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Recent Advances in Microextraction Methods for Sampling and Analysis of Volatile Organic Compounds in Air: A Review

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Human exposures to volatile organic compounds (VOCs) are associated with a wide range of health problems. Due to the adverse effects of VOCs on the human health, determination of trace levels of VOCs is very important for accurate assessment of indoor and outdoor exposure. Solid phase microextraction (SPME), needle trap device (NTD), and hollow fiber-liquid phase microextraction (HF-LPME) are increasingly used for accurate determination of VOCs in air. In this paper, authors have reviewed new developed forms of SPME, NTD and LPME techniques for the sampling and analysis of VOCs in air with a main focus on SPME coating fibers and NTD sorbents. The effects of some environmental and device parameters on SPME and NTD samplers are also reviewed. Moreover, several analytical parameters such as carryover effect, storage time, limit of detection (LOD) and limit of quantitation (LOQ) of these new technologies are discussed. Finally, the applicability, limitations and future trends of these methods are reviewed.

Keywords: Volatile organic compounds (VOC), Solid phase microextraction (SPME), Needle trap device (NTD), Air

INTRODUCTION

Volatile organic compounds (VOCs) are among the major indoor and outdoor pollutants. VOCs and their degradative products are considered as important agents in the epidemiology of respiratory disorders and various types of cancers [1,2]. Nowadays, the presence of these compounds at workplaces has become as a major concern for many scientists worldwide. VOCs are globally used in many products, such as solvents, cleaning and degreasing agents, polymerization, blowing agents, and disinfecting agents. The products containing VOCs can release them into the air when they are used and stored [3,4]. Because of their high vapor pressure, they can be easily released into the environment and workplace. Previous studies have defined several definitions for VOCs [5,6]. Generally, VOCs can be defined by two following definitions: in the

first definition, they are known as organic compounds contributing to photochemical ozone creations. The second definition is based on their physical-chemical properties such as pressure and temperature [7]. In this case, VOCs are organic compounds containing carbon atoms with boiling temperature below 373.15 K at 101 kPa and vapor pressure higher than 13.3 Pa at 25 °C [8]. In another definition provided by EU Solvents Directive (1999/13/EC), VOCs are organic compounds with vapor pressure of at least 10 Pa at 20 °C [9]. Halogenated hydrocarbon compounds (HVOCs) as a group of VOCs are also known to be hazardous. These compounds can enter the body through skin contact, inhalation, ingestion and hand-to-mouth contact. HVOCs can then enter the bloodstream and accumulate in various organs [10]. Due to these adverse effects of VOCs on the human health, it is necessary to develop simple and cost-effective technologies with high sensitivity and accuracy for the detection of these harmful compounds in air, especially in workplace air. Based on our

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knowledge, there is no review focusing on the new advances of microextraction methods for sampling and analysis of VOCs in air. Therefore, with respect to the previous reviews on the SPME applications for detecting VOCs in air, the main objective of this article is to review all of the new developed technologies for the sampling and analysis of VOCs in air [9,11]. Main literature sources in this study consist of published articles on developed technologies for the sampling and analysis of VOCs in air.

AIR SAMPLING AND ANALYSIS OF VOCs

Sampling and analysis of analyte are the most important steps for detecting analyte of interest in the matrix samples. In recent years, several studies have been conducted to develop new technologies for measuring VOCs from air in trace analysis [7,12-14]. Sampling of VOCs can be carried out by active or passive methods. The passive methods are used for sampling the indoor and outdoor air pollutants in trace analysis. Due to the fact that the passive methods are easy to use and handle and require cheap instruments, there has been growing interest in the use of them for the assessment of occupational exposures at low concentrations [14]. It should be noted that these methods are only suitable for long-term sampling periods and they are less commonly used to quantify indoor pollutants [15,16]. While active sampling methods can be used for short-term periods. Passive badges, canisters, sorbent traps, active samplers and diffusive samplers are commonly used for sampling the VOCs in air [16,17]. According to the NIOSH 1501 method, adsorbent tube and GC-FID have been recommended for the sampling and analysis of VOCs in workplaces [18]. Moreover, the use of containers and GC-MS has been also recommended by the USEPA for outdoor determination of VOCs [19]. Most of the previous conventional methods are based on drawing air through a sorbent or impinger trap followed by a solvent desorption process and injecting the solvent into the detective device to detect the extracted analytes. These sampling methods have many disadvantages such as low sensitivity, costly, non-reusable and solvent requirements [20]. In this regard, the development of new technologies is necessary to overcome the disadvantages of previous methods.

NEW DEVELOPED TECHNOLOGIES FOR SAMPLING AND ANALYSIS OF VOCs

Solid-phase Microextraction (SPME)

Solid-phase microextraction (SPME) is one of the extraction techniques that can be used for the sampling and extraction of VOCs and semi-VOCs, especially in water aqueous. SPME application for the sampling and analysis of VOCs in air has been relatively less studied [21,22]. This method was first introduced by Pawliszyn and his coworkers [21]. In the first SPME design, it was consisted of a Hamilton syringe attached to optical fiber with epoxy glue (Fig. 1a). In this method, a film coating of sorbent was used for extracting analytes from matrix [23]. SPME technique can be applied for a wide range of VOCs and semi-VOCs at trace concentrations, which has many advantages in comparison to the previous conventional methods, such as simplicity, low cost, solvent-free, time-efficient, sensitive, and effectiveness in rapid sampling, flexibility, and high enrichment factor [24]. In SPME method, all steps of extraction, pre-concentration, desorption and analysis are combined in one step [25]. It is structurally similar to a syringe consisting of different parts including a small fiber with a silica core in tip of the syringe coated with a stationary phase for trapping target analytes, metal sheath, springs and septum, and pressure piston [23,26]. Figure 1 shows a schematic of conventional SPME device. Depending on the target analytes, various fibers are used in SPME, such as polyacrylate (PA), polydimethylsiloxane (PDMS), carbowax-polydimethylsiloxane (CAR-PDMS), and polydimethylsiloxane-divinylbenzene (PDMS-DVB). These coating fibers are commercially available and offer a high efficiency for the extraction of their specific compounds [27]. However, these coating fibers suffer from several drawbacks like high cost, friability and required high temperature [28]. Previous studies have reported that PDMS-DVB fiber is more efficient for extracting VOCs under non-equilibrium conditions and short sampling times [29]. To identify an appropriate fiber, physico-chemical characteristics of the target analyte should be considered including boiling point, molecular weight, vapor pressure, polarity, detector type, analyte concentration and functional groups [30]. The characteristics of the coating fiber are also

