

ARTICLE

FABRICATION OF SILICA NANOPARTICLE-PEG-IONIC LIQUID
SPME FIBER FOR DETERMINATION OF PESTICIDE RESIDUES IN
TOMATOJavad Norooz Haghi, Syed Waqif Husain*, Parviz Aberoomand Azar, Mohammad Saber Tehran²¹Department of Chemistry, Science and Research Branch, Islamic Azad University, IRAN

ABSTRACT



A novel SPME fiber was prepared for determination of pesticides in tomato samples. Different materials were synthesized as absorbent layer with Sol-Gel technology. These different adsorbing layers essentially were different combinations of polyethylene glycol (PEG), (Trimethoxysilyl) propyl methacrylate (TMSPA), polydimethylsiloxane (PDMS) with Silica Nanoparticles (Silica-NPs) and 1-Butyl-4-methylpyridinium tetrafluoroborate (BMPT) as the ionic liquid. These final synthesized adsorbing layers were attached to the modified surface of porous copper self-assembled monolayer (SAM) with simple immersion. Then the fibers were used to extract 6 types of pesticides in tomato samples and the extraction parameters such as extraction temperature and time, ionic strength, pH, desorption temperature and time were optimized. The fabricated fibers were compared with each other in terms of extraction efficiency and the selected fiber with best performance was PEG-Ionic Liquid-Silica NPs. The selected fiber was examined by SEM and figures of merit like LOD, LOQ, LDR, r^2 for each individual pesticide were calculated for this proposed technique under optimum conditions.

INTRODUCTION

Pesticide residue analysis in environmental and biological samples has received increasing attention in the last few decades as can be deduced by the great number of papers published dealing with this subject [1]. Pesticides are substances intended for preventing, destroying, repelling or mitigating any pest and are widely used on a variety of crops in the current agricultural practices. In this regard, the pesticide residues are found in foods [2]. It has been shown that the majority of pesticides cause acute high toxicity in human beings [3-4]. The residues are harmful not only for human being but also for all living organisms. The ongoing research in this area indicates the presence of pesticide residues in most agricultural products. When the contaminated products are taken by humans, they cause different diseases and may even be lethal.

Various methods such as supercritical fluid extraction, accelerated solvent extraction microwave-assisted extraction, ultrasonic extraction, and matrix solid phase dispersion have been employed to separate and measure these compounds in various matrices [5-9]. Many of these methods are time-consuming and require large amounts of organic solvents. In the literature, the need for rapid sample preparation methods for extraction and separation of analytes with high selectivity for the composition in matrix is emphasized [10-15]. To evaluate food safety and potential risks to human health, development of analytical methods to identify pesticide residues in aqueous and biological samples, fruits, and vegetables is necessary. A common sample preparation technique is solid-phase micro extraction (SPME). The technique was first described in 1990 by Pawliszyn et al [16] as a solvent-free pre-concentration and sample preparation method. It was introduced as a new way to insert the samples into the chromatography system. It is based upon development of a balance between the analyte in the sample solution and the fiber. After fulfillment of the extraction the analyte is desorbed into an analytical instrument such as GC or HPLC [17-20].

The fiber coated with typically an immobilized polymer, a solid adsorbent or a combination of them [17, 21] for sample introduction to GC and GC-MS, has been successfully and routinely applied to a wide variety of compounds from environmental, biological, and food samples [14, 21-24]. Among disadvantages of the commercial fibers used in SPME we can consider the large thickness of the stationary phase, fragility, high price, and lack of chemical bonding between the stationary phase and the substrate surface that causes low thermal stability of the aforementioned fibers. To tackle these disadvantages, a large number of home-made fibers have been prepared using different ways. Some of these methods include electrochemical deposition of conductive polymers, sol-gel technology, and using ionic liquids and nanoparticles [25]. Another approach to improve extraction efficiency in SPME is to use metals like Pt, Ni-Ti [26], Al [27], and Cu [28] as substrates to prevent the fragility of silica substrates. Increased porosity in the metallic substrate leads to higher thermal stability of the fiber and stronger bonding with the polymer network [28]. Metal substrate porosity has been achieved by electro deposition of a Cu thin layer on clean surface of Cu wire by applying a negative potential [29]. Other methods to enhance the extraction efficiency is promoting the formation of a covalent bond between the porous copper substrate and the polymer network (3-mercaptopropyl) trimethoxysilane (3MPTS) as binder using self-assembled monolayer (SAM) [30] as well as using carbon nanotubes [31-32]. Employment of silica nanoparticles is another way to improve the performance of SPME fibers [33].

