AMECJ

A review: Total vaporization solid-phase microextraction procedure in different matrixes

Yunes M. M. A. Alsayadi [a,*], and Saahil Arora[b]
[a] *University Institute of Pharmaceutical Sciences, Chandigarh University, Punjab-140413, India*
[b] *University Institute of Pharmaceutical Sciences, Chandigarh University, Punjab-140413, India*

A B S T R A C T

Total vaporization solid-phase microextraction (TV-SPME) is a type of extraction technique in which a specific solvent dissolves the analyte. Then a tiny amount of solvent is taken to the vial of SPME. Then, the solvent vaporizes in the SPME vial, and sampling is carried out on the headspace of the SPME fiber. As a result, the partitioning phase of the analyte between the headspace and liquid sample is omitted. The equilibrium phase remains the analyte partitioning between the headspace and SPME. TV-SPME was introduced in 2014 by Goodpaster to increase the recovery compared to the liquid injection method. This review discusses different aspects of TV-SPME, including its impact on sampling techniques, theoretical part, sampling procedure, and method optimization. Special attention was paid to its applications. A comprehensive literature study was conducted in the relevant databases to summarize the research work that has been done on this technique. In TV-SPME, the liquid samples completely vaporized and had a less matrix effect and better adsorption. This method needs no sample preparation, consumes less supply, and can be done automatically. Also, TV-SPME enables a cost-effective and efficient extraction for different matrixes. This review summarizes aspects related to TV-SPME including its sampling procedure, method optimization, and its preference for conventional liquid methods. Special attention was paid to its applications of the vacuum-assisted total vaporization solid-phase microextraction procedure (VA-TV-SPME).

1. Introduction

Solid-phase microextraction technique (SPME) is widely used for pre-concentration/separation of analyte from the sample, analytes are absorbed on a fiber and then, it desorbed before determined by analytical instrument such as GC-FID [1,2]. SPME was introduced in 1989, and since then, it has been used extensively in the field of environmental chemistry, with more than 1500 publications. SPME

is a technique with off-column pre-concentration sampling that facilitates the trace analysis of the occurring abundance of matrices and samples. This technique depends on a polymer fiber with surface chemistry designed to increase targeted compounds' adsorption [3, 4, 5]. SPME was initially presented as a solvent-free technique combining the prepared sample into one-step sampling, sample introduction extraction, and concentration [1,6]. Two processes are involved in the SPME extraction: (1) the analytes partitioning between the fiber coating and the sample, and (2) the desorption process occurs by the concentrated analytes from the coated fiber

*Corresponding Author: Yunes M. M. A. Alsayadi
Email: yunes20171@gmail.com

to the instrument to be used for the analysis. The extraction is performed by placing a solid sample containing volatile analytes and an aqueous sample containing organic analytes into a vial, then closed with a septum and cap [7]. The main advantages of SPME are a simple extraction method, efficient, selective, and fast. SPME followed with less amount of sample volumes and no-solvent consumption. For those advantages, it was implemented quickly in many disciplines of analytical chemistry, like bioanalysis, environmental science, and chemical analysis [8,9,10]. In addition, SPME can be coupled and automated with instruments like gas chromatography, which easily estimates the organic compound [11]. Direct analysis of complex matrixes mostly cannot be performed in a manner that attains the sensitivity and selectivity needed for many trace analysis applications. To solve this issue, SPME techniques were used so that preconcentrating of analytes occurs selectively before placing it into ion trap mass spectrometric/ gas chromatographic analysis. This approach was introduced to be used in the trace analysis of the metabolites of explosives in seawater [6]. The SPME technique includes exposing a fiber of fused silica coated with a solid phase to an aqueous solution containing organic compounds [12]. It involves using a silica fiber coated with a polymer film to adsorb compounds of interest from their matrices. Such a technique is a solvent-free, reliable, and inexpensive method that can be used practically for aqueous sample analysis/headspace and shows good sensitivity and excellent selectivity [13]. The SPME technique is used for multiple sampling, and sample preservation leads to minimizing the risk of contamination of the sample because the technique affords a simplified sample handling [14]. SPME is mainly carried out in one of the two modes; either headspace or immersion technique. In headspace SPME mode, the extraction of analytes by fibers occurs from the headspace above a sample. While in immersion SPME mode, the extraction of analytes by the fiber takes place directly from a liquid sample [15]. In headspace SPME, the partition of analytes occurs between the headspace above the

sample and the coating fiber of SPME [16,17]. The main criteria for applying headspace solid-phase microextraction (HS-SPME) was to prevent the fiber of SPME coatings from being tricked by the components of sample matrices [18]. In HS-SPME, the fiber is placed into the vial of the sample, the volatile organic compounds that are available in the headspace, are bound to the coating, and then the fiber is to be taken to the site of injection of the Gas Chromatography (GC) for desorption and further analysis [13] HS-SPME compounds having analytes with low volatility from complex aqueous samples can be used by the manner of increasing the temperature of the sample. Still, some SPME coatings made from some adsorbent substances may face difficulties due to their low stabilities, particularly in a hot medium like a steam of hot water. It is the preparation of super hydrophobic metal-organic framework (MOF) that is obtained from decoration nodes of the amino-functionalized UiO-66(Zr) with phenyl silane was needed and then successfully improved to be used in a novel fiber coating of SPME [15]. The scientists of food flavors have appreciated the ease of use and sensitivity of the headspace technique mode by using it in analyzing the volatile compounds in many food products [19]. Headspace SPME sampling was widely used in analyzing of some intact explosives like triacetone triperoxide (TATP) which was detected from headspace applying planar SPME with the help of an ion mobility spectrometer[20]. HS-SPME is a pre-sampling technique that does not need complicated apparatus or solvents [21]. HS-SPME can integrate the concentration, extraction, and introduction in a single step. Combing HS-SPME with GC–MS is employed to determine the volatile components in different plants like tea samples [22]. In the immersion SPME sampling technique, the fiber is directly placed into a liquid sample and the compounds of interest absorb/ adsorb to the fiber coating. After the absorption/ adsorption, the fiber is then placed for desorption in the inlet of a LC or GC for further analysis [23]. Immersion SPME sampling has been utilized practically in the applications of environmental

studies for extracting organic explosives that are present in aqueous soil extracts and/or water to be later analyzed by GC-MS and GC-electron capture detection [6,16]. Some explosives examples that have been detected and recognized in this method like PETN, 2,6-dinitrotoluene, RDX (composition C-4), TNT, and NG (dynamite) [24,25]. Both the techniques either headspace or immersion SPME cannot be smoothly applied to the detection and identification of some explosive residues especially those present on post-blast debris, regardless of many previously reported descriptions of its unique use, for example, the detection of a single particle of smokeless powder [2] or the residue extraction of the explosives that obtained from soil samples collected from the blast site after an explosion [25,26]. In fact, headspace and immersion SPME methods have been used to analyze a various analytes [27]. TV-SPME is almost a new technique that is being utilized in analytical chemistry. It is always in comparison with conventional techniques including HS-SPME in the motive of determination of the superior technique. That comparison is highly appreciated as it plays a critical turn in the superiority of the method that is to be adopted. And in the case of TV-SPME and HS-SPME, it is important to compare them to see if one is superior, as it helps to choose a method with specific samples [28]. These two methods are among the advanced micro extraction methods as they require least to almost no sample preparation compared to other liquid methods which require a high amount of

the sample [29]. They involve placing the samples directly into the headspace in place of placing them to do individual extraction techniques to a sample ahead of being directly injected into the GC. Table .01 shows the differences between the HS-SPME and TV-SPME [30]. The comparison concentrates on the sample volumes, analysis time, and matrix effects as these parameters are critical for analysis samples.

Environmentally, TV-SPME has been used to analyze drugs and their metabolites in saliva, urine, and hair. This valuable simple technique has also been used in analyzing lipids, fuel samples, street drugs, lipids, and pollutants in water and post-blast explosive residues [30], [33], [36-38]. TV-SPME has been used to identify illegal adulterants in tiny samples (microliter quantities) of alcoholic beverages [39-40]. Both gamma-butyrolactone (GBL) and gamma-hydroxybutyrate (GHB) were identified at levels that would be found in spiked drinks [34]. There were techniques being used, including Membrane protected micro-solid-phase extraction (μ-SPE), which was used for the first time in 2006 with the motive of replacing multistep SPE. The principle of μ-SPE lies in taking a minimal amount of the sorbent and packing it inside a porous membrane paper having edges that are heat sealed for the fabrication of a μ-SPE device. This device can perform pre-concentration and extraction in a single step. Such techniques seem to have the best extracting method, especially for complex

Table 1. Differences between the HS-SPME and TV-SPME

Parameter	HS-SPME	TV-SPME
Sample volumes	Sample utilization is at least 1mL.[29,31-33].	**Almost 1 μl - 100 μl as TV-SPME vaporizes the sample completely [31,34].
Matrix effect	The effect of matrix is higher as it is between two phases only [32, 33].	less matrix effects are there as it results in fully vaporizing the analyte and its matrix[34].
Analysis time.	***HS-SPME and other liquid injection, need that the analyte to be reacted with the derivatizing agent in solution [33, 35].	As TVSPME allows for the analyte to be derivatized during the extraction process which reduces analysis time [27, 34].

**Almost 1 μl - 100 μl as TV-SPME vaporizes the sample completely, analyte partitioning will be there between the vapor and only the fiber, which lead forcing more amount of the sample to adsorb into the fiber and large amount of the sample can be exposed to the vapor. And that can cause minimizing the sample size [31,34].