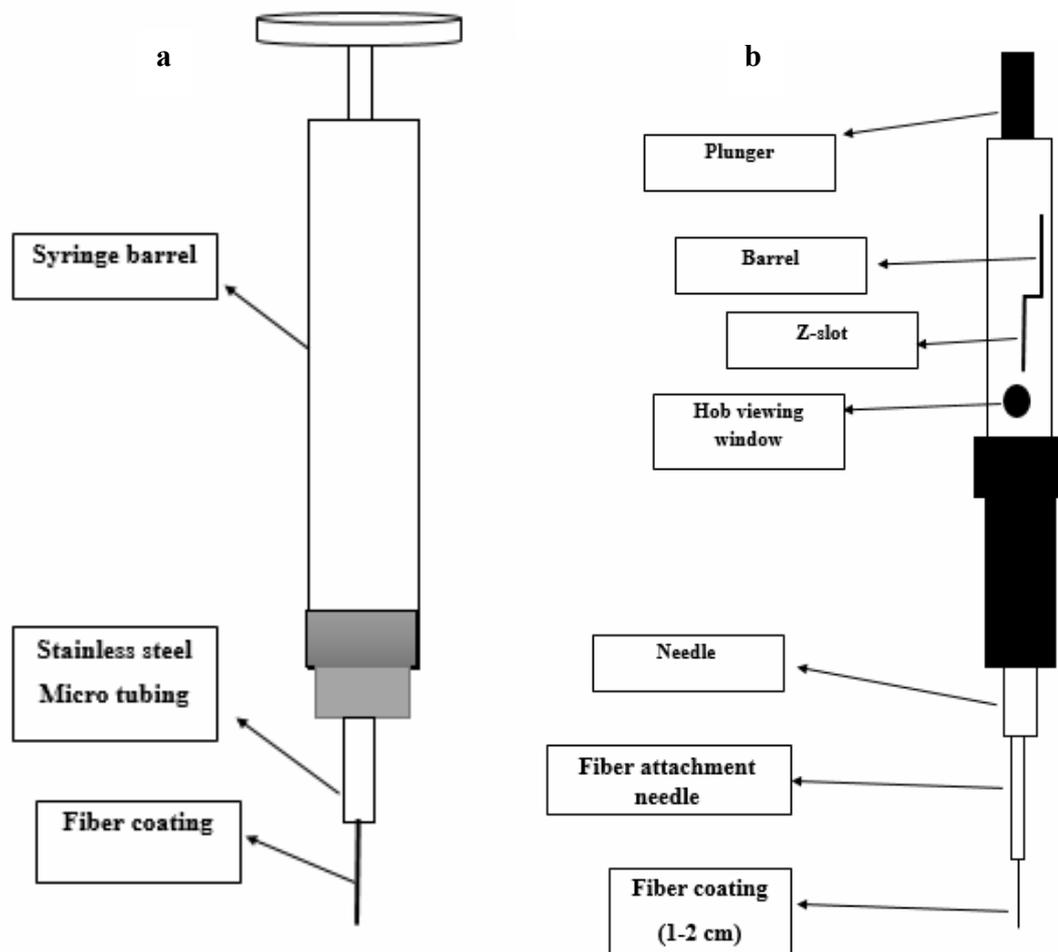


Fig. 1. Schematic diagram of SPME device: (a) Customized SPME device (the first form of SPME based on Hamilton syringe), (b) Conventional or commercial SPME device.

important for selecting an appropriate fiber in SPME method, such as porosity, thickness, and polarity [31]. SPME sampling can be performed by attaining equilibrium of analyte between the matrix and a stationary phase, and it is not based on the complete extraction. After equilibrium, by increasing the contact time, further extraction does not occur. SPME sampling can also be performed under non-equilibrium conditions, which is classified into two exposed and retracted modes for sampling. In the retracted mode, the SPME technique is applied as a Time Weighted Average (TWA) sampler [15].

In recent years, different types of SPME have been developed such as fiber introduction mass spectrometry

(FIMS) in which a portable mass spectrometer is used along with SMPE for detecting trace levels of VOCs in air [9], and derivatization techniques occurring in the coating SPME fiber or in the injector port of analyzer for increasing the extraction efficiency and limit of detection (LOD) [32]. Moreover, Mangani *et al.*, introduced a new technique of SPME for the determination of HVOCs in air after sampling by steel containers. In this method, the output of the sampler is connected to the GC inlet with a packed column. The SPME fiber is inserted into the GC injection port [33].

Needle Trap Device (NTD)