Using SPME with ionic liquid coated fibers are highly proposed because ILs have some unique properties including negligible vapor pressure, good thermal stability, tunable viscosity and miscibility with water and

KEY WORDS

solid-phase micro extraction, sol-gel, ionic liquids, self-assembled monolayer (SAM), pesticide, silica nanoparticle

Received: 7 Sept 2016
Accepted: 22 Oct 2016
Published: 15 Oct 2017

*Corresponding Author

Email:
syedwaqfhusain@yahoo.com

organic solvents, as well as good extractability for various organic compounds and metal ions [34]. Recently, solid-phase micro extraction (SPME) with ionic liquid (IL) coating was developed for headspace extraction of BTEX [35]. Liu and co-workers introduced the use of ILs in preparation of SPME fiber for the first time [36]. There are several reports of the ionic liquids application in SPME such as extraction of polycyclic aromatic hydrocarbons (PAHs) in water samples by Nafion membrane based on ILs [37], extraction of various organic compounds and metal ions [38-39], headspace extraction of BTEX [40], and determination of amphetamine metabolite [41].

Conventional SPME including suffer from some drawbacks like operating temperature problems, instability, and swelling in organic solvents [34, 42]. Sol-gel technology which was suggested by Malik and co-workers [34] provides efficient approach by incorporation of the organic component into the inorganic polymeric structure in solution under very mild thermal condition [43]. Among many inherent advantages of sol-gel technology are the followings: i) high thermal stability achieved by strong adhesion of the coating to the substrate due to chemical bonding; ii) porous structure that provides high surface area and possibility of the use of thinner coatings to achieve acceptable stationary phase loading, sample capacities, and fast mass transfer characteristics; and iii) high degree of flexibility in coating composition and selectivity by varying the proportion of the sol solution ingredients or using a deactivation reagent [44].

In this study Cu porous wire was prepared by electro deposition of Cu thin layer on Cu substrate and metal surface was modified using SAM of (3-mercaptopropyl) trimethoxysilane (3MPTS) covalently bonded to the Cu substrate. Different combination of organic polymers, ionic liquids and silica NPs were prepared by sol-gel chemistry and the final synthesized mixtures were coated on the surface of the modified Cu-porous by SAM. Incorporation of silica NPs and ionic liquids enhances the fiber performance. Analysis of the surface morphology characteristics of the coated fibers was performed using SEM. Extraction efficiency of these fibers were investigated by direct immersion of the fibers in the aqueous sample for extraction of some pesticides in tomato samples. The most suitable fiber was PEG-Ionic Liquid-Silica NPs that caused highest extraction efficiency.

MATERIALS AND METHODS

Reagents

(3-Mercaptopropyl) trimethoxysilane (3MPTS) (95%) was purchased from Fluka (Buchs, Switzerland). Hydroxyl-terminated poly dimethyl siloxane (OHTSO), tetra ethylortho silicate (TEOS), tri fluoroacetic acid (TFA, 98%), poly methyl hydro siloxane (PMHS), silica NPs (10–20 nm), and 1-butyl-4-methylpyridinium tetra fluoro borate were obtained from Aldrich (Stein heim, Germany). Polyethylene glycol (PEG) (mono methyl ether, MW; 5000), and Superox-4 (PEG) were purchased from Sigma-Aldrich (Chemie, Stein heim, Germany), 3-(Trimethoxysilyl)propyl methacrylate (TMSPA), ionic liquid (1-butyl-4-methylpyridinium tetra fluoro borate) was purchased from Fluka (Buchs, Switzerland). All these materials were used as received, except TFA that was diluted to 95% and 99% with water. Before use, all plastic and glassware were decontaminated overnight in 20% nitric acid and thoroughly washed with Milli-Q quality (Millipore, Billerica, MA) deionized water. Target pesticides include Phosmet, parathion, Phorate, desethylatrazine and terbutylazine [Table 1] were supplied from Riedel-deHaen (Seelze-Hannover, Germany) with purity higher than 95.5%. Sodium chloride (extra pure), ethanol, methanol and acetonitrile (all of analytical reagent grades) were purchased from Merck (Darmstadt, Germany). Characterize of pesticides used in this work are summarized in [Table 1].