***Other methods including HS-SPME and other liquid injections, need that the analyte to be reacted with the derivatizing agent in solution prior to being injected into the GC. And that lead to minimize the time of analysis[33, 35].

samples, since extraneous matter does not adsorb over the sorbent as it is protected effectively inside the Membrane [39]. Direct Immersion-Solid Phase Microextraction (DI-SPME) is preferred for aqueous samples as the fiber is introduced directly to the sample solution. However, when applied to a complex matrix, the sample must be pretreated; otherwise, some interfering substances from the matrix can bind irreversibly to the fiber. As a result, choosing the mode is not preferred in the case of complex samples, including samples arising from food, sludge, and biological origin

[39-40]. To overcome such issues, HS-SPME can be used, although it has some limitations, including it can work better only for volatile compounds and that compounds having good volatility even with almost moderate heat. Therefore, nonvolatile or low volatile compounds cannot be extracted by applying such an approach. So, something should be developed for extracting compounds with less or no volatility from complex samples by adopting a mode of direct immersion [41]. Differences between DI-SPME, HS-SPME, and Membrane Protected SPME, are shown in Figures 1 (a and b).
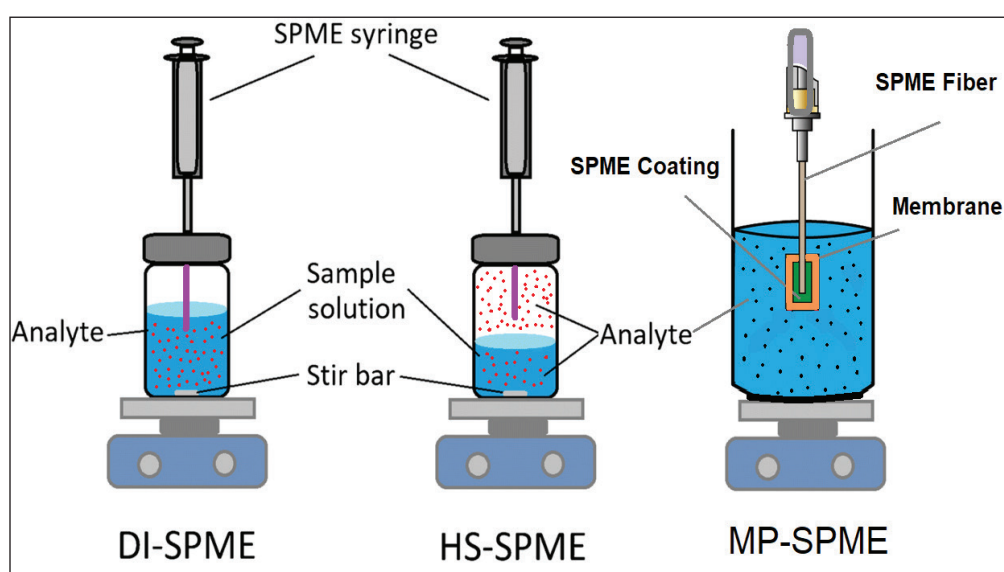

Fig. 1a. DI-SPME, HS-SPME and membrane protected SPME
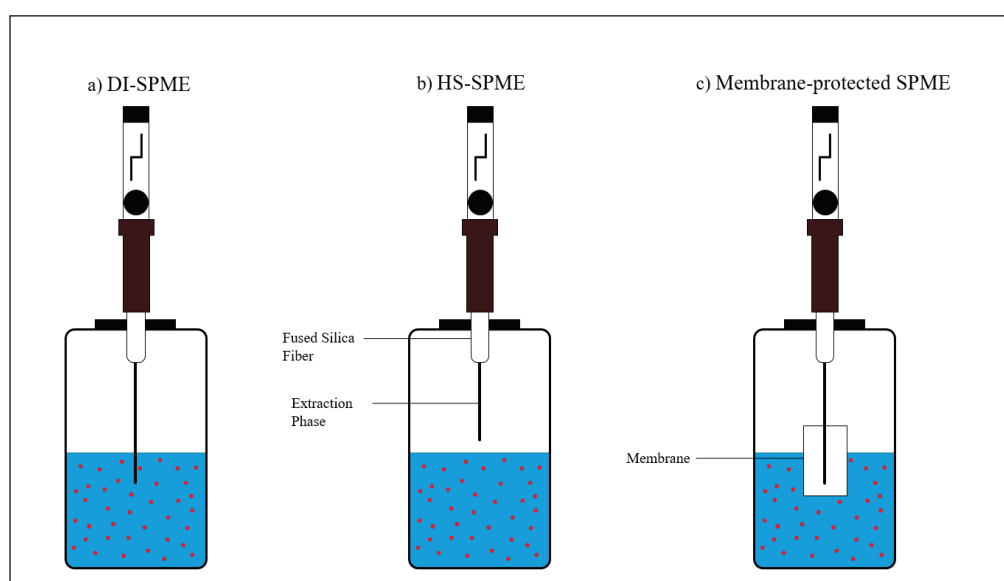

Fig. 1b. DI-SPME, HS-SPME and membrane protected SPME

SPME and its derivative techniques are a well-recognized method of extraction which utilize zero solvents and has a wide scope and applications, including biomedical, food, forensic, and environment [35,41]. Moreover, they can be applied in organic contaminants extraction like; pesticides, Pharmaceutical compounds, emerging pollutants, and persistent organic pollutants [42-53]. Total vaporization (TV) is a technique that can be practically utilized in conjunction fused with headspace sampling. The residual solvents will be released from the matrix by applying TV to a solid sample. Furthermore, applying it to the liquid samples allows the whole sample to be vaporized before the headspace sampling [54]. TV technique applies to many samples like solid samples (e.g., residual solvents), [55], aqueous solutions (e.g., odor compounds) [56] and fermentation liquor (e.g. ethanol) [57]. The approach of coupling TV and SPME (TV-SPME) offered great sensitivity and even low detection limits for compounds present in the hair of some users of tobacco such as nicotine and cotinine. In the TV-SPME technique, a sample extract needs to be heated until it gets vaporized and fiber of SPME is utilized for pre-concentrating analytes from the produced vapor [53]. In TV-SPME, a complete vaporing of the liquid samples gives a fewer matrix effect and better adsorption. This method does not need any sample preparation, utilizes less supplies and can be done automatically, enabling it to be both a cost-effective and efficient method [58]. SPME is a sensitive technique where the liquid portion is totality vaporized before being placed for sampling, easing to attain equilibria inside the sample vial and increasing the analyte's availability in the headspace, leading to making the analyte quantity more [53,59]. TV-SPME is an effective technique that does not require derivatization while being used to analyze controlled substances, either with or without on-fiber. Total vaporization is a technique that has been utilized in simple headspace sampling. Still, matrix effects that result between two phases in headspace sampling are a matter of concern. One important method to remove matrix

effects is completely evaporating the analyte and its matrix. Total vaporization headspace is applicable in determining ethanol in fermentation liquor, methanol in wood pulp, odor compounds in aqueous samples, and volatile organic compounds in biological samples [56,60-62]. The matrix effects in SPME can be eliminated by extracting analytes (quantitatively) from complex matrixes. This method is known as cooled fiber SPME, and it has been applied for extracting polycyclic aromatic hydrocarbons (PAHs) from heated soil samples [3]. Also, the urine extracts in solvent and have been evaporated in a headspace vial. The residue was heated until analytes derivatize, vaporize, and absorb to a SPME fiber [63].

2. Experimental
2.1. TV-SPME sampling procedure and practical TIPs
SPME fiber format was one of the most commonly used forms of the technique for many years [64]. In SPME fiber format, a small amount of the extracted phase is coated by a thin and short fused-silica rod, which is revealed for a specific time directly to the headspace above the sample or to the sample itself. Analytes of interest were taken from the sample to be analyzed in the SPME fiber coating, and then the sample was extracted till the point when the quantity of analyte extracted by the fiber remained constant even if the sampling time increased i.e., the analyte concentration attained partition equilibrium state between the fiber coating and sample [65]. Generally, the time needed to attain equilibrium relies on the characteristics of the fiber coating, matrix, and target analyte, and its range varies from a few minutes to many hours [66]. SPME sampling includes two stages of the equilibrium mechanism, which occur between the headspace/sample (first stage) and the fiber coating/headspace (second stage). In the TV-SPME technique, the equilibrium process between the sample/headspace is no longer needed since the analytes can be directly partitioned from the fiber coating and headspace [67]. Figure 2 shows the sample preparation of HS-SPME and TV-SPME. For HS-SPME, the extraction of volatile analytes
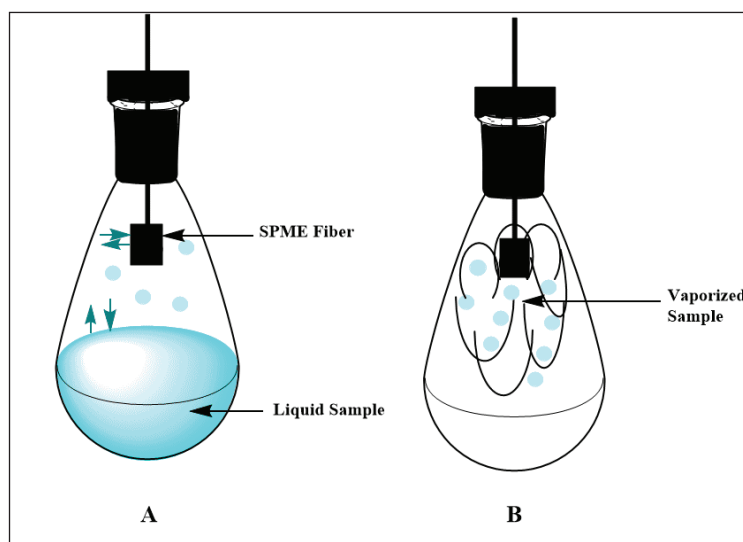
Fig. 2. Samples preparation of HS-SPME and TV-SPME

is noticed to happen faster than analytes with semi volatiles nature [15]. For that, the longer equilibration times could be less in various ways, including agitating the sample, heating the sample, maximizing the headspace/sample interface, and implementing the cold fiber HS-SPME proposal to cool the fiber coating and heating the sample matrix occurs simultaneously [13]. The effects of the matrix that can be produced between two phases while sampling in the headspace technique is a matter of concern. An important method to remove such effects from the matrix is applying heat to evaporate the analyte and its matrix fully. An excellent example of the use of total vaporization headspace involves estimation of volatile organic compounds in biological samples, methanol in wood pulp, odor compounds in aqueous samples, and ethanol in fermentation liquor [27]. In TV-SPME, the extracted aliquot of the sample is sentenced for heating till the point where both the analytes and solvent are completely vaporized; after that, the analytes partition between the SPME fiber and the vapor phase [16]. TV-SPME extraction of analytes from a sample of interest was performed by applying a specific solvent in this approach. Then, a small part of this extract is fully vaporized inside a headspace vial inserted into an SPME fiber. Also, the VOCs in water samples based on fiber coating on the needle were determined after HS-SPME and TV-SPME were coupled to the GC-MS (Fig.3).
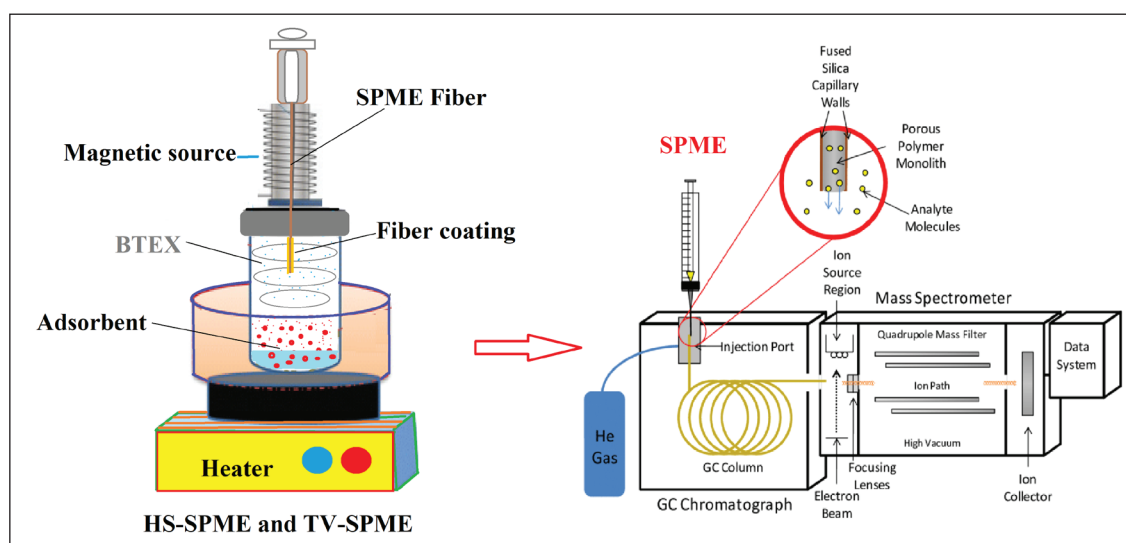