Needle trap device (NTD) is also one of the novel

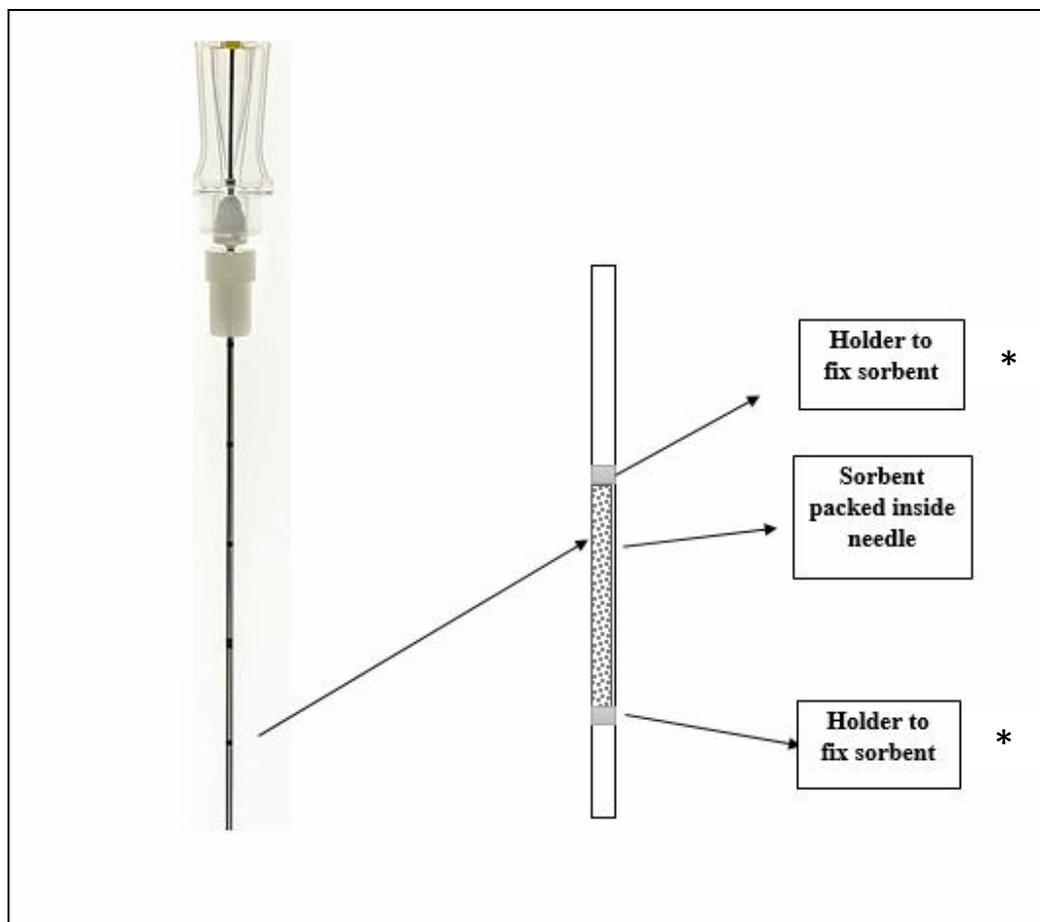


Fig. 2. Schematic diagram of NTD (* in recent studies on NTD applications glass wool is successfully used to keep the sorbent fixed).

extraction methods that its first principal was introduced by Qin *et al.*, [34]. In the NTD method, a syringe needle packed with charcoal adsorbent was used for sampling and analysis of methanol, ethanol, acetone and pentane in breath air (Fig. 2). Then, the needle was placed in the gas chromatograph injector to desorb the adsorbed analytes [34]. This technique was also introduced by Koziel *et al.*, in 2001 as a simple, environmental friendly, user friendly, small, inexpensive and solvent-less method. In the mentioned study, both NTD and SPME were used for measuring air born particulate matter and aerosol. They combined the concept of both active and passive methods with newly created microextraction methods [29]. NTD is a combination of the concepts of liquid phase microextraction

(LPME), SPME and sorbent tube. In NTD, sorbent particles are protected inside a steel needle, which makes it more robust technique than SPME. This technique is based on the microextraction of analytes using a small gauge needle packed with sorbents demonstrating a high sensitivity compared to the conventional extraction methods. Its high sensitivity is attributed to high enrichment into small volume of solid extraction phase [35]. In this method, direct desorption occurs by inserting the needle inside the GC/GC-MS port. NTD has very important advantages over SPME, such as lack of fragile fiber, inexpensive device and high sorption capacity [36,37]. Also, in SPME method, a tiny volume of analyte is extracted in comparison to the matrix volume, which requires complex calibration and careful

development [38]. NTD can be applied for both active and passive sampling and its capacity increases with the increase of sorbent quantity [37]. Its high capability for using as an active sampler can reduce the sampling time compared to SPME. A NTD packed with an appropriate and strong sorbent can also be used as a passive TWA sampler. Recent studies have reported that NTD coupled with GC-MS device acts as a sensitive technology for quantitative on-site analysis of VOCs [39]. It has also been reported that the relatively low amount of sorbent inside needle can cause the breakthrough volume in the air volume range 10-100 ml. For this reason, the design parameters of NTD must be carefully optimized to prevent occurring breakthrough and analyte loss during sampling [40]. Within research activities on NTD application, different methods have been suggested for packing sorbent inside the NTD. Most of the packing methods are based on a general rule that involves placing a 1.5 cm sorbent from the tip of the steel needle and fixing the sorbent using a holder such as glass wool (as can be seen in Fig. 2) [7,12,37]. In passive sampling, diffusion is the only mechanism for transporting analyte to the extraction phase [41]. In addition, NTD can act as a filter for trapping particulate material in the matrix [42]. Four mechanisms have a major role in the collection of particles from air streams including interception, inertial impaction, diffusion and gravitational settling. However, the effect of gravitational settling is negligible in comparison with other mentioned mechanisms [43]. Previous studies have investigated the effects of some fundamental parameters on the performance of NTD, such as packing density, sorbent type, sorbent size, air temperature, air velocity, air relative humidity, storage time, carryover effect, and desorption time [7,37,44]. In a fundamental study conducted by Lord *et al.*, it was found that the effects of sorbent type and high retention time are more important on NTD performance than those of the particle size, sorbent amount and sorbent density [38]. In the present review, the effects of some environmental and device parameters on the performance of SPME and NTD are discussed.

Hollow Fiber-liquid Phase Microextraction (HF-LPME)

Liquid-liquid extraction (LLE) as a solvent extraction method is commonly used as a classical and common

standard approach for pre-concentration of a wide range of compounds prior to analysis. In this method, the analyte of interest is extracted from one phase to another phase through a separating funnel to pre-concentrate and prepare the sample for chromatographic analysis. In the LLE method, a large volume of organic solvent is used for the pre-concentration and separation of the target analytes [45]. In recent years, there has been a growing tendency to use single-step and microextraction methods instead of the conventional methods that can be used for both sampling and separation of analytes in samples [46]. LPME has been recently used to improve the LLE performance for efficient sampling and extraction of the compounds. Indeed, LPME is a solvent-minimized preparation method of LPE, which has all advantages of the traditional LPE procedure and has overcome its drawbacks [47]. There are many advantages to employ LPME technique, such as being fast, effective, one-step preparation, and solvent-free sample pretreatment. In LPME procedure, the compounds of interest are extracted from the matrix, through a very small volume of organic solvent (a few microliters), when the acceptor phase is an aqueous phase [46-49]. This method can be divided into three categories including: (1) single drop microextraction (SDME), (2) dispersive liquid-liquid microextraction (DLLME), and (3) hollow fiber-based liquid phase microextraction (HF-LPME). In SDME technique, typically 1-3 μl of an organic solvent at the tip of a syringe is used for sampling and extraction of the target analytes [47]. This kind of LPME is only used for aqueous samples, because the drop in the tip of the syringe should be immersed in a stirred aqueous solution, and then the solvent drop is collected with a microsyringe. Afterward, the collected solvent containing target analytes is injected into the detector system. DLLME as a LPME method, introduced by Assadi *et al.* [50], is based on the use of a small volume of extraction solvent (μl) along with a few ml of dispersive solvents. In this technique, the dispersive solvent plays an important role in the extraction of analytes of interest and helps the extraction solvent for extracting the analytes from aqueous solutions. An appropriate mixture of extraction and dispersive solvent is injected into the matrix containing analytes of interest to extract them from liquid matrix [47]. Finally, the mixture containing analyte trapped is injected into the analyzer. SDME and DLLME have been applied