Table 1: Specifications of the pesticides used

	S (mg/L)	Log Kow	VP (mPa)	MW	VP (mPa)
Terbutylazine	6.6	3.4	0.12	229.71	0.12
Desethylatrazine	3200	1.51	12.44	187.63	12.44
Phorate	44	3.66	85.5	260.36	85.5
Parathion	11.75	3.73	2.3	291	2.3
Phosmet	15.2	2.96	0.065	317.323	0.065

Water solubility (S), vapor pressure (VP), Henry's law constant (H); data from Footprint Pesticide Properties Database.

Apparatus

A Hewlett-Packard (HP, Palo Alto, USA) HP 6890 plus series GC equipped with a split/split less injector and a Flame ionization detector system were used. Helium (99.999%) was employed as carrier gas and its flow velocity was constantly adjusted to 70 cm S⁻¹. The separation of pesticides was performed on a 30m × 0.25 mm HP-5 (0.25 μm film thickness). The column was held at 40 °C for 2 min, increased to 290 °C at a rate of 25 °C min⁻¹ and kept constant for 4 min and then raised to 290 °C at 40 °C min⁻¹ and kept at this temperature for 4 min. The injector temperature was set at 260 °C and fiber desorption was carried out in the split less mode.

Fiber Fabrication

Preparation of SPME fibers

A Cu wire with a length of 2cm and diameter of $200\mu\text{m}$ was prepared and its physical contamination was removed by washing with acetone, ethanol and distilled water respectively. For achieving a porous Cu surface a system of two electrodes (anode and cathode; both copper) with an electrolyte solution of 10% v/v H_2SO_4 and 5% W/W CuSO_4 was applied by a voltage to -500 mv – DC for 5 min. All porous wires were kept in ethanol for later use. Then the wires were placed in a solution of 3-MPTS (10-3 M) in ethanol for two hours. In the following, the wire was immersed in a solution of 0.1 M NaOH for 90 min and then in a solution of HCl for 60 min and finally rinsed with distilled water. Cu surface porosity highly increases the level of adhesion of polymer network which was attached through 3-MPTS with SAM procedure. [Fig. 1A] shows SEM images of Cu wire without electro deposition of the porous layer, 1B shows Cu-porous layer, 1C shows Cu-porous layer 3-MPTS modified and 1D shows Cu-porous- 3MPTS-PEG-IL-silica NPs fiber.

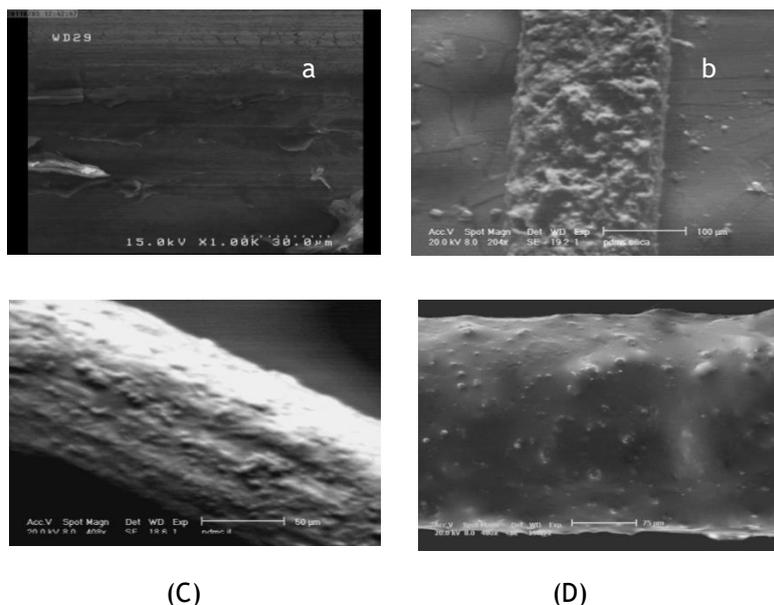


Fig. 1: A Cu wire without electro deposition of porous layer and - B shows Cu- porous layer – C shows Cu-porous layer 3-MPTS modified and D shows Cu-porous- 3MPTS – PEG-IL-silica NPs fiber.