Fig.3. Determination VOCs in water samples based on fiber coating on needle after HS-SPME and TV-SPME coupled to the GC-MS

These results are a simple two-phase system. In particular, patterns occur when the analytes partition between the extract and the headspace is removed and when the analyte partitioning occurs directly between the vapor phase and the SPME fiber. In general, combining the total vaporization technique with SPME increase preconcentrating analytes onto the fiber. For example, the estimation of an organic analyte in an organic solvent is not accessible by either immersion or headspace SPME. For that, the solvent should get vaporized and the analyte absorbed into the fiber of SPME. So, when the analyte gets distributed (in TV-SPME) at a solid/vapor interface, it has been found that the extraction time is less important than the sample volume and extraction temperature for the analytes to be recovered efficiently. In TV-SPME, extracts of the sample do not have to get filtered, which gives it a significant advantage compared to liquid injection. Nonvolatile compounds or solids that may have the chance to be laid within an extract of the sample will stay on the surface of the vial. That may lead to minimize extensively the contamination and the quantity of buildup that may take place in the inlet and the column of GC. Furthermore, the boiling point of the analytes plays an essential role in the selectivity of the GC inlet in liquid injection. TV-SPME can add a level of chemical selectivity because of the advantage of the fiber that can enable it to select the targeted analyte specifically. Finally, the volumes for the liquid injection are almost 1 to 2 μL; thus, only a tiny portion of the sample extract is needed for the injection. The Large-volume injection (LVI) techniques have thus been developed to be used in the GC. However, LVI needs some changes to meet the requirements for the instrument and other analysis parameters. So, TV-SPME needs no modification in instruments and other parameters, enabling the use of large volumes of the sample for the analysis in GC, which ultimately concluded in great sensitivity over the liquid injection [27]. The idea of combining total vaporization with SPME is almost similar to that of LVI techniques in those large volumes of the sample (e.g., 200 mL) which lead to an increase the sensitivity. However, TV-SPME is an essential technique because it does not require any modification in the GC instrument, such as exits for solvent vapor or adding retention gaps.

Additionally, the sample extracts require no filtration as any non-volatile or volatile components float above and within the surface of the vial. A critical feature of TV-SPME is that although it evaporates the liquid sample completely, resulting in a much larger volume, it plays a vital role in pre-concentrating the analytes more than compensates for this dilution. In addition, a clear choice of fiber chemistry used in SPME can add remarkable selectivity to the analysis [16].

2.2. TV-SPME method optimization

HS-SPME is a process of multi-stage equilibrium [68] where the extracted analytes in the headspace partition with the adsorptive surface on the fiber after the compounds get extracted from the matrix to the sample headspace by the help of some external force, including ultrasound, agitation and rising the temperature. These strategies shorten the time needed to attain equilibrium. In 2014, a novel separation technique was introduced by Goodpaster in which sampling was to be performed only in the headspace [53]. In this technique, the extraction of the analyte occurs by a solvent. Then a tiny amount of the solvent is taken to the SPME vial by total vaporization of the transferred solvent in the vial used in SPME, and sample processing is taken place on the SPME fiber from the headspace [23]. Therefore, the phase of partitioning the analyte extracts between the headspace and liquid sample is omitted, and the only equilibrium phase that remains is the partitioning of the analyte between the headspace and SPME [69]. Reflecting that the partitioning process of the analyte is to occur between the vapor and solid, it was noticed that in comparison with extraction temperature and sample volume, the extraction time parameter has less significance [67]. In addition, all non-volatile and solid compounds stay on the surface of the

SPME vial and are not taken to the injection portion or the GC column. Therefore, it reduces contamination in GC, and the sample extracts require no filtration [16]. Also, the evaporation of the sample is almost more, and a proper fiber of SPME is used for the preconcentration of the analytes to enable the TV-SPME technique to have a greater sensitivity compared to the traditional SPME [69]. The TV-SPME method depended on the vaporization of the total portions of the sample, containing volatile, non-volatile, and semi-volatile components. Therefore, it is noticed that semi-volatile and non-volatile compounds require more heat, and the sample volume needed is a more significant amount. Consequently, it was reported that the SPME fiber is heated and that heat does not cause any fault in the absorption of the analytes on the SPME fiber [67]. Maybe this is one of the limitation factors, but it is considered to be among the main reasons why this valuable technique is not more widely used. As a result, few publications based on TV-SPME have been written [70]. The TV-SPME technique should be coupled with another method to ease the vaporization; surpassing the preparation steps and minimizing the required heat would be helpful [71]. Various factors must be investigated and optimized, such as the desorption temperature, the extraction time and temperature, and the salt concentration. Such factors significantly affect thermal desorption and extraction efficiencies [15]. For controlled substances that are not thermally stable and not sufficiently volatile while being analyzed by GC-MS, derivatization is used to improve their characteristics to match the required conditions in the method optimization in GC-MS. The performance of GC-MS is significantly improved by the use of such derivatizing compounds [71]. Although derivatization has many benefits, techniques of the conventional solution phase work are time-consuming and intensive. However, derivatization was adapted to a sampling technique that is called TV-SPME to automate and simplify the process. SPME is

a technique in which the analytes of interest are placed for pre-concentration onto a fiber coated in adsorptive or absorptive material. TV-SPME is a unique and novel technique in which a tiny amount of solution is poured into a vial and heated until complete vaporization occurs [53]. A fiber of SPME is then introduced, and the adsorption of the sample onto the fiber coating takes place. TV-SPME belongs to immersion SPME in that both are two-phase systems which differ from headspace SPME, which is a three-phase system [69]. Calculating the maximum volume for total vaporization of a given solvent can be easily obtained by the vial volume, molecular weight, solvent vapor pressure, and temperature [53]. For example, the calculated maximum volume of methanol for total vaporization in a 20-mL vial at 60°C is 24 μL [53].

When TV-SPME is used for sampling, it can be streamlined the process of derivatization by enabling it to be taken place simultaneously with the extraction step in a process called on-fiber derivatization (Fig.4). This On-fiber derivatization was used before in conjunction with immersion or headspace SPME [72]. However, it could be desirable to use the advantages brought by TV-SPME to bear for on-fiber derivatization. In the process of derivatization on-fiber with TV-SPME, an SPME fiber is introduced to the headspace of a vial that contains a small aliquot of liquid derivatization agent. The fiber is then taken to the heated headspace of a vial that contains the sample. The reaction between the derivatization agent and analyte takes place directly in the headspace surrounding the fiber or on the SPME fiber. After sufficient time for adsorption and reaction, the fiber is taken to the inlet of the GC for desorption. The use of an autosampler can make this a fully automated process wherein the only sample prep necessary is to dissolve the sample in a suitable solvent and place an aliquot into the vial [73].

Several parameters are in direct touch with TV-SPME method, involving desorption time, SPME fiber type, extraction time, sample volume and desorption temperature [16,69].
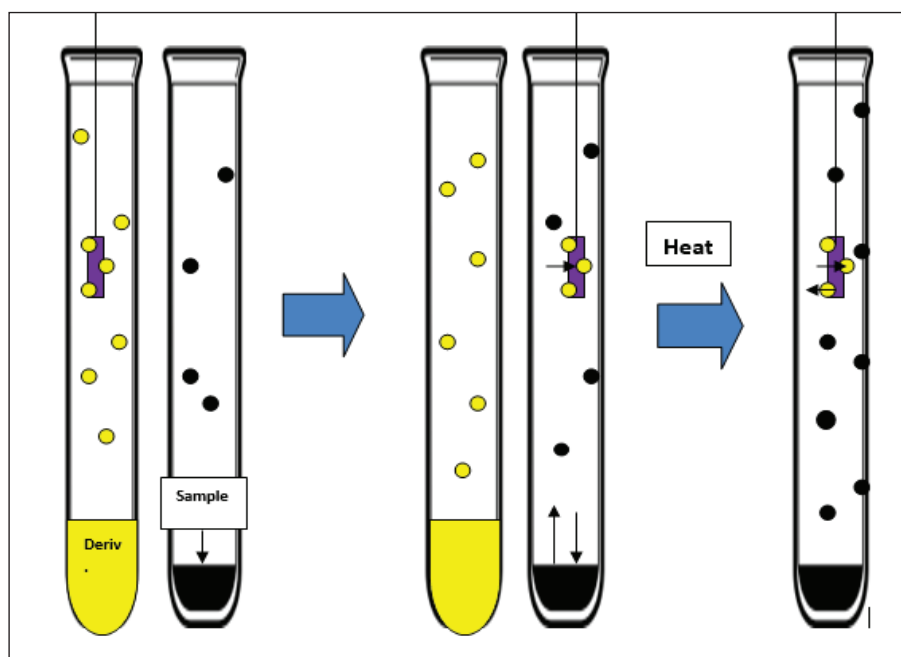
Fig. 4. Derivatization on-fiber in TV-SPME

2.3. TV-SPME based on liquid method

Although Gas Chromatography – Mass Spectrometry (GC-MS) is considered to be one of the most frequently used techniques in the laboratories, it has some limitations since compounds need to be volatile as well as thermally stable. Without these two characteristics, GC-MS cannot be used for regular routine analysis. For that some compounds have to undergo derivatization before injecting them into the gas chromatograph (GC) to meet and satisfy these requirements of thermostability and volatility. In SPME technique, a sample is taken into a vial and then heat is applied on the vial to initiate a site of the analyte to get vaporized into the headspace. A polymeric material such like polydimethylsiloxane-divinylbenzene (PDMS/DVB) used to coat SPME fiber, the coated SPME fiber is placed into the headspace of the sample or immerged graphene-Fe_3SO_4–SPME Fiber in water samples and the analyte is adsorbed onto the fiber concluding that the formation of a thin coating of the analyte on the fiber (Fig.5). The fiber is then introduced to the inlet of the GC for desorption [74]. TV-SPME technique is almost similar to that of headspace SPME but it differs by the complete vaporization of a liquid sample prior getting adsorbed onto the fiber. Such adsorption

permits the occurrence of partitioning of the analyte between only the coating of the fiber and the vapor. By this technique, more portion of the sample is exposed for the adsorption onto the fiber lead to minimize the sizes of the sample (e.g., $1 – 200$ µL) can be utilized [75-76].