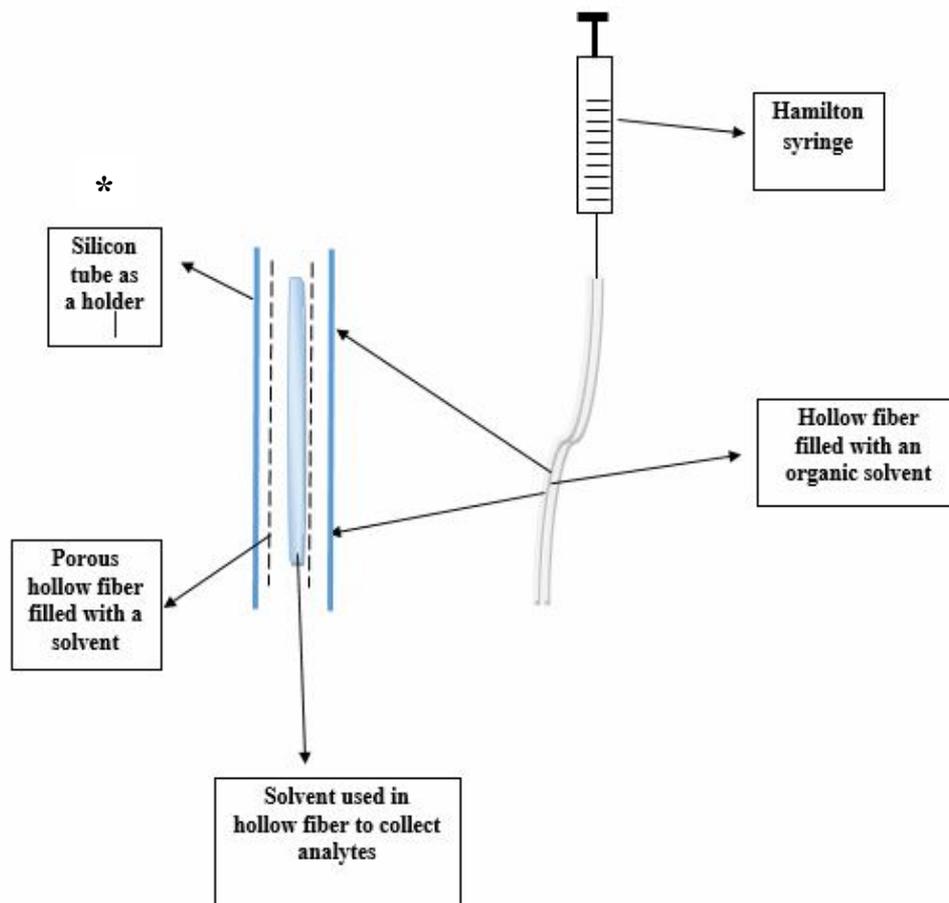


Fig. 3. Schematic diagram of HP-LPME (*A recent study has used silicon tube as a holder).

only for aqueous samples, and to our knowledge, no previous studies have been undertaken to use the application of these techniques for sampling the analytes from air.

HF-LPME as one of the LPME techniques is used as a miniature and novel method for simultaneous sampling and pre-concentration of organic pollutants from various matrices [51]. The HF-LPME was first introduced by Pedersen-Bjergaard and Rasmussen [52]. In this method, a suitable organic solvent fills the HF pores to allow the HF to absorb the analytes from air. Polypropylene is usually used as HF membrane in the HF-LPME technique. Meanwhile, various solvents can be applied in this method to develop its application for sampling the different compounds [53]. Overall structure and schematics of HF-LPME is shown in Fig. 3. There have been few studies on

the use of LPME for the sampling and analysis of VOCs in air. Most of the previous studies have focused on the use of LPME for sampling and pre-concentration of analytes from aqueous samples [54,55]. In some previous studies, HF-LPME has been successfully applied for the sampling and analysis of various VOCs from water samples [53-55]. A recent study reported that HF-LPME with hydrochloric acid (0.1%) as the solvent could efficiently be used for TWA determination of 1,1-dimethylhydrazine (UDMH) in air followed by spectrophotometric analysis [56].

FIBER/SORBENT TYPE

Various fibers and sorbents are used in SPME and NTD for sampling and analysis of different analytes from air

samples. A variety of materials have been used in SPME and NTD as fibers and sorbents, respectively. PDMS belongs to a group of polymeric organ silicon compounds widely used as the solid phase in SPME method. The efficiency of PDMS along with other materials for the determination of VOCs has been extensively investigated [29,57]. Nowadays, several types of coating fibers are commercially available, such as PDMS, Carboxen/PDMS and PDMS/Divinylbenzene (PDMS/DVB) [13-15]. Despite all benefits of these coating fibers, they suffer from several drawbacks such as instability at high temperature and high cost. For example, thermal stability of PDMS is lower than 300 °C. In addition to these commercial coatings fibers, different synthesized fibers have been studied in SPME such as nano-tubes of carbon and graphene [58,59], cobalt and zinc oxide nano-particles [60], and molecular imprinted polymers [61]. In this case, the nano-tubes of carbon and graphene revealed many inherent advantages like high surface area, high thermal stability and long lifetime [59]. Earlier studies revealed that PDMS/DVB coatings are more efficient in the sampling of VOCs over other common fibers [62]. The use of tetra-quinoxaline cavitand functionalized with methylenoxy bridges at the upper rim as solid phase in SPME method showed very low LOD (0.4-1.2 ng m⁻³) for sampling and analysis of BTEX compounds from air samples [63]. This new proposed coating fiber in SPME method also showed a good repeatability and sensitively for the sampling and analysis of BTEX compounds in air. Also, SPME coated with CAR/PDMS in the retracted mode can successfully be applied as a TWA sampler for occupational exposure assessments [64]. Under the retracted mode, SPME coated with CAR-PDMS is also suited for TWA determination of epichlorohydrin from air [15]. In this mode, SPME can be used as a passive sampler and the analyte concentration on the SPME samples are calculated according to the following equation:

$$N = \frac{D_g A}{L} \cdot C \cdot t$$

where, N indicates the amount of analyte adsorbed on the SPME fiber (ng), D_g is diffusion coefficient of gas phase or sampling rate, which could be obtained theoretically based on Fuller *et al.*, study, cm² s⁻¹, A is diffusion area (cm²), L is

diffusion path length (cm), and C and t are analyte concentration (ng cm⁻³) and sampling time (min), respectively [15,65].