Polyethylene glycol (PEG), (Trime thoxysilyl) propyl methacrylate (TMSPA), poly dimethylsiloxane (PDMS) with Silica Nanoparticles (Silica-NPs) and 1-Butyl-4-methylpyridinium tetra fluoroborate (BMPT) as the ionic liquid were the raw materials which was prepared with Sol-Gel procedure as PDMS, PDMS-IIs, PDMS-IIs-silica NPs, PA, PA-IIs, PA-IIs-silica NPs, PEG, PEG-IIs, and PEG-IIs-silica NPs. After preparing the Sol-Gel solution, the previous treated copper wire was simply immersed in it and after about 60 minutes the covalent bonding of absorbing layer with metallic substrate will be accomplished.

SPME procedure

Before extraction, all the fibers were conditioned in the inlet of GC at the temperature of $280\text{ }^{\circ}\text{C}$ with helium carrier gas for one hour. For real sample analysis 300 g tomato (purchased from the local market) was crushed, homogenized and diluted with 500 mL of distilled water.

The stock solution of the pesticides contains terbuthylazine, desethylatrazine, Phorate, Parathion, and Phosmet were prepared in methanol at the concentration of 1000 ppm and was kept in the refrigerator and the standard solutions were prepared from that on daily basis. To spike a certain amount of pesticides in tomato samples 50 ml of chopped and homogenized tomato samples were mixed with appropriate values of standard solutions in a 100-ml flask and brought to the volume using double distilled water and became uniform by placing in an ultrasonic bath for 30 min. Then, 10 ml of the top solution was transferred to a Falcon tube, blended smoothly, and was centrifuged at 8000 rpm for 10 min. After that few milliliters of the supernatant in the test tube was transferred to a glass vial and the fabricated fibers were placed in it for 45 min at $30\text{ }^{\circ}\text{C}$. Then the fibers were removed and injected into the GC device. [Fig. 2] shows chromatogram obtained after SPME of pesticides at 500 ppb. As can be seen main peaks started from around 6 min and ended at 9 min. These five peaks represent desethylatrazine, Phosmet, terbuthylazine, Phorate and parathion respectively.

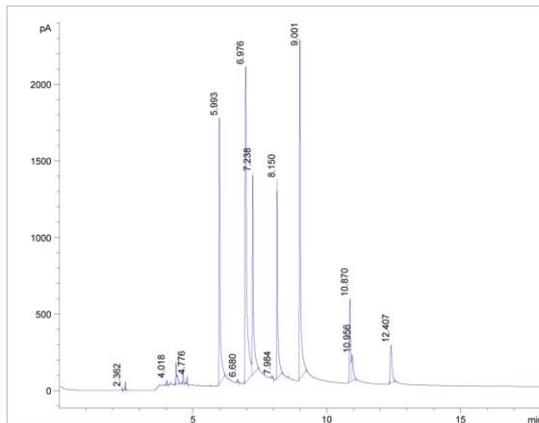


Fig. 2: Final chromatogram after SPME procedure for extracted pesticide from tomato samples. Five main peaks from 6 min to 9 min are desethylatrazine, Phosmet, terbuthylazine, Phorate and parathion respectively

RESULTS

For optimization of effective parameters of extraction, the concentration of 500 ppb of the pesticides was spiked in to the tomato samples. According to the results demonstrated in [Fig. 3], absorbent fiber with PEG-IL-silica NPs was selected as the most suitable fiber for extraction. The extraction parameters including extraction time and temperature, pH, ionic strength, stirring speed for the solution, and time and temperature of desorption were evaluated and the extraction efficiency values were compared under various condition.