TV-SPME showed its ability to be an efficient technique especially when used for the analysis of controlled substances in both the ways either with or without on-fiber derivatization. A summarized table for the results is presented below: Table 2. Brief of results for TV-SPME and liquid injection methods. + denotes that a single chromatographic peak is formed. 0 denotes that multiple chromatographic peaks are formed, and – denotes that no any chromatographic peak is formed [72,77].

even it could not be applied for all analytes, TV-SPME with on-fiber derivatization can serve as a powerful technique for amine, GHB and hydroxylamine-controlled substances [78]. The technique can increase the efficiency of the analyst by minimizing the time required for preparation of the sample for these types of analytes. Since GHB cannot be analyzed directly in its native state by GC/MS, this method is particularly well-suited to overcome such limitation [72,79].

Table 2. liquid injection methods based on V-SPME

Drug	TV-SPME	Liquid Injection
Methamphetamine	+	+
Amphetamine	+	+
Methamphetamine + TFAA	+	+
25I-NBOH	0	-
Gabapentin	+	+
Psilocin	+	+
25I-NBOH + TFAA	+	+
Pregabalin	+	-
Ephedrine	+	+
Ephedrine + TFAA	0	+
Lorazepam	+	+
Vigabatrin	-	-
GHB	-	-
Gabapentin + DMF-DMA	0	+
GHB + BSTFA + 1% TMCS	+	+
Vigabatrin + DMF-DMA	-	+
Pregabalin + DMF-DMA	-	0
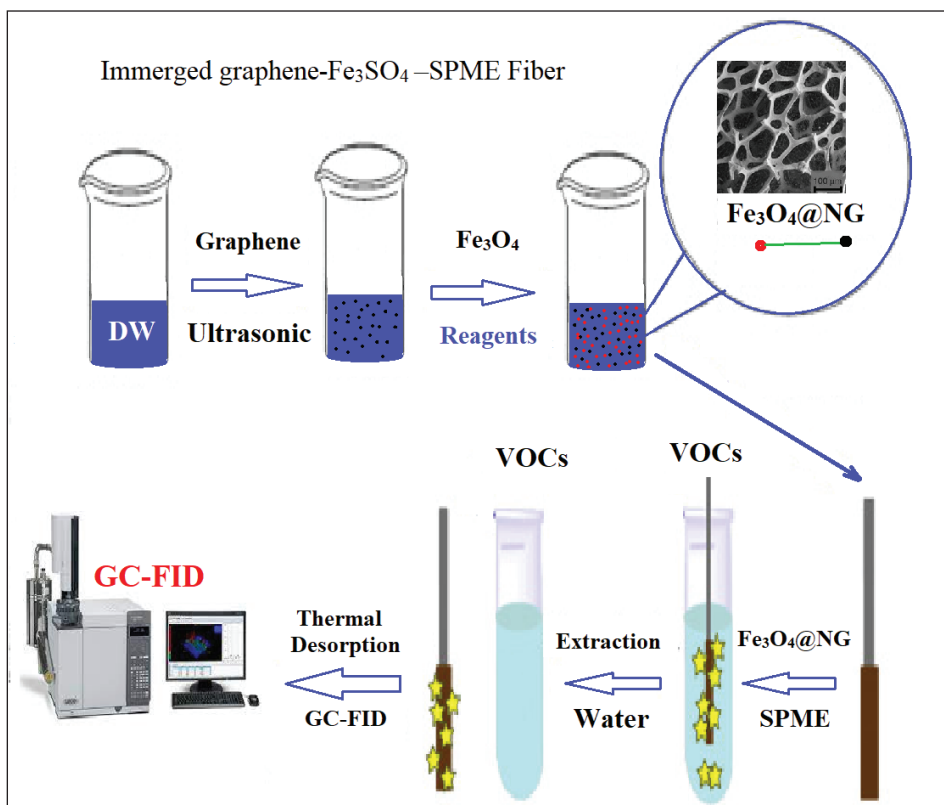
Fig.5. Immerged (graphene-Fe$_3$SO$_4$–SPME Fiber) in water and adsorbed the BTEX from water onto the fiber

2.4. Application of TV-SPME procedure
2.4.1. Ascertainments of lipid profiles of Phormia regina

Pupae of Phormia regina was the sample used in this study which basically belongs to a kind of blow fly species; while doing the inquiries of death, the forensic entomologists commonly found this type. which is commonly found by forensic entomologists during the investigations of death. Conventionally, the insect species analysis in a forensic backdrop has been falling within the prospect of biologists along with entomologists. Nevertheless, considerable effect has been done by the chemistry domain for the evaluation of these specimens by LC-MS, GC-MS and likely analytical techniques [80]. Studies that rely on liquid extraction are more commonly used for such analysis. Usually, the pest is placed in a non-polar solvent by the mean immersion for a particular time, allowing the extraction process of the cuticular and internal lipids. Derivatization is a kind of needful for these excerpts to improve performance and sensitivity within subsequent separation steps [81-82]. Unavoidably, single or multifold rounds of chromatography follows: liquid chromatography (LC), gas chromatography (GC) and thin layer chromatography (TLC) are some of the techniques that have been used. This wide-ranging method has been applied to the analysis of pupae [83-86].

Some experiments have been sought for the evaluation of the Volatile Organic Compounds (VOCs) that emitted by pupae using HS-SPME at elevated temperatures, unfortunately, the experiments were unsuccessful. For that, attentions have been exerted towards developing a new technique for the liquid extraction of pupae in order for the isolation of any hydrocarbons and lipids subsequent to TV-SPME analysis. The derivatization by trimethlysilyl was also performed internally within the sample vial immediately before GC-MS analysis took place, such derivatization would come very handy and with potential advantage to future analysts in order to rundown on blow fly pupae [23].

A new-fangled technique has been developed for the evaluation of sterols, fatty acids and other naturally occurring lipids within pupae of the blow fly Phormia regina. Such method counted on liquid extraction in a solvent (non-polar), followed by derivatization using N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) w/ 1% trimethylchlorsilane (TMCS) carried out inside the sample vial. The facilitation of this rundown was done by total vaporization solid-phase microextraction (TV-SPME), along with gas chromatography-mass spectrometry (GC-MS) which served as the instrumentation for analysis. The TV-SPME delivery technique was considered to be sensitive and effective approximately five times more than traditional liquid injection, this higher sensitivity may ease the reconstitution requirement, rotary evaporation, and collection of high-performance liquid chromatography fractions, and many of the other pre-concentration steps that are commonplace in the current literature. In addition to that, the ability of this method to derivatize the liquid extract in just single step while ensuring good sensitivity represents an improvement over present derivatization method. Various saturated and unsaturated fatty acids were the lipids present by and large in fly pupae, ranging from lauric acid (12:0) to arachinoic acid (20:4), as well as cholesterol. The concentrations of myristic acid (14:0), palmitelaidic acid (16:2), and palmitoleic acid (16:1) emerged as the most reliable indicators of the age of the pupae [23, 87-88].

2.4.2. Detection of ɣ-butyrolactone (GBL) and ɣ-hydroxybutyric acid (GHB) in alcoholic beverages via TV-SPME and GC-MS

ɣ-butyrolactone (GBL) and ɣ-Hydroxybutyric acid (GHB) are important drugs since the can be spiked into a victim's beverage to facilitate sexual assault(surreptitiously). These drugs may cause sedation, memory loss, and are difficult to be detected especially in plasma and biological samples. The challenge related to their analysis of these drugs lies on that they may be prone to readily interconvert in aqueous samples, which was showed in samples that required longer time to stand at room temperature. A volume required

for the study of GBL in water was performed with volumes that ranged from 1µl to 10mg as compared to the efficacy of headspace SPME, immersion SPME and TV-SPME. Lastly, water, liquor, wine beer, and mixed drinks were spiked with either GBL or GHB along with realistic concentrations (mg/ml) and microliter quantities were analysed using a combination of the TV-SPME and GC/MS method. The volume study of GBL exhibited a great sensitivity in the detection of GBL when TV-SPME was used. In addition to that, GBL and GHB were recognized in many beverages at realistic concentrations. Overall, TV-SPME is a method of benefits since it does not require sample preparation and uses lesser sample volume as compared to the immersion and headspace SPME [73].

2.4.3. Detection of both cotinine and nicotine in hair

TV-SPME can be used in detection of both cotinine and nicotine in hair as biomarkers of tobacco users whereas the cotinine detection was not possible in the past by using conventional SPME [89]. Only few research papers have published in using headspace SPME in the detection of nicotine in human hair by using. It was reported for first time that both cotinine and nicotine are efficiently detected using TV-SPME from a hair sample collected from a tobacco user. Incidentally, full scan data detect many other important compounds relied on a library search [53]. These involves phenacetin (an analgesic), squalene (a hair lipid that occurs naturally), 1,4-benzenediamine (a precursor of hair dye), and homosalate (type UV filter seen in shampoos). The hair taken from a two more smokers had nicotine concentrations of 21 and 29 ng mg^{-1} hair, which is almost same as that the concentrations reported from other studies [24,25]. A detailed studies of validating the TV-SPME for the use of hair analysis showed its ability to detect both the cotinine and nicotine even in a small portion of the hair from the tobacco users which could serve as a good method for the researchers of toxicology and other medical backgrounds [53].

2.4.4. Tracking explosive residues on the places of bombing

The detection of the residues seen on bombing places and that arising from a debris of post-blast has a great role for the explosive's investigators. This can be used on the determining of explosive type, which may be used to catch a link about some suspect. To solve the issue of not finding a particle of explosives, some standard methodology can be used including the extraction of some pieces of debris with specific solvent (i.e., acetone and/ or dichloromethane) and then the extract(s) is to be analyzed via liquid injection GC/MS and/or infrared spectroscopy [16,90]. A TV-SPME method for the analysis of explosive residues on pipe bomb fragments has been designed and optimized. Optimization of this method was done by the following parameters incubation temperature, extraction time, and sample volume of the TV-SPME method. For the nitroglycerin, method optimization parameters were a 70 mL sample volume, a 30-minute extraction time and a 65 C incubation temperature. In addition to that, TV-SPME showed great sensitivity as compared to conventional liquid extraction methods as it was found to be 13-fold more sensitive and it has a very low detection limit (i.e., less than 10 ng mL^{-1}). When this developed method was used to actual pipe bombs, the recovery of the estimated NG mean mass was 1.0 mg and the mean concentration of NG on the fragments of steel was almost 0.26 ppm (w/w). It was noticed that end caps fragments yielded higher amount of NG and DPA. These findings could contribute to understand how IEDs functioning and it help the analysts regarding the required sensitivity for the analysis smokeless powder from post-blast fragments.

Fragments from the end caps yielded the highest amount of DPA and NG. These results of this study contributed by the meaning of understanding of how small IEDs function as well as inform analysts regarding the sensitivity that is required for post-blast analysis of smokeless powder. It is expected that many other types of smokeless powder could be analyzed by this technique. This technique also can be used for the analysis of some other types of containers like PVC [16].