In recent uses of SPME, nano-materials were used as the coating fibers for the sampling and analysis of various compounds in air [14,66]. Due to the high surface area of carbon nanotube, SPME coated with single and multi-walled carbon nanotubes might be a good option for sampling and analysis of a wide range of VOCs. Single and multi-walled carbon nanotube/silica composite fiber synthesized by sol-gel technology could increase the performance of SPME method for the determination of VOCs [66].

The use of sol-gel method as a new technique is used for synthesizing new sorbents with a high surface area [67]. In recent years, this technique has been also examined for the preparation of new and various types of fibers in SPME [68, 69]. Several operational parameters should be considered in the synthesis of new SPME fibers through sol-gel technique, such as thickness, surface area, solvability, stability, polarity, absorption capacity, and absorption rate [14]. Single and multi-walled carbon nanotube/silica composite fiber synthesized by sol-gel technologies are suited for measuring HVOCs compounds in air with a high extraction efficiency and sensitive analysis. The application of these new advanced fibers allows the quantification of the trace level of HVOCs in air (with LOD range of 0.09-0.2) [14,66].

Different materials have been so far tested in NTD to increase its sensitivity in the sampling and analysis of various analytes. In the first applications of NTD, charcoal was used as sorbent into a needle for the extraction of methanol, ethanol, acetone and pentane from human breath [34]. The use of charcoal as sorbent in NTD demonstrated a rapid and simple procedure with high sensitivity (LOD in the range a few ppb) [34]. In addition, the use of common coating SPME fibers in NTD [70] showed an appropriate efficiency in the sampling and analysis of a whole range of volatile compounds, such as aldehydes, ethanol, methanol, butadiene, acetone, and mono aromatic hydrocarbons [70]. Therefore, single layer organic polymer of methacrylic acid and ethylene glycol dimethacrylate are suited in NTD as sorbent for sampling aldehydes and hydrocarbons in air (with LOD and LOQ range of some ng l⁻¹) [70].

Table 1. A Summary of New Developed Techniques for Sampling and Analysis of VOCs in Air

	Microextraction device	Analyte	Fiber/sorbent	Detection device	LOD*	LOQ*	Precision	LDR*	Ref.*
1	SPME	BTEX in indoor air at environmental levels	CAR	HRGC-FID	0.4-2 mg m ⁻³	-	6.6-12.8%	-	[72]
2	SPME	aldehydes in exhaled breath of patients with lung cancer	PDMS/DVB	GC-MS	1 × 10 ⁻¹² M	3 × 10 ⁻¹² M	7.2-15.1%	3.3-333.3 × 10 ⁻¹² M	[73]
3	SPME	volatile and semi-volatile pollutants	PDMS	GC-MS	1.3-273.9 ng l ⁻¹	4.3-913 ng ml ⁻¹	5.6-15.2 ng ml ⁻¹	1-100 ng ml ⁻¹	[74]
4	SPME	Airborne Particulate Matter and Aerosols in diesel exhaust air	PDMS	GC/MS	-	-	-	-	[29]
5	SPME	PAHS in atmospheric particulate matter	PDMS	GC-MS	5-20 pg	-	-	-	[57]
6	SPME	aldehydes in human breath	PDMS/DVB	GC-MS	0.01-0.03 nM	0.02-0.10 nM	9-24%	0.002-20 nM	[75]
7	SPME	Sinus mucus volatiles	DVB/CAR/P Stableflex	GC-MS	-	-	-	-	[76]
9	SPME	Epichlorohydrin	CAR/PDMS	GC-MS	0.8 ng	-	6.9%	-	[15]
10	SPME	Halothane, isoflurane, and sevoflurane in operating room air.	CAR/PDMS	GC-MS	4.2-5.1 ppb	-	2.2-7.4%	-	[64]
11	SPME	perchloroethylene in dry cleaning	CAR/PDMS	GC-MS	0.08 ng	-	8.9%	-	[77]
12	SPME	VOCs (Benzene, ketones and aldehydes) in human exhaled breath vapor	NPAA fiber	GC-MS	0.7 and 3.4 ng l ⁻¹	-	1.8-14%	0.005-40 ng ml ⁻¹	[78]
13	SPME	BTEX	Cavitand-coated	GC-MS	0.4-1.2 ng m ⁻³	1.1-2.9 ng m ⁻³	-	0.4-1.2 ng m ⁻³	[63]

Table 1. Continued

14	SPME	Carbontetrachloride, Benzotrichloride, Chloromethyl methyl ether and Trichloroethylene in air	CAR/PDMS	GC-MS	0.09-0.2 ng ml ⁻¹	0.25-0.7 ng ml ⁻¹	0.1-100 ng ml ⁻¹	[14]
15	SPME	Perchloroethylene, benzotrichloride, chloromethyl methyl ether and trichloroethylene	Single-walled carbon nanotube/silica composite fiber based on sol-gel technology	GC-MS	0.11-0.2 ng ml ⁻¹	0.34 and 0.7 ng ml ⁻¹	1-100 ng ml ⁻¹	[79]
16	SPME	carbon tetrachloride	Synthesized multi- walled carbon nanotube based on sol-gel method		0.09 ng ml ⁻¹	0.21 ng ml ⁻¹	4-4.3% 1-100 ng ml ⁻¹	[66]
17	NTD	Methanol, ethanol, acetone and pentane in human breath and in the ambient air	Charcoal adsorbent (trade name CNH charcoal)	GC	< 0.1 nmol ⁻¹			[34]
18	NTD	C1-C10 aldehydes, 2- propenal and 2-butenal, formaldehyde, acetaldehyde, methanol, ethanol, 2-methyl-1,3- butadiene, acetone, 2- propenal, acetonitrile, 2- butanone, benzene, 2- butenal, toluene, chlorobenzene, 1,2- dimethylbenzene, 4,7,7- trimethylbicyclohept-3- ene, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene	PDMS, DVB and Carbopack X and Carboxen 1000 and single layer organic polymer of methacrylic acid and ethylene glycol dimethacrylate	GC-MS	In the range of some ng l ⁻¹	In the range of some ng l ⁻¹	0.27-961.5 ng l ⁻¹	[70]

