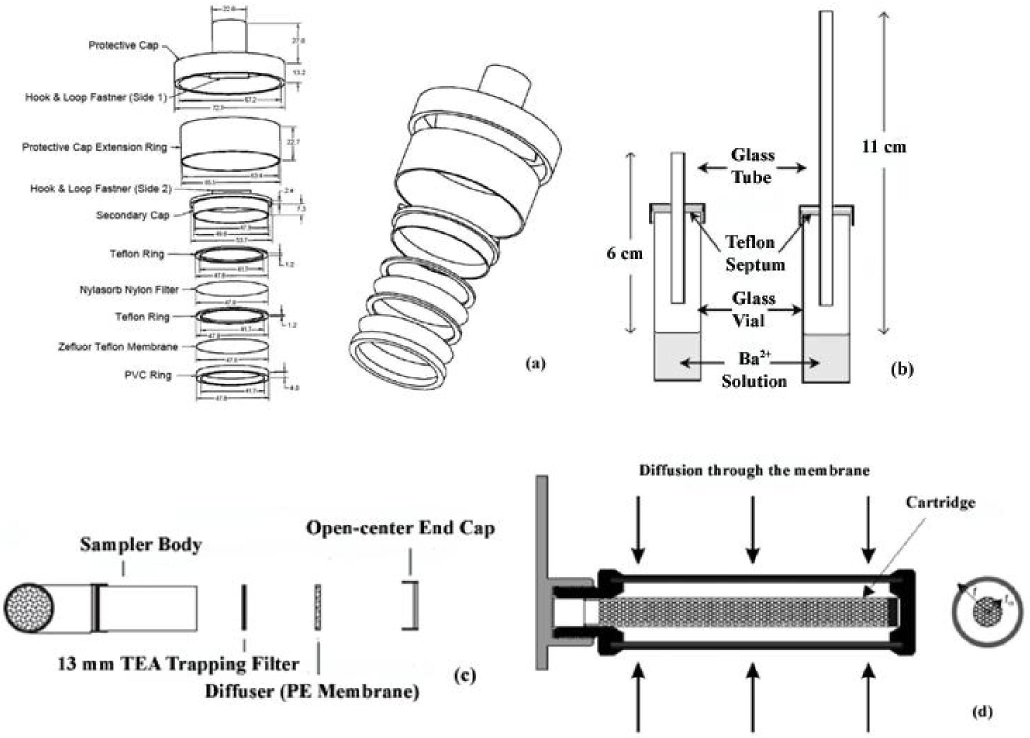

Figure 4. Diagram of the passive sampler for monitoring the inorganic (a) nitric/nitrous acid (Bytnerowicz et al., 2005) (b) CO_2 (Bertoni et al., 2004) (c) NO_2 (Sekine et al., 2008) (d) O_3(Plaisance et al., 2007) (reproduced with permission)

Organic Compounds

Volatile Organic Compounds

Volatile organic compounds (VOCs) are pollutants commonly found in both indoor and outdoor air. Some of them *e.g.* benzene, formaldehyde has been a human carcinogen. Since the human could easily expose these compounds, through breathing, many researches in the field of air monitoring focused on them. Passive sampling has been reported as a tool to achieve VOCs analysis using porous adsorbent with/without derivatizing agent coated as a receiving phase. These porous adsorbent would carefully select to be suitable with the interested pollutants. Most literature involved with diffusive-type passive sampler, although permeation-type has also been reported.