2.4.5.Identification and Automated Derivatization of Controlled Substances via TV-SPME and Gas Chromatography/Mass Spectrometry (GC/MS)

Due to polarity, many compounds that present in biological and environmental samples are not suitable to be analyzed by GC. In addition to that, some compounds have the tendency to have decomposing and adsorbing properties on the injector or columns and to show non-reproducible peak areas, shapes and heights [91]. To overcome such issues, the need of introducing derivatization reactions arises [92]. The importance of derivatization comes from its ability to decrease the polarity of the compounds of interest and increase the volatility and improve the analytes thermo stability. The derivatization also can improve the process of selecting of compounds behavior towards selective detectors, such as the spectrometry (MS) and electron capture detector (ECD). One of the main purposes from the formation of derivatives is to enhance the selectivity of the compounds, limit of detection (LOD) or both [93]. Before applying the analytical method, the targeted compounds placed for a procedure of sample preparation that involves a derivatization, concentration, or clean-up step procedures[26]. Combining extraction technique with derivatization result in enhancing the separation characteristics, detectability, and analyte recovery [94]. Generally, derivatization has been performed to promote the extractability of the analytes, reduce polarity, improve the GC characteristics of compounds, and make them compatible with the analytical system and/or to increase the detection sensitivity [91]. In forensic science laboratories, controlled substances units are placed under pressure for analyzing samples adapting methods that can show cost-effectiveness and high throughput. Additional to that, it is recommended in the field of analytical chemistry that that new chemical compounds appear in forensic chemists and exhibits must react to this by developing instrumental methods have great selectivity and high specificity [95]. It was observed that TV-SPME offering greater sensitivity for controlled substances as compared

to traditional liquid injection. Additionally, TV-SPME technique was easily applied to involve either a post-extraction or a pre-extraction on-fiber derivatization step species with thermally labile. Promising results were obtained for almost all categories of drugs that were analyzed successfully by the meaning of on-fiber derivatization as solutions. This important discovery may increase the use of this novel technique, because controlled substances are existed mostly in their solid forms in the laboratories of forensic science. This technique can be applied in the determination of solid drug powders and beverage sample, since these applications include a significant decrease in the amount of sample preparation. Although not applicable ideally for all analytes, TV-SPME with on-fiber derivatization could serve as an important technique for the determination of hydroxylamine and amine, controlled substances, and GHB. Thus, this work results in a set of optimized derivatization methods that can serve in TV-SPME and even in liquid injection. This approach presents a possible method for automated derivatization and sampling for a wide variety of thermally labile compounds and for analyzing compounds that need no derivatization [72,74,96]. Many applications exist for extraction analyte by the TV-SPME which was shown in Figure 6.

2.4.6.VA-TV-SPME procedure

Considering that SPME is that method depended on vaporizing the whole portion of the sample of interest, including volatile, nonvolatile and semi-volatile components. However semi-volatile and non-volatile compounds needs more heat, for that more amount of the sample volume is required. As a resultant of that, the SPME fiber get heated and that fiber has not affected the absorption of the analytes on the SPME fiber [53]. It could be a limiting factor, and considered to be the main reason behind this important extraction technique is not more used widely. For that reason, publication studies based on TV-SPME technique are less [23,69,70]. To solve such limitations, TV-SPME is coupled with another technique to encourage the analytes vaporization
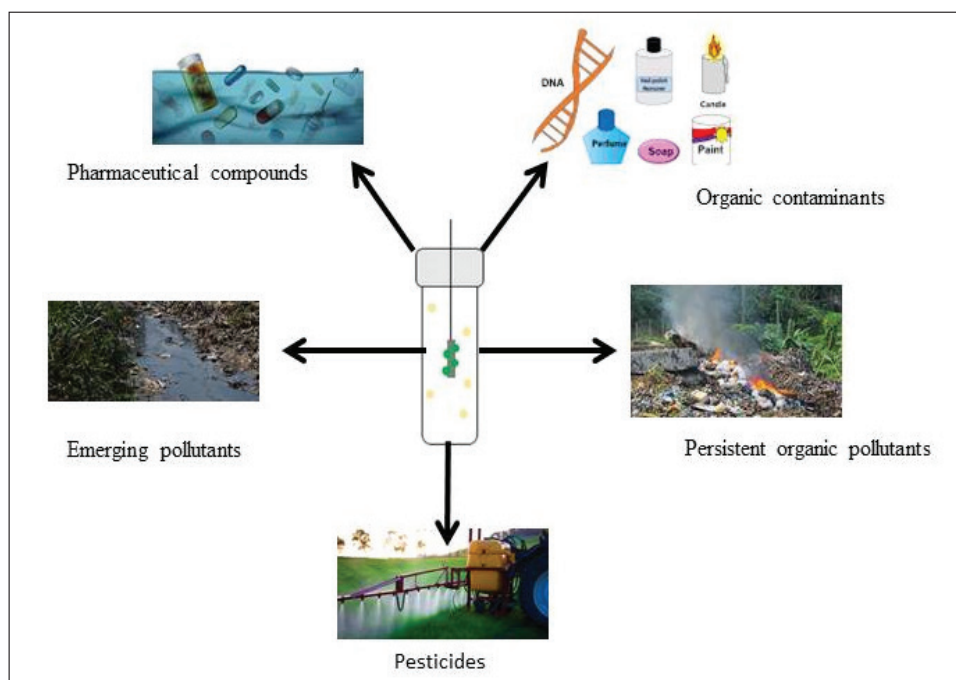
Fig. 6. Some applications of TV-SPME

and the preparation steps are omitted lead to a great reduction in the required heat which would assist a great benefit. In 2001, Brontun explained that when there is inhibition of the vessel pressure, it will lead to effect positively on the sampling [19]. One more explanation revealed that by decreasing the pressure, the analytes gets released from the matrix of the sample. Additional to that, decreased pressure reduces the boundary layer that attached to the fiber and strengthens the analyte absorption on the surface of the absorbent [49]. Recently, new extraction technique was introduced by Psillakis called Vac-HS-SPME as a new method depends on reduction of the pressure of the vessel used for sampling [76]. They revealed that when the vacuum conditions are applied, HS-SPME the extraction rate of analyte will be increased be speeding up the conversion from the aqueous matrix to the headspace. As a result of that, the vaporization of the analytes increased attributed to vacuum removal and faster equilibrium of the air from the headspace. This technique could not be able to extract analytes from the sample in solid phase and soil without preparation [77]. The sample may be lost due to the direct contact between the vacuum and the sample while evacuation period occurring.

To overcome such risk, the need of using a novel setup for the sampling vessel, Vacuum Assisted HS-SPME (VA-HS-SPME) was introduced to be used in the extraction of Polycyclic Aromatic Hydrocarbons (PAHs) from polluted soil without the need of preparation and the risk of analytes loss is less [52]. In that proposed technique, for the first time, a low-cost, sample, reliable and fast setup was developed by using both VA-HS-SPME (low pressure) [78] and TV-SPME techniques. One of the main advantages of VA-TV-SPME, more temperature can be applied for the extraction of analyte from the matrix of the sample without increasing the fiber temperature, which results in the increasing the of analyte extraction, as compare to conventional TV-SPME. One more advantage is that the time of sample vaporization is shorter. Also, when vacuum-assistance and total vaporization are simultaneously used, it maximizes the rate of analyte extraction in a complex matrix, with no need of any preparation. To evaluate the PAHs extraction from polluted water samples, a PDMS fiber is used, then the determination is done by GC-FID [67]. The main purpose of coupling TV-SPME with the VA-TV-SPME system (Fig.7) was to increase the sensitivities
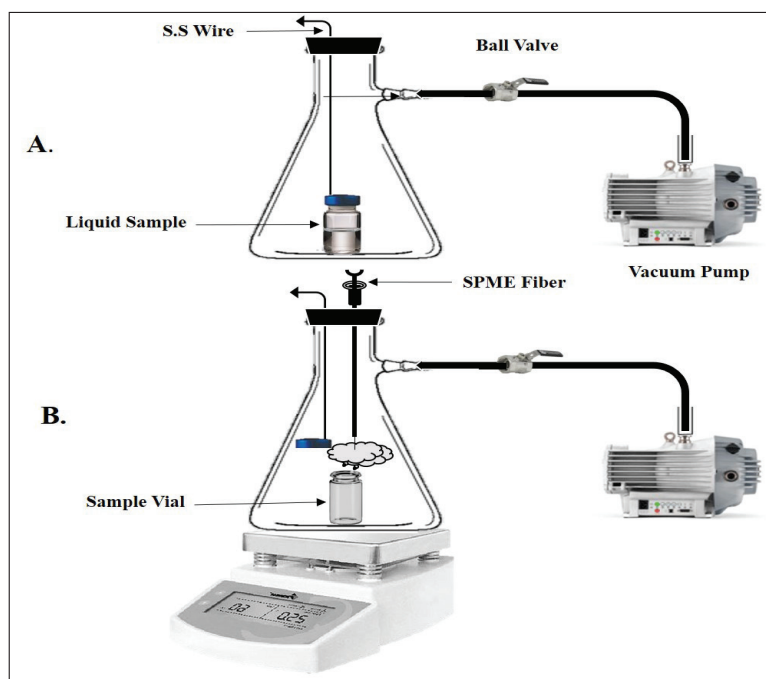
Fig. 7. Diagram of the VA-TV-SPME Assembly: in [A.] the cap of the sample is caped in close system while in [B.] the cape of the system is opened

in shorter times, which lead to lower extraction time and temperature, as compared to the conventional TV-SPME technique [67]. Such technique offers a new method to solve the warm of the SPME fiber caused by the heating process needed for separating the analyte from the matrix avoiding the use of complicated equipment and the sample is vaporized totally with lower duration as well as low heat energy. Additional to that, the total vaporization of the sample presents highly efficiency due to the increasing of the mass transfer in just one step. In addition to that, it is possible to use of homemade and commercial SPME fiber, and there is potential for coupling with other SPME techniques and automation, such as an inside needle capillary adsorption trap (INCAT) or a needle trap device (NTD [79].

2.5. Estimation of BTEX Compounds present in Polluted water using GO-APTES Fiber and Novel VA-TV-SPME Method

Isomers of benzene, toluene, ethylbenzene and xylene, all together known as BTEX (Fig.8), are highly volatile aromatic hydrocarbons and considered to be among the most serious human health and environmental risk issues.[32,97-98].