Table 1. Continued

19	NTD	Carbon tetrachloride, trichloroethylene, bis (chloromethyl) ether and chloromethyl methyl ether in air	Single wall carbon nanotubes sol-gel sorbent	GC-MS	0.001-0.01 ng ml ⁻¹	0.007-0.03 ng ml ⁻¹		0.01-100 ng ml ⁻¹	[7]
20	NTD	Carbon tetrachloride, trichloroethylene, bis (chloromethyl) ether and chloromethyl methyl ether in air	Sol-gel derived, multi-walled carbon nanotubes/silica composite	GC-MS	0.01-0.05 ng ml ⁻¹	0.039-0.173 ng ml ⁻¹		0.01-100 ng ml ⁻¹	[12]
21	NTD	Perchloroethylene in the air	Graphene	GC-MS	0.023 and 0.25 ng ml ⁻¹	0.08 ng ml ⁻¹		0.01-70 ng ml ⁻¹	[37]
22	NTD	Carbon tetrachloride in air	Graphene nanoplatelets silica composite, prepared by sol-gel	GC-MS	0.021-0.25 ng ml ⁻¹	0.08-0.75 ng ml ⁻¹		0.01-80 ng ml ⁻¹	[71]
23	NTD	BTEX compounds	Carbotrap B	GC-MS	0.03-0.04 ng ml ⁻¹	0.1-0.13 ng ml ⁻¹	4.3-13.3%	0.01-50 ng ml ⁻¹	[80]
24	NTD	vapor mercury in ambient air	Gold wire	GC-MS	0.23 ng ml ⁻¹		1.9-7.1%		[81]
25	NTD	Aromatic amines	Amberlite/silica composite	GC-FID	0.01-0.02 ng ml ⁻¹	0.05-0.08 ng ml ⁻¹	0.60-12.15%	0.01-20 ng ml ⁻¹	[82]
HF-LPME		1,1-dimethylhydrazine (UDMH)	hydrochloric acid (0.1 N) as solvent	Spectrophotometry	0.002 ng ml ⁻¹	0.006 ng ml ⁻¹	0.082-0.12 ng ml ⁻¹	-	[56]

*LOD indicates limit of detection. *LOQ initiates limit of quantitation. *Ref. means references.

In a recent NTD study, graphene and its nano-platelet silica composite prepared by sol-gel technique were used in NTD for the sampling and analysis of organo halogen compounds in air [37,71]. The NTD packed with graphene

nano-platelets and its silica composite showed a high sensitivity for determination of VOCs and HVOCs in air [70]. Also, single and multi-wall carbon nanotubes/silica composites prepared by sol-gel technique have been applied

as efficient sorbents in NTD. In this case, the NTD packed with single and multi-wall carbon nanotubes/silica composites showed a higher efficiency over SPME CAR-PDMS fiber for sampling and analysis of HVOCs in air [7, 12].

EFFECT OF ENVIRONMENTAL PARAMETERS

Environmental Temperature

The ambient temperature at the time of sampling is one of the important parameters affecting the absorption rate of the analyte on the fiber/adsorbent. In Koziel and Pawliszyn study, it was found that the change in sampling temperature is a main reason for obvious errors during sampling with SPME [83]. According to the Wang *et al.*, theory (2009), the sampling rate of nonpolar VOC is correlated to $T^{1.085}$. In this theory, any change in the ambient temperature at the sampling time from 25 °C and in the range $\pm 10^\circ$ can cause about 4% error in the final measured concentration [84,85]. In the use of HS-SPME method, temperature changes in the range 25-65 °C showed a dramatic effect on the area obtained by GC-MS device, and the strongest response was at 50 °C. The effect of environmental temperature on SPME coated with CAR/PDMS fiber in 0.5 retracted mode showed that there is no relationship between temperature changes (under 5 °C) and analyte adsorption rate. While, temperature changes more than 10 °C demonstrated a dramatic effect on the SPME performance [15,77,78]. Increasing sampling temperature from 30 to 50 °C showed an increase in the sampling efficiency of NPAA coated fibers in SPME. However, an obvious reduction was observed with increasing temperature over 50 °C [78]. The use of synthesized multi-walled carbon nanotube coating prepared by sol-gel method showed that the peak response decreased with increasing temperature sampling [14,64,66].

This decrease is attributed to the influence of temperature on the adsorption of analytes onto the coating fiber. Indeed, the vapor pressure of the analyte increases with increasing sampling temperature, and thereby its volatility increases. As a result, it has a negative effect on the analyte extraction efficiency. Similarly, in NTD sampling, an increase in the sampling temperature can cause an obvious decrease in the sampler efficiency [7,12,80]. In

the use of NTD packed with graphene/silica composite for the determination of perchloroethylene, the efficiency of the proposed sampler decreased with increasing sampling temperature. Comparison of the effect of sampling temperature between the SPME and NTD methods revealed that the increase in the sampling temperature reduces the efficiency of the both samplers, which this reduction in SPME is greater than that of NTD [37,71]. This may be attributed to the effect of the sampling temperature on the distribution equilibrium in SPME sampler.