Among VOCs pollutants, volatile aromatic hydrocarbons *i.e.* benzene, toluene, ethylbenzene, xylene (BTEX) received a great interesting. Charcoal pad (Elke et al., 1998), Tenax TA (polydiphenylene oxide) (Thammakhet et al., 2004; Thammakhet et al., 2006), Carbopack X (intermediate between graphitized carbon and molecular sieve) and Carbograph 5 (graphitized carbon) (Strandberg et al., 2006), Carbograph 4 (graphitized carbon) (Pennequin-Cardinal et al., 2005), Chromosorb 106 (polystyrene) had been employed as a trapping phase. The VOCs would physisorption onto a porous solid sorbent during exposure. After exposure, these adsorbed aromatic hydrocarbons normally thermally desorbed before analysis using gas chromatography. Often, the back diffusion phenomenon occurred due to inversion of concentration gradient between the adsorbent surface and ambient air when the sampler was exposed to strong concentrations variations in ambient air. The bias of measurement from this phenomenon was investigated (Pennequin-Cardinal et al., 2005). It was found that exposing the sampler (carbograph 4 as an adsorbent) in medium and high level of BTEX for 7 days with a relative humidity of 50±3%, temperature of 20±2 °C, wind velocity of 0.5±0.1 m s^{-1} did not show the significant effect. Thus, the daily variations of BTEX concentration did not seem to affect on the sampling rate (Pennequin-Cardinal et al., 2005).

1, 3-Butadiene is another VOC usually emitted from road traffic and industry. It was suspected to be a carcinogenic compound (group 2A for IARC classification (IARC, 1999)). Carbopack X and Carbograph 5 were reported as adsorbents (Martin et al., 2003; Martin et al., 2005; Strandberg et al., 2005; Strandberg et al., 2006). Carbopack X provided more adsorption efficiency than carbograph 5 and showed no effect of humidity, wind velocity, even minor temperature effect (Strandberg et al., 2006). In addition, adsorbed 1,3-butadiene in the sampler did not appear to react with ambient ozone (Martin et al., 2005).

Another groups reported the use of the passive sampler was carbonyl compounds. Difference from others, this group usually required a coated adsorbent. 2, 4-Dinitrophenylhydrazine (DNPH) is common derivatizing agent of carbonyl compounds to form hydrazone derivatives (Uchiyama et al., 2004; Shinohara et al., 2009). After exposure, the derivatives usually extracted and followed analyzed using high performance liquid chromatography. This DNPH could be coated either on filter (Grosjean and Williams Ii, 1992) or porous adsorbents *e.g.* silica gel (Uchiyama et al., 2004), Carbotrap B (Shinohara et al., 2009). Part per billion (ppb) level of 21 carbonyl compounds was achieved using silica gel coated DNPH with design as in Figure 5 (Uchiyama et al., 2004).

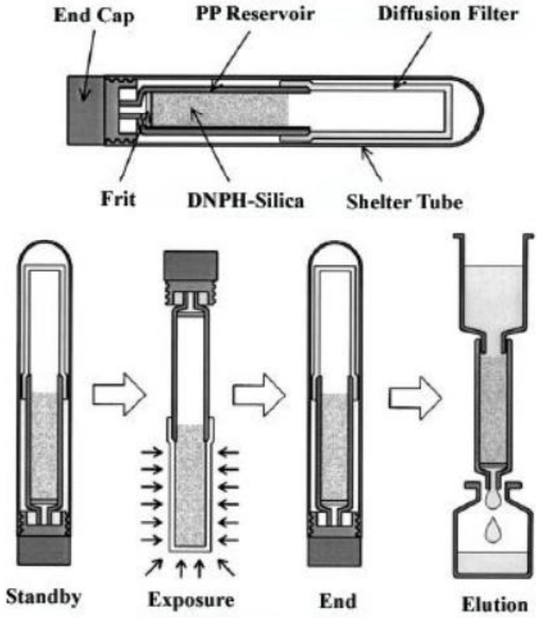

Figure 5. The DNPH coated silica passive sampler for carbonyl measurement and the method of the collection/ elution (Uchiyama et al., 2004) (reproduced with permission)

For other VOCs, volatile organo halogen compounds in indoor air in Japan has been surveyed using passive sampler with activated charcoal adsorbent (Olansandan et al., 1999), while VOCs emitted from building materials was sampled using SPME fiber (PDMS/carboxen) as a passive sampler (Nicolle et al., 2009). Permeation-type passive sampler has also been reported for VOCs in indoor air. Badge-type permeation passive sampler with silicone membrane and activated charcoal sorption media was employed (Zabiegala et al., 2002). This sampler provided no different results with active sampling. However, the calibration constant of the sampler slightly change over time, thus recalibration was recommended.