When these organic compounds are exposed in higher concentrations, they cause a harmful effects on central nervous systems, respiratory and skin [89-100]. Leakage of oil pipelines may be resulted by accidental fuel spills, and the disposal contamination of oil companies effluents and petrochemical, such pollutants have been released into groundwater and other water sources [97]. As a result of that, many analytical methods were developed such as a consequence, a wide variety of analytical methods, such as narrow-bore tube DLLME [38], ultrasound-assisted emulsification microextraction [101] and in syringe dispersive liquid–liquid microextraction (IS-DLLME). These methods have been developed with motive of extracting and determining of BTEX compounds from water [102]. For the determination of BTEX from contaminated water without using ant additional steps for the extraction and the preparation of the aqueous samples, microextraction techniques were used. VA-SPME removed one of the most partitioning steps in the conventional HS-SPME and that can increase the speed and the sensitivity of the method [102]. A novel and reliable microextraction technique was used for the fast determination of
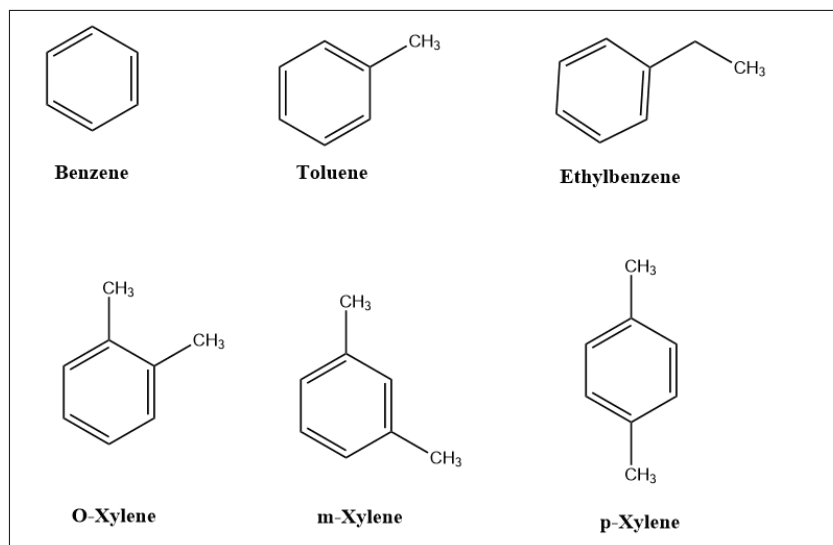
Fig. 8. Structures of BTEX

benzene, toluene, ethylbenzene and xylenes (BTEX) from contaminated water without any extra steps for the preparation or extraction of the aqueous sample. Vacuum-assisted-total vaporization-solid-phase microextraction (SPME) eliminated one of the partitioning steps in conventional headspace SPME and caused an increase in the sensitivity and speed of the method. A special nanocomposite SPME fibre made of grapheme oxide/3-aminopropyl-triethoxysilane fiber was utilize as the extraction phase to attain an efficient extraction. Numerous parameters were considered for the optimization, the extraction time, temperature, and desorption conditions. The optimized method exposed acceptable a good validity aspects according to the ICH guidelines with acceptable range. In this study, BTEX that present in aqueous samples were determined by the use of VA-TV-SPME method. It was observed that effect of adsorption time is less in the extraction efficiency of VA-TV-SPME [102]. Additional to that, in order to preconcentrate and extract the analytes, an affordable and home-made GO-APTES SPME fiber was utilized and it was observed that it has reliable and a powerful sorbent, compared with that fibres obtained from the market commercially. For achieve a précised analyte determination, this method was hyphenated with a GC-FID instrument. According the outcomes of this method, an analytical parameters such as LDR,

LOD and RSD were within the acceptable range, and it was observed this method is suitable for the determination of BTEX in polluted water[32,47,59].

3. Conclusion

The coupling TV with SPME arises from the need for a technique where a complete vaporing of the liquid samples gives a fewer matrix effect and better adsorption. Such a method requires less sample preparation, utilizes the least supplies, and can be done automatically, enabling it to be both a cost-effective and efficient method. TV-SPME is a sensitive technique where the liquid aliquot is totality vaporized prior to sampling, easing to attain the equilibria inside the sample vial and increasing the quantity of analyte available in the headspace. TV-SPME is an effective technique for analyzing controlled substances with and without on-fiber derivatization. The approach of coupling TV and SPME (TV-SPME) offered great sensitivity and even low detection limits for compounds present in the hair of tobacco users, such as nicotine and cotinine. A sample extract needs to be heated until it gets vaporized, and fiber of SPME is utilized for pre-concentrating analytes from the matrix.

4. Acknowledgement

5. List of abbreviation

TV-SPME: Total Vaporization Solid Phase microextraction

SPME: Solid Phase Microextraction

GC: Gas Chromatography

HS-SPME: Headspace Solid Phase Microextraction

MOF: Metal-Organic Framework

TATP: triacetone triperoxide

I-SPME: Immersion Solid Phase Microextraction

LC: Liquid Chromatography

IR: Infrared Spectroscopy

UV: Ultraviolet Spectroscopy

TV: Total Vaporization

PAHs: Polycyclic Aromatic Hydrocarbons

LVI: Large-Volume Injection

MS: Mass spectrometry

GC/MS: Gas Chromatography/ Mass Spectrometry

PDMS/DVB: Polydimethylsiloxane-divinylbenzene

LC-MS: Liquid Chromatography- Mass Spectrometry

TLC: Thin Layer Chromatography

VOCs: Volatile Organic Compounds

BSTFA: Bis(trimethylsilyl)trifluoroacetamide

TMCS: Trimethylchlorosilane

GLB: ɣ-butyrolactone

GHB: ɣ-hydroxybutyric acid

DPA: Diphenylamine

NG: Nitroglycerin

ECD: Electron Capture Detector

LOD: Limit of Detection

VA-TV-SPME: Vacuum Assisted Total Vaporization Solid Phase Microextraction

VA-HS-SPME: Vacuum Assisted Headspace Solid Phase Microextraction

PDMS: Polydimethylsiloxane

GC-FID: Gas Chromatography Flame Ionization Detector

CAT: Capillary Adsorption Trap

INCAT: Inside Needle Capillary Adsorption Trap

6. References

[1] C. L. Arthur, J. Pawliszyn, Solid phase microextraction with thermal desorption using fused silica optical fibers, Anal. Chem, 62 (1990) 2145-2148. https://doi.org/10.1021/ac00218a019.

[2] M. Lashgari, V. Singh, J. Pawliszyn, A critical review on regulatory sample preparation methods: Validating solid-phase microextraction techniques, TrAC Trends Anal. Chem., 119 (2019). https://doi.org/10.1016/j.trac.2019.07.029.

[3] E. Martendal, E. Carasek, A new approach based on a combination of direct and headspace cold-fiber solid-phase microextraction modes in the same procedure for the determination of polycyclic aromatic hydrocarbons and phthalate esters in soil samples, J. Chromatogr., A 1218 (2011) 1707-1714. https://doi.org/10.1016/j.chroma.2011.01.074.

[4] E. Yiantzi, N. Kalogerakis, E. Psillakis, Vacuum-assisted headspace solid phase microextraction of polycyclic aromatic hydrocarbons in solid samples, Anal. Chim. Acta., 890 (2015) 108-116. https://doi.org/10.1016/j.aca.2015.05.047.

[5] J. S. Elmore, M. A. Erbahadir, D. S. Mottram, Comparison of dynamic headspace concentration on Tenax with solid phase microextraction for the analysis of aroma volatiles, J. Agric. Food Chem. 45 (1997) 108-116. https://doi.org/10.1021/jf960835m.

[6] S. A. Barshick, W. H. Griest, Trace analysis of explosives in seawater using solid-phase microextraction and gas chromatography/ ion trap mass spectrometry, Anal. Chem., 70 (1998) 3015-3020. https://doi.org/10.1021/ac980060b.

[7] S. A. Scheppers Wercinski, J. Pawliszyn, Solid Phase Microextraction Theory, Solid Phase Microextraction., Boca Raton, 257 pages, 1999. https://doi.org/10.1201/9780367803223

[8] S. Huang, Monitoring of persistent organic pollutants in seawater of the Pearl River Estuary with rapid on-site active SPME sampling technique, Environ. Pollut, 200 (2015) 149-158. https://doi.org/10.1016/j.envpol.2015.02.016.

[9] S. Risticevic., Protocol for solid-phase microextraction method development,

Nat. Protoc., 5 (2010) 122-139. https://doi.org/10.1038/nprot.2009.179.

[10] É. A. Souza-Silva., A critical review of the state of the art of solid-phase microextraction of complex matrices III, Bioanalytical and clinical applications. TrAC Trends Anal. Chem., 71 (2015) 249-264. https://doi.org/10.1016/j.trac.2015.04.017.

[11] S. Lv, The study of fingerprint characteristics of Dayi pu-erh tea using a fully automatic HS-SPME/GC-MS and combined chemometrics method, PLOS ONE, 9 (2014) e116428. https://doi.org/10.1371/journal.pone.0116428

[12] C. L. Arthur, Automation and optimization of spme. Anal. Biochem., 64 (1992) 1960-1966. https://doi.org/10.1021/ac00041a034

[13] J. Ai, Solid phase microextraction for quantitative analysis in nonequilibrium situations, Anal. Chem., 69 (1997) 1230-1236. https://doi.org/10.1021/ac9609541.

[14] K. G. Furton, Application of solid-phase microextraction to the recovery of explosives and ignitable liquid residues from forensic specimens, J. Chromatogr., A 885 (2000) 419-432.   https://doi.org/10.1016/s0021-9673(00)00368-x.

[15] G. Liu, Headspace solid-phase microextraction of semi-volatile ultraviolet filters based on a superhydrophobic metal–organic framework stable in high-temperature steam, Talanta 219 (2020) 121175. https://doi.org/10.1016/j.talanta.2020.121175.

[16] D. Bors, J. Goodpaster, Mapping explosive residues on galvanized pipe bomb fragments using total vaporization solid phase microextraction (TV-SPME), Anal. Methods, 7 (2015) 9756-9762. https://doi.org/10.1039/C5AY02358K.

[17] R. Technologies, A review of: Static headspace – Gas chromatography theory and practice, J. Liq. Chromatogr. Relat. Technol., 21 (1998) 434-436, https://doi.org/10.1080/10826079808000503.

[18] M. Tabibpour, Carbon fibers modified with polypyrrole for headspace solid phase microextraction of trace amounts of 2-pentyl furan from breath samples, J. Chromatogr. A, 1609(2020) 460497. https://doi.org/10.1016/j.chroma.2019.460497.

[19] N. P. Brunton, D. A. Cronin, F. J. Monahan, The effects of temperature and pressure on the performance of Carboxen/PDMS fibres during solid phase microextraction (SPME) of headspace volatiles from cooked and raw turkey breast, Flavour Fragr. J. 16 (2001) 294-302. https://doi.org/10.1002/ffj.1000.

[20] A. Mehdinia, M. O. Aziz-Zanjani, Advances for sensitive, rapid and selective extraction in different configurations of solid-phase microextraction, TrAC Trends Anal. Chem., 51 (2013) 13-22. https://doi.org/10.1016/j.trac.2013.05.013.

[21] W. Q. Xie, Y. Gong, K. Yu, Enhancing the sensitivity of full evaporation technique using multiple headspace extraction analysis, Chromatographia, 80 (2017) 1263-1268. https://doi.org/10.1007/s10337-017-3343-x.

[22] C. Wang, Oolong tea made from tea plants from different locations in Yunnan and Fujian, China showed similar aroma but different taste characteristics, Springerplus, 5 (2016) 576. https://doi.org/10.1186/s40064-016-2229-y.

[23] W. Kranz, Optimization of total vaporization solid-phase microextraction (TV-SPME) for the determination of lipid profiles of Phormia regina, a forensically important blow fly species, Anal. Bioanal. Chem., 409 (2017) 6349-6357.   https://doi.org/10.1007/s00216-017-0573-6.

[24] J. L. Thomas, Application of a co-polymeric solid phase extraction cartridge to residues containing nitro-organic explosives, Forensic Chem., 11 (2018) 38-46. https://doi.org/10.1016/j.forc.2018.08.006.

[25] S. Calderara, D. Gardebas, F. Martinez, Solid phase micro extraction coupled with on-column GC/ECD for the post-blast analysis of organic explosives, Forensic Sci. Int., 137 (2003) 6-12. https://doi.org/10.1016/s0379-0738(03)00256-1.

[26] A. Jim, Application of solid-phase microextraction to Virgin olive oil quality control, J. Chromatogr A, 1121 (2006) 140-144. https://doi.org/10.1016/j.chroma.2006.05.005.

[27] C. L. Rainey, D. E. Bors, J. V. Goodpaster, Design and optimization of a total vaporization technique coupled to solid-phase microextraction, Anal. Chem., 86 (2014) 11319-11325. https://doi.org/10.1021/ac5030528.

[28] K. G. Furton, Application of solid-phase microextraction to the recovery of explosives and ignitable liquid residues from forensic specimens, J. Chromatogr. A, 885 (2000) 419-432. https://doi.org/10.1016/s0021-9673(00)00368-x.

[29] M. A. LeBeau, M. A. Montgomery, M. L. Miller, S. G. Burmeister, Analysis of biofluids for gamma-hydroxybutyrate (GHB) and gamma-butyrolactone (GBL) by headspace GC-FID and GC-M, J. Anal. Toxicol., 24 (2000) 421-428. https://doi.org/10.1093/jat/24.6.421.

[30] K. E. Davis, L. D. Hickey, J. V. Goodpaster, Detection of ɣ-hydroxybutyric acid (GHB) and ɣ-butyrolactone (GBL) in alcoholic beverages via total vaporization solid-phase microextraction (TV-SPME) and gas chromatography–mass spectrometry, J. Forensic Sci. 66 (2021) 846-853. https://doi.org/10.1111/1556-4029.14660.

[31] D. N. Konanov, UniqPy: A tool for estimation of short-chain fatty acids composition by gas-chromatography/mass-spectrometry with headspace extraction, J. Pharm. Biomed. Anal., 212 (2022) 11468. https://doi.org/10.1016/j.jpba.2022.114681.

[32] M. Beiranvand, Determination of BTEX compounds in contaminated water using the novel vacuum-assisted-total vaporization SPME method and GO-APTES fiber, J. Chromatogr. Sci., 60 (2022) 486-492. https://doi.org/10.1093/chromsci/bmab111.

[33] K. E. Davis, J. V. Goodpaster, Gas chromatography-mass spectrometry paired with total vaporization solid-phase microextraction as a forensic tool, J. Vis. Exp., 171 (2021) 1-6. https://doi.org/10.3791/61880.

[34] M. Llompart, M. Celeiro, C. García-Jares, T. Dagnac, Environmental applications of solid-phase microextraction, TrAC Trends Anal. Chem., 112 (2019) 1-12. https://doi.org/10.1016/j.trac.2018.12.020.

[35] G. Sauzier, Optimisation of recovery protocols for double-base smokeless powder residues analysed by total vaporisation (TV) SPME/GC-MS, Talanta, 158 (2016) 368-374. https://doi.org/10.1016/j.talanta.2016.04.048.

[36] L. Hickey, Automated derivatization and identification of controlled substances in solution via total-vaporization solid-phase microextraction (TV-SPME), SSRN Electron. J., (2021), https://doi.org/10.2139/ssrn.3888661.

[37] O. M. Fayemiwo, M. O. Daramola, K. Moothi, Btex compounds in water – Future trends and directions for water treatment. Water South Africa, 43 (2017) 602-613. https://doi.org/10.4314/wsa.v43i4.08.

[38] M. Rahmani, M. Kaykhaii, E. Ghasemi, M. Tahernejad, Application of in-syringe dispersive liquid–liquid microextraction and narrow-bore tube dispersive liquid–liquid microextraction for the determination of trace amounts of BTEX in water samples, J. Chromatogr. Sci., 53 (2015) 1210-1216, https://doi.org/10.1093/chromsci/bmu163.

[39] M. Sajid, Porous membrane protected micro-solid-phase extraction: A review of features, advancements and applications, Anal. Chim. Acta., 965 (2017) 36-53. https://doi.org/10.1016/j.aca.2017.02.023.

[40] M. Sajid, Development of natural sorbent based micro-solid-phase extraction for determination of phthalate esters in milk samples, Anal. Chim. Acta, 924 (2016) 35-44. https://doi.org/10.1016/j.aca.2016.04.016.

[41] C. Basheer, H. K. Lee, Hollow fiber membrane-protected solid-phase microextraction of triazine herbicides in bovine milk and sewage

sludge samples, J. Chromatogr., A 1047. (2004) 189-194. https://doi.org/10.1016/j.chroma.2004.06.130.

[42] S. Merkle, K. Kleeberg, J. Fritsche, Recent developments and applications of solid phase microextraction (SPME) in food and environmental analysis—A review, Chromatogra. 2 (2015) 293-381. https://doi.org/10.3390/chromatography2030293

[43] H. Piri-Moghadam, F. Ahmadi, J. Pawliszyn, A critical review of solid phase microextraction for analysis of water samples, TrAC Trends Anal. Chem., 85 (2016) 133-143. https://doi.org/10.1016/j.trac.2016.05.029.

[44] X. Wang, Zinc(II)-based metal–organic nanotubes coating for high sensitive solid phase microextraction of nitro-polycyclic aromatic hydrocarbons, Talanta, 186 (2018) 561-567. https://doi.org/10.1016/j.talanta.2018.02.062.

[45] M. Merdivan, V. Pino, J. L. Anderson, Determination of volatile polycyclic aromatic hydrocarbons in waters using headspace solid-phase microextraction with a benzyl-functionalized crosslinked polymeric ionic liquid coating, Environ. Technol., 38 (2017) 1897-1904. https://doi.org/10.1080/09593330.2016.1240242.

[46] H. Mokbel, Simultaneous analysis of organochlorine pesticides and polychlorinated biphenyls in air samples by using accelerated solvent extraction (ASE) and solid-phase micro-extraction (SPME) coupled to gas chromatography dual electron capture detection, Environ. Sci. Pollut. Res. Int., 23 (2016) 8053-8063. https://doi.org/10.1007/s11356-016-6072-z.

[47] M. Espina-Benitez, Development of a new microextraction fiber combined to on-line sample stacking capillary electrophoresis UV detection for acidic drugs determination in realwater samples, Int. J. Environ. Res. Public Health,, 14 (2017) 1-16. https://doi.org/10.3390/ijerph14070739.

[48] R. López-Serna, Multiresidue analytical method for pharmaceuticals and personal care products in sewage and sewage sludge by online direct immersion SPME on-fiber derivatization – GCMS, Talanta, 186 (2018) 506-512. https://doi.org/10.1016/j.talanta.2018.04.099.

[49] N. Ochiai, K. Sasamoto, A. Hoffmann, K. Okanoya, Full evaporation dynamic headspace and gas chromatography-mass spectrometry for uniform enrichment of odor compounds in aqueous samples, J. Chromatogr. A, 1240 (2012) 59-68. https://doi.org/10.1016/j.chroma.2012.03.097.

[50] S. R. Kim, Method validation for measurement of hair nicotine level in nonsmokers, Biomed. Chromatogr., 23 (2009) 273-279. https://doi.org/10.1002/bmc.1110.

[51] J. Kim, Association between secondhand smoke in hospitality venues and urinary 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanol concentrations in non-smoking staff, Int. J. Environ. Res. Public Health, 13 (2016) https://doi.org/10.3390/ijerph13111101.

[52] C. L. Arthur, J. Pawliszyn, Solid phase microextraction with thermal desorption using fused silica optical fibers, Anal. Chem., 62 (1990) 2145-2148. https://doi.org/10.1021/ac00218a019,

[53] J. You, BTEX degradation by a newly isolated bacterium: Performance, kinetics, and mechanism, Int. Biodeterior. Biodegrad., 129 (2018) 202-208. https://doi.org/10.1016/j.ibiod.2018.02.012.

[54] N. De Giovanni, D. Marchetti, A systematic review of solid-phase microextraction applications in the forensic context, J. Anal. Toxicol., 44 (2020) 268-297. https://doi.org/10.1093/jat/bkz077.

[55] D. M. Mana Kialengila, Full evaporation headspace gas chromatography for sensitive determination of high boiling point volatile organic compounds in low boiling matrices, J. Chromatogr. A, 1315 (2013) 167-175. https://doi.org/10.1016/j.chroma.2013.09.058.

[56] N. Ochiai, K. Sasamoto, A. Hoffmann, K. Okanoya, Full evaporation dynamic headspace

and gas chromatography-mass spectrometry for uniform enrichment of odor compounds in aqueous samples, J. Chromatogr. A, 1240 (2012) 59-68. https://doi.org/10.1016/j.chroma.2012.03.097.

[57] E. Goudsmits, The analysis of organic and inorganic gunshot residue from a single sample, Forensic Sci. Int., 299 (2019) 168-173. https://doi.org/10.1016/j.forsciint.2019.03.049.

[58] S. Dugheri, N. Mucci, Advanced solid-phase microextraction techniques and related automation: A review of commercially available technologies J. Anal. Methods Chem., 2022(2022) 8690569. https://doi.org/10.1155/2022/8690569

[59] D. Bors, J. Goodpaster, Mapping smokeless powder residue on PVC pipe bomb fragments using total vaporization solid phase microextraction, Forensic Sci. Int., 276 (2017) 71-76. https://doi.org/10.1016/j.forsciint.2017.04.002.

[60] Q. Guan, Rapid determination of total acid content of oils resulting from sub/supercritical water liquefaction of lignite by headspace gas chromatography, Energy Fuels, 27 (2013) 5135-5137. https://doi.org/10.1021/ef401020c.

[61] M. Chan , H. Sy, Determination of ethanol content in kombucha using headspace gas chromatography with mass spectrometry detection: Single-laboratory validation, J. AOAC Int., 5 (2021) 122-128. https://doi.org/10.1093/jaoacint/qsaa094.

[62] J. Schuberth, A. Full, A full Evaporation headspace technique with capillary GC and ITD: A means for quantitating volatile organic compounds in biological samples, J. Chromatogr. Sci., 34 (1996) 314-319. https://doi.org/10.1093/chromsci/34.7.314.

[63] C. Pistos, J. T. Stewart, Direct injection HPLC method for the determination of selected benzodiazepines in plasma using a Hisep column, J. Pharm. Biomed. Anal., 33 (2003) 1135-1142. https://doi.org/10.1016/s0731-7085(03)00426-6.

[64] J. Pawliszyn, S. Pedersen-Bjergaard, Analytical microextraction: Current status and future trends, J. Chromatogr. Sci., 44 (2006) 291-307. https://doi.org/10.1093/chromsci/44.6.291.

[65] J. Pawliszyn, Theory of solid-phase microextraction, J. Chromatogr. Sci., 38 (2000) 270-278. https://doi.org/10.1093/chromsci/38.7.270

[66] G. Vas, K. Vékey, Solid-phase microextraction: A powerful sample preparation tool prior to mass spectrometric analysi, J. Mass Spectrom., 39 (2004) 233-254. https://doi.org/10.1002/jms.606.

[67] M. Beiranvand, A. Ghiasvand, Design and optimization of the VA-TV-SPME method for ultrasensitive determination of the PAHs in polluted water, Talanta, 212 (2020) 120809. https://doi.org/10.1016/j.talanta.2020.120809.

[68] X. Sun, Detection of polycyclic aromatic hydrocarbons in water samples by annular platform-supported ionic liquid-based headspace liquid-phase microextraction, J. Anal. Methods Chem., 2018 (2018) 3765682. https://doi.org/10.1155/2018/3765682.

[69] D. Bors, J. Goodpaster, Chemical analysis of racing fuels using total vaporization and gas chromatography mass spectrometry (GC/MS), Anal. Methods, 8 (2016) 3899-3902. https://doi.org/10.1039/C6AY00539J.

[70] G. Sauzier, Optimisation of recovery protocols for double-base smokeless powder residues analysed by total vaporisation (TV) SPME/GC-MS, Talanta, 158 (2016) 368-374. https://doi.org/10.1016/j.talanta.2016.04.048.

[71] C. Jurado et., Rapid analysis of amphetamine, methamphetamine, MDA, and MDMA in urine using solid-phase microextraction, direct on-fiber derivatization, and analysis by GC-MS, J. Anal. Toxicol., 24 (2000) 11-16. https://doi.org/10.1093/jat/24.1.11.

[72] L. D. Hickey, Automated derivatization and identification of controlled substances via total vaporization solid phase microextraction (TV-SPME) and gas chromatography/mass spectrometry (GC/MS), forensic and

investigative science program, Thesis, 2019. http://dx.doi.org/10.7912/C2/2387

[73]   K. E. Davis, L. D. Hickey, J. V. Goodpaster, Detection of ɣ-hydroxybutyric acid (GHB) and ɣ-butyrolactone (GBL) in alcoholic beverages via total vaporization solid-phase microextraction (TV-SPME) and gas chromatography–mass spectrometry, J. Forensic Sci., 66 (2021) 846-853. https://doi.org/10.1111/1556-4029.14660.

[74]   A.V. de Bairros, Determination of low levels of benzodiazepines and their metabolites in urine by hollow-fiber liquid-phase microextraction (LPME) and gas chromatography–mass spectrometry (GC–MS), J. Chromatogra. B, 975 (2015) 24-33. https://doi.org/10.1016/j.jchromb.2014.10.040

[75]   G. S. Groenewold, J. R. Scott, C. Rae, Recovery of phosphonate surface contaminants from glass using a simple vacuum extractor with a solid-phase microextraction fiber, Anal. Chim. Acta, 697 (2011) 38-47. https://doi.org/10.1016/j.aca.2011.04.034.

[76]   E. Psillakis, Vacuum-assisted headspace solid-phase microextraction: A tutorial review, Anal. Chim. Acta, 986 (2017) 12-24. https://doi.org/10.1016/j.aca.2017.06.033.

[77]   N. Reyes-Garcés, Advances in solid phase microextraction and perspective on future directions, Anal. Chem., 90 (2018) 302-360. https://doi.org/10.1021/acs.analchem.7b04502.

[78]   M. Beiranvand, A. Ghiasvand, Simple, Low-cost and reliable device for vacuum-assisted headspace solid-phase microextraction of volatile and semivolatile compounds from complex solid samples, Chromatographia, 80 (2017) 1771-1780. https://doi.org/10.1007/s10337-017-3422-z.

[79]   A. Ghiasvand, F. Zarghami, M. Beiranvand, Ultrasensitive direct determination of BTEX in polluted soils using a simple and novel pressure-controlled solid-phase microextraction setup, J. Iran. Chem. Soc., 15 (2018) 1051-1059. https://doi.org/10.1007/s13738-018-1302-6.

[80]   R. Telles-Romero, Effect of temperature on pupa development and sexual maturity of laboratory Anastrepha obliqua adults, Bull. Entomol. Res., 101 (2011) 565-571. https://doi.org/10.1017/S0007485311000150.

[81]   B. Frere, GC-MS analysis of cuticular lipids in recent and older scavenger insect puparia. An approach to estimate the postmortem interval (PMI), Anal. Bioanal. Chem., 406 (2014) 1081-1088. https://doi.org/10.1007/s00216-013-7184-7.

[82]   J. E. Baker, D. R. Nelson, C. L. Fatland, Developmental changes in cuticular lipids of the black carpet beetle, Attagenus megatoma. Insect Biochem., 9 (1979) 335-339. https://doi.org/10.1016/0020-1790(79)90015-5.

[83]   M. Gołębiowski, Comparison of free fatty acids composition of cuticular lipids of Calliphora vicina larvae and pupae, Lipids, 47 (2012) 1001-1009. https://doi.org/10.1007/s11745-012-3702-1.

[84]   M. Gołębiowski, Cuticular and internal n-alkane composition of Lucilia sericata larvae, pupae, male and female imagines: Application of HPLC-LLSD and GC/MS-SIM, Bull. Entomol. Res., 102 (2012) 453-460. https://doi.org/10.1017/S0007485311000800.

[85]   M. Gołębiowski, The composition of the cuticular and internal free fatty acids and alcohols from Lucilia sericata males and females, Lipids, 47 (2012) 613-622. https://doi.org/10.1007/s11745-012-3662-5.

[86]   M. Gołębiowski, M. I. Boguś, M. Paszkiewicz, P. Stepnowski, Cuticular lipids of insects as potential biofungicides: Methods of lipid composition analysis, Anal. Bioanal. Chem., 399 (2011) 3177-3191. https://doi.org/10.1007/s00216-010-4439-4.

[87]   J. A. Yoder, G. J. Blomquist, D. L. Denlinger, Hydrocarbon profiles from puparia of diapausing and nondiapausing flesh flies (Sarcophaga crassipalpis) reflect quantitative rather than qualitative differences, Arch. Insect Biochem. Physiol., 28 (1995) 377-385. https://doi.org/10.1002/arch.940280407.

[88] S. R. Kim, Method validation for measurement of hair nicotine level in nonsmokers, Biomed. Chromatogr., 23 (2009) 273-279. https://doi.org/10.1002/bmc.1110.

[89] J. Kim, Association between secondhand smoke in hospitality venues and urinary 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanol concentrations in non-smoking staff, Int. J. Environ. Res. Public Health, 13 (2016) 1101. https://doi.org/10.3390/ijerph13111101.

[90] TWGFEX, Laboratory explosion group standards and protocols, Recommended guidelines for forensic identication of intact explosives, 2007. https://moodle.cranfield.ac.uk/pluginfile.php/408151/mod_resource/content/0/Guidelines_for_ident_of_post_blast_expl_residues-TWGFEX.pdf) (2007) 1-9.

[91] M. A. Farajzadeh, N. Nouri, P. Khorram, Derivatization and microextraction methods for determination of organic compounds by gas chromatography, TrAC Trends Anal. Chem., 55 (2014) 14-23. https://doi.org/10.1016/j.trac.2013.11.006.

[92] F. Pena-Pereira, I. Lavilla, C. Bendicho, Miniaturized preconcentration methods based on liquid–liquid extraction and their application in inorganic ultratrace analysis and speciation: A review, Spectrochim. Acta, B, 64 (2009) 1-15. https://doi.org/10.1016/j.sab.2008.10.042.

[93] R. M. Smith, Before the injection- Modern methods of sample preparation for separation techniques, J. Chromatogr. A, 1000 (2003) 3-27. https://doi.org/10.1016/s0021-9673(03)00511-9.

[94] A. Balinova, R. Mladenova, D. Shtereva, Solid-phase extraction on sorbents of different retention mechanisms followed by determination by gas chromatography-mass spectrometric and gas chromatography-electron capture detection of pesticide residues in crops, J. Chromatogr. A, 1150 (2007) 136-144. https://doi.org/10.1016/j.chroma.2007.02.002.

[95] J. M. DuBois, A mixed-method analysis of reports on 100 cases of improper prescribing of controlled substances, J. Drug Issues., 46 (2016) 457-472. https://doi.org/10.1177/0022042616661836.

[96] M. Lashgari, Y. Yamini, An overview of the most common lab-made coating materials in solid phase microextraction, Talanta, 191 (2019) 283-306. https://doi.org/10.1016/j.talanta.2018.08.077.

[97] T. O. Egbuchunam, G. Obi, F. E. Okieimen, F. Tihminlioglu, Removal of BTEX from aqueous solution using Organokaolinite, Int. J. Appl. Environ. Sci., 11 (2016) 505-513. http://www.ripublication.com

[98] M. H. Dehghani, Source apportionment of BTEX compounds in Tehran, Iran using UNMIX receptor model, Air Qual. Atmos. Health, 10 (2017) 225-234. https://doi.org/10.1007/s11869-016-0425-0.

[99] K. Khodaei, BTEX biodegradation in contaminated groundwater using a novel strain (Pseudomonas sp. BTEX-30), Int. Biodeterior. Biodegrad., 116 (2017) 234-242. https://doi.org/10.1016/j.ibiod.2016.11.001.

[100] M. Hashemi, N. Jahanshahi, A. Habibi, Application of ultrasound-assisted emulsification microextraction for determination of benzene, toluene, ethylbenzene and o-xylene in water samples by gas chromatography, Desalination., 288 (2012) 93-97. https://doi.org/10.1016/j.desal.2011.12.017.

[101] W. S. Khayoon, Micro-solid phase extraction with liquid chromatography-tandem mass spectrometry for the determination of aflatoxins in coffee and malt beverage, Food Chem., 147 (2014) 287-294, https://doi.org/10.1016/j.foodchem.2013.09.049.

[102] F. Leusch, M. Bartkow, A short primer on benzene, toluene, ethylbenzene and xylenes (BTEX) in the environment and in hydraulic fracturing fluids, Smart Water Res. Cent., (2010) 1-8. https://www.ehp.qld.gov.au/management/coal-seam-gas/pdf/btex-report.pdf