Relative Humidity

Humidity has a critical role on the sampling efficiency. In sampling of breathing air, high levels of humidity can affect the sampling efficiency through its effect on extraction and desorption of analytes [86]. There is no consensus among researchers regarding the influence of humidity on SPME/NTD efficiency. The effect of relative humidity is related to the type of analyte and coating fiber/sorbent. Chen and Pawliszyn have reported that the relative humidity did not affect the SPME coated with Car/PDMS under saturated conditions [85]. This is due to the hydrophobic properties of Car/PDMS and is not affected by competition of water molecules in retracted mode. It has been also reported that 10% increase in humidity can decrease the sampling efficiency of SPME [86,87]. Namiesnik *et al.* reported that the relative humidity in the range 0-92% can cause 20-80% decrease in the sampling efficiency [88]. Similarly, in the use of SPME coated with CAR/PDMS, increasing the relative humidity from 20 to 40% causes a 25% reduction in mass loading of the fiber [15]. Humidity can occupy the active free sites of the sorbent or fiber, and thereby decreases its surface area. In a study on the use of SPME coated with CAR/PDMS, it was found that the increase of relative humidity has a negative effect on sampling performance of the SPME sampler [77]. This finding may be attributed to the polarity of analyte and SPME coating. According to the previous studies on the use of NTD for sampling and analysis of air pollutants, increasing relative humidity causes a decrease in sampling efficiency [12]. This phenomenon may occur because of two probably reasons; increasing humidity decreases the active free sites on the sorbent surface, and water molecules in high humidity can cause adhesion among absorbent

particles. As a result, decreasing free sites on the sorbent surface and sticking of sorbent particles can clog the needle and, thereby, causes a pressure drop into the needle. The clogging causes a decrease in the amount of extracted analyte, subsequently reduces the peak area responses [7, 12,71].

Velocity

Air velocity is another environmental factor that can be effective on the sampling rate. The changes of air velocity in sampling sites can affect the sampling efficiency, especially in passive samplers such as SPME. Isetun *et al.*, (2004) reported that in exposed mode of SPME, linear velocities higher than 7 cm s^{-1} do not have significant influence on the sampling efficiency [89]. In SPME coated with CAR/PDMS, the effect of air velocity in the range $0-0.5 \text{ m s}^{-1}$ showed a significant influence on the sampler efficiency [15]. In another application of SPME, it was found that the air velocities higher than 0.1 m s^{-1} have no significant effect on the sampling efficiency [64]. This may be attributed to the inclinable role of boundary layer on mass transfer. In addition, in this process, passive diffusion is the limiting step. In retracted SPME, the effect of air velocity can be less than other passive samplers, due to its structure and aspect ratio of the fiber. In NTD, the effect of air velocity has not been studied yet.

EFFECT OF DEVICE PARAMETERS

Desorption Temperature

Desorption temperature has a key role in the sensitivity and reproducibility of the SPME and NTD methods. Desorption temperature should be selected based on the type of fiber/sorbent used and target analyte [37], because high desorption temperature has adverse effects on the fiber/sorbent and target analytes [15]. In the use of Cavitated-coated SPME, it was found that the desorption of aliphatic hydrocarbons occurs in the temperature range $50-100 \text{ }^\circ\text{C}$, while the desorption of BTEX compounds occurs at $200 \text{ }^\circ\text{C}$ and the desorption operation can be completed at $250 \text{ }^\circ\text{C}$ [63]. This contradiction in the optimal desorption temperature concerns to the analyte type. In the development of SPME coated with Anodic alumina for the determination of VOCs in human exhaled breath vapor,

$265 \text{ }^\circ\text{C}$ was determined as the best thermal desorption temperature [78]. The study of thermal desorption temperature ranging from $230-275 \text{ }^\circ\text{C}$ on the application of SPME coated with N-phenylanthranilic acid (NPAA) for sampling and analysis of VOCs in human exhaled breath vapor showed that the sampler efficiency increased with increasing desorption temperature until $265 \text{ }^\circ\text{C}$, and the best area response was obtained at $265 \text{ }^\circ\text{C}$. After that, the peak area decreased obviously [78]. In the use of NTD packed with PDMS as a sorbent, the largest peak areas were observed at a desorption temperature of $290 \text{ }^\circ\text{C}$ [70]. This result is in agreement with other applications of NTD packed with graphene [37], graphene Nano-platelets silica composite sol-gel [71], single and multi-walled carbon nanotubes sol-gel [7,12].

NTD packed with double bed containing PDMS showed a better efficiency at desorption temperature of $290 \text{ }^\circ\text{C}$ compared to $250 \text{ }^\circ\text{C}$ for the sampling and analysis of a wide range of volatile compounds, such as aromatic compounds, pentane, hexane, isoprene, propanal, E-2butenal, and aldehydes [70]. In addition, in the use of NTD packed with DVB/Carboxen, peak area responses of the target analytes increased with increasing desorption temperature from 180 to $250 \text{ }^\circ\text{C}$ [70].

Desorption Time

Desorption time in the injection port of the analyzer system is another important factor playing a significant role on the sensitivity and reproducibility of the SPME/NTD methods. Desorption time varies depending on the type of analyte and adsorbent. By increasing desorption time, the carryover effect decreases, while, the risk of damage to the analyte and sorbent increases. To avoid carryover effect and damage the target analyte, the desorption time in the GC injector should be optimized [90]. Generally, in these microextraction methods, the desorption process lasts few minutes and does not require much time for most VOCs. Although, some compounds with a high boil point may require further desorption time for complete desorption. Using SPME coated with DVB/PDMS showed that there was no significant difference in the sampler efficiency with changing desorption times in the range 1-2 min. In this case, desorption time of 3 min at $200 \text{ }^\circ\text{C}$ was selected as optimal conditions for analysis of BTEX using SPME with a

disposable ionic liquid coating [90]. In sampling and analysis of HVOCs using SPME coated with SWCNTs/silica composite, the influence of desorption time in the range 1-5 min was investigated on the SPME performance, and its results implied that the maximum performance of SWCNTs/silica composite coated SPME was observed at 5 min of desorption time. In another research, the effect of thermal desorption time (in the range 1-7 min) was evaluated on the efficiency of nano-porous as coating fiber in SPME method. In this study, after 6 min of desorption time, the tapped analytes were well desorbed from the used fiber [83].

In some of NTD studies, the desorption time has been considered to be 30 s without further optimization [70]. In another study, the effect of desorption time in the range 1-5 min was investigated on the NTD packed with graphene Nano-platelets silica composite prepared by sol-gel method, and the maximum peak area response of the target analyte was observed at 3 min, and then the increase of the desorption time did not increase the peak area response of the analyte indicating that further increase in the desorption time did not affect the sampling efficiency [71]. A similar result has been also reported by other studies on the use of NTD packed with various sorbents for the sampling and analysis of VOCs in air.