<u>*Semi-Volatile Organic Compounds*</u>

Semi-volatile organic compounds (SVOCs) composed many priority pollutants such as polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs), etc. These compounds are toxic as they have ability to bioaccumulate in fatty acid tissue and can cause a range of health problems in the immune, endocrine, nervous and reproductive systems of animals and humans (Klánová et al., 2006). They are also persistent that made them named as persistent organic pollutants (POPs). They are also ubiquity and their primary distribution throughout the environment mainly via the atmosphere (Bartkow et al., 2005). Although, some SVOCs, *e.g.* hexachlorobenzene (HCB), polychlorinated biphenyl (PCB), has been banned for many years, their concentrations have still been observed in production and application area and to a lesser extent in rural and remote area (Van drooge et al., 2005). This cause SVOCs was monitored by the use of passive samplers.

A large number of SVOCs measurement involved with various types of passive sampler, such as semi permeable membrane device (SPMD), polyurethane foam (PUF) disk, XAD-resin passive sampler, SPME passive sampler, and coated stir bars passive sampler (Petty et al., 1993; Bartkow et al., 2004; Paschke and Popp, 2005; Harner et al., 2006; Paschke et al., 2006; Hazrati and Harrad, 2007; Levy et al., 2009; Wang et al., 2009). The most commonly used are SPMD and PUF disk.

SPMD consisted of a low density polyethylene (LDPE) tube (70-90 mm wall thickness) that filled with 20% w/w 1,2,3-tris[cis-9-octadecenoyl]glycerol (triolein). SVOCs would freely diffuse through polymeric membrane bag, and then accumulated in lipophilic solvent. The membrane's transient polymeric cavities were about 1 nm in diameter. Pollutants can be sequestered in an SPMD by cavity size and non-polarity of the membrane (Levy et al., 2009). Since both membrane and adsorbing phase are hydrophobic, the SPMD is good for hydrophobic pollutants (log K_{OW} > 3) (Huckins et al., 2006). It has been used for passive sampling of PAHs (Bartkow et al., 2004; Söderström et al., 2005; Bartkow et al., 2006; Choi et al., 2007) and organochlorine compounds (Petty et al., 1993; Van drooge et al., 2005; Levy et al., 2009). Good agreement with high-volume active sampling for organochlorine monitoring was obtained, even in the atmospheric of remote high mountain site (1600, 2240, 2600 m above sea level) (Van drooge et al., 2005), while there were slightly different for PAHs monitoring (Bartkow et al., 2004). It was owing to PAHs could be absorbed on particle leading to lower amount in SPMD (Lohmann et al., 2001). Moreover, photodegradation of PAHs might be occurred (Bartkow et al., 2006). Thus, sunlight protected chamber was recommended for passive sampling of photo sensitive compounds *e.g.* PAHs using SPMD. Even though SPMD was simple, the diverse and variable environmental conditions can cause unpredictable pollutant uptake rates by influencing diffusion rate and membrane permeabilities (Petty et al., 1993). The SPMD sampling rate was affected by the physicochemical properties of sampled compounds, while high wind speeds/turbulences, temperature, and amount of bound particle (Lohmann et al., 2001; Söderström and Bergqvist, 2004; Levy et al., 2009).

Polyurethane foam (PUF) disk, which acts as a sampling medium in high volume active sampling, is the most used diffusion-type passive sampler for SVOCs monitoring. This PUF disk would be placed in the bottom bowl of connected two stainless steel bowl, shown in Figure 6. The space between two bowls and the opened bottom bowl would lead air and interested pollutants move in and out, while upper bowl acts as a precipitation and light protection. This passive sampler showed good agreement results with active sampler for POPs (Harner et al., 2006; Mari et al., 2008). Many factors showed the influence to the sampling rate of PUF disk. Temperature affected the sampling rate as average factor of 2.7 times higher in summer than winter. Thus, differential ambient and deployment chamber temperature should also be considered when PUF disk is used (Kennedy et al., 2010). Wind speed also affected the sampling rate (Tuduri et al., 2006). It resulted substantially different of time-weighted average and integrated period. Thus, a special sampler configuration (like Figure 6) was recommended to reduce this effect. The sampling rate of the same analytes from different design sampler deployed in each environmental conditions would be varied, thus it should not be extrapolated (Hazrati and Harrad, 2007). Gas-particle partitioning has also been reported to affect the uptake rate (Chaemfa et al., 2009) and the knowledge of this is still required to correct this effect, and to improve predicted uptake rates.