CARRY OVER

SPME and NTD methods could be reused several times (20-150 times), and this is one of the most important advantages of these technologies over the conventional methods. Since carryover effect can affect the reusability of these methods, it should be carefully inspected [9]. Carry over varies between different type of NTDs. In general, increasing the desorption temperature and desorption time could lead to the complete desorption of analytes from the sorbent bed. PDMS as a commercial sorbent that can be packed inside NTD has shown a large amount of carry over even at high levels of desorption time and temperature [70]. In previous studies, the effect of carryover has been investigated with changing desorption time or desorption temperature [70,89,90]. The sampling and analysis of BTEX from polluted air using Cavitand-coated fiber showed that the carryover effect was not observed after

thermal desorption at 250 °C [63]. In the extraction of VOCs in human breath vapor using SPME coated with anodic alumina, it was reported that no carryover effect was observed at 265 °C and 6 min of desorption temperature and time, respectively [78]. In another application of simple SPME in TWA mode, temperatures above 260 °C were used to remove carryover effect for future applications [86]. The use of SPME coated with CAR/PDMS for sampling perchlorethylene from dry cleaning shops, desorption temperature of 280 °C for 2 min was applied to remove the carryover effect for consecutive sampling [77]. In NTD packed with PDMS, desorption temperature of 290 °C was recommended to remove the carryover effect [70]. In NTD packed with graphene, at 3 min of desorption time and 290 °C of desorption temperature, no peak was observed for studied analytes [37,91]. A similar trend was also observed for NTD packed with Carbotrap for the sampling and analysis of BTEX from air [80].

STORAGE TIME

Storage capability of the sampling methods is one of the most important operating factors. In SPME exposed mode, poor storage ability is the main limitation in its application for field sampling, because a large amount of analyte can be evaporated from the coating fiber [72]. Svensson *et al.*, (2007) reported that exhaled breath samples on SPME coated with PDMS/DVB is storable up to 48 h at -20 °C [75]. The application of SPME as a TWA sampler for the determination of inhalation anesthetics in the air showed that the samples on capped SPME fibers could be stored in sealed glass tubes at 4 °C for three days without significant losses [64]. NTD packed with PDMS/Carbopack X/Carboxen 1000 showed less than 80% of recovery after 48 h. NTD packed with DVB/Carbopack X/Carboxen 1000 showed poor recoveries for oxygenated compounds and hydrocarbons after 48 hours. In this NTD, aromatic compounds had more than 90% recovery after 8 days, except for benzene, which its recovery was only 26% [70]. In general, it can be concluded that both of the SPME and NTD methods as new proposed technologies have poor storage stability in comparison with OSHA 103 and NIOSH 1501 methods. Although, in the newly developed NTDs, acceptable recoveries of adsorbed analytes were observed

even up to 7 days after sampling indicating a good storage stability [12,37].

ANALYTICAL PARAMETERS

In analytical chemistry, LOD is the lowest level of analytes that can be determined and distinguished from the absence of the analytes [92]. In analytical methods coupled with chromatography, the value of LOD is estimated as the lowest concentration of target analyte corresponding to the peak area responses with signal to noise ratio of 3 [80,93]. Moreover, limit of quantitation (LOQ) is the lowest concentration of target analyte that can be reliably determined. In chromatography coupled methods, LOQ is estimated based on the lowest concentration of target analyte corresponding to the peak area responses with signal to noise ratio of 10 [80,94]. As shown in Table 1, NTD can detect lower concentrations of HVOCs in air compared to SPME. According to the table, 0.001 ng ml⁻¹ and 0.007 ng ml⁻¹ of HVOCs have been reported as LOD and LOQ values of the NTD packed with single wall carbon nanotubes sol-gel sorbent, respectively. While the LOD and LOQ values of SPME methods are obviously higher than those of NTD methods. This finding implied that NTD offers a higher sensitivity than SPME for the detection of VOCs in air.

LIMITATIONS AND FUTURE TRENDS

Despite all the developments in the microextraction methods including SPME, NTD and HF-LPME for the determination of VOCs in air, there are still some limitations for applying them as TWA samplers. For example, the fragility of SPME fiber coatings in exposed mode has not yet been overcome in the recent advances of SPME. In NTD, the low flow of air passing through the sorbent packed in NTD is the main limitation of this method as a TWA sampler. The larger needle diameter in this method compared to the standard Hamilton syringes, which causes the leakage of the carrier gas in the injection port of GC system, is another limitation of this method. These limitations have been addressed in some of the latest studies on NTD development [80,82]. The low capacity of the liquid absorbent and possibility of damage to the HF

body have been reported as the main drawbacks of HF-LPME method for applying as TWA sampler [56]. Hence, future studies must be specifically focused on these strategies to overcome their limitations and improve their performance as the field samplers.

CONCLUSIONS

SPME and NTD are two useful and developing methods in sampling and analysis of VOCs from air. A recent study has also examined the use of HF-LPME method for sampling and analysis of an organic pollutant in air followed by spectrophotometric detection. In SPME and NTD, the type of coating fiber and sorbent has an obvious effect on their efficiency, respectively. In addition to the commercially coating fibers, various new coatings can be also used in SPME method to increase its sensitivity, such as single and multi-walled carbon nanotubes prepared by sol gel method. In the NTD method, various materials have been successfully used for the sampling and analysis of VOCs in air, such as charcoal, single layer organic polymer of meth acrylic acid and ethylene glycol dimethacrylate, graphene, and graphene Nano-platelets. Single and multi-walled carbon nanotubes prepared by sol gel method are also suited for the sampling and analysis of HVOCs in air. Comparing the effect of sampling temperature on the SPME and NTD showed that their efficiency decreased with increasing the sampling temperature, and this reduction in SPME method is greater than NTD. In the both SPME and NTD methods, increasing relative humidity causes a decrease in sampling efficiency. Air velocity as a sampling factor has no significant effect on SPME efficiency. Increasing desorption temperature until a specific level could increase the efficiency in the both SPME and NTD methods. The highest performance of SPME is affected by desorption temperature, and depends on the type of sorbent inside NTD. Increasing desorption time (until a specific level) has also positive effects on the SPME and NTD efficiency in the determination of VOCs. In the most applications of SPME, desorption time in the range 5-6 min and desorption temperature in the range 250-265° can completely remove carryover effect. While in NTD, higher temperature (290°) and lower desorption time (3 min) can be used for removing the carryover effect. Comparing the

storage time among the new proposed technologies showed that the NTD has better storage stability.

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