This PUF passive sampler has been used for SVOCs monitoring in air in many region such as for polybrominated diphenyl ethers in urban and rural area in Toronto (Harner et al., 2006), OCPs, PAHs, PCBs (POPs) in processing plants and chemical factory in Czech republic (Klánová et al., 2006), pesticides in Ontario (Gouin et al., 2008), POPs in indoor and outdoor air in Mexico, Sweden, and UK (Bohlin et al., 2008), POPs in Spain (Mari et al., 2008), PCBs (due to Balkan War) in Yugoslavia (Klánová et al., 2007).

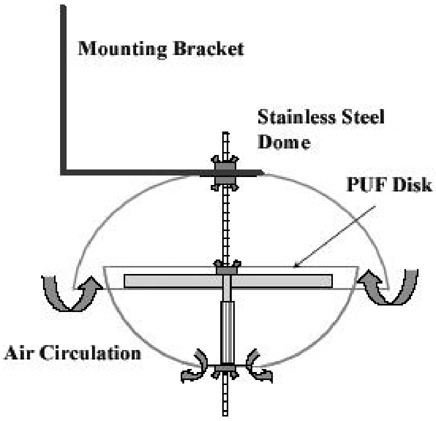

Figure 6. The PUF disk passive sampler (Harner et al., 2006) (reproduced with permission)

Conclusions

A number of researches applied passive sampler as a important tool for air monitoring. Heavy metal, inorganic and organic compounds were sampled from air media with a wide area ranging from individual exposure to global issues of climate change. In addition to pollutant species, the design of sampler should be concerned, since it significantly affects to sampling rate. Badge and radial diffusion –type passive sampler provide higher uptake rate than tube and cartridge – type. They are suitable for short-term monitoring. The other kind of sampler, permeation-type passive sampler is widely used for many works, including SVOCs sampling. For the VOC, most of them were collected by the passive sample containing with the sorbent coated/uncoated derivatizing agent. The acidic receiving phase was used to trap the NH_3 vapor, while basic solution was applied for CO_2 gas and some ambient acids. Triethanolamine (TEA) plays an important role for adsorbing NO, NO_2 and SO_2 in the sampler. For O_3 measurement, many reagents were used, but they were not specific and could be interfered by NO_x. Researchers recommend to use 1,2-bis(4-pyridyl) ethylene (DPE) and nitrite as derivatizing agent coated on filter. Although there were a few studies on a heavy metal passive air sampler, the cation-exchange membrane was employed for sampling the mercury vapor. Environmental conditions, *e.g.* wind velocity, relative humidity and temperature, were important parameter that should be concerned, since they could extremely affect to the sampling efficiency. The limitation of passive sampling was summarized in Table 1.

Table 1. Obvious limitation of passive sampling for various sample type

Type of sample	Limitation
Heavy metal	Sampling rate was affected by wind speed
Gaseous ammonia	There was a saturation of the sampler when sampling was at extremely high ammonia concentration
Acid vapor	There was an interference caused by dust particles and high humidity as well as an activity of ambient photochemical processes resulting in the lost of acid vapor
Carbon, nitrogen and sulphur dioxide	The precision of the method increases along with the time exposure and with a faster sampling rate
Ozone	Lack of specificity as the used reagent can be interfered with other atmospheric oxidants *e.g.* NO_x and peroxyacetyl nitrate (PAN)
VOCs	Sampling rate was affected by wind speed and some publication reported quite high %RSD e.g. 22% (accepted was 25%)
SVOCs	Sampling rate was affected by wind speed with depended on sampler configuration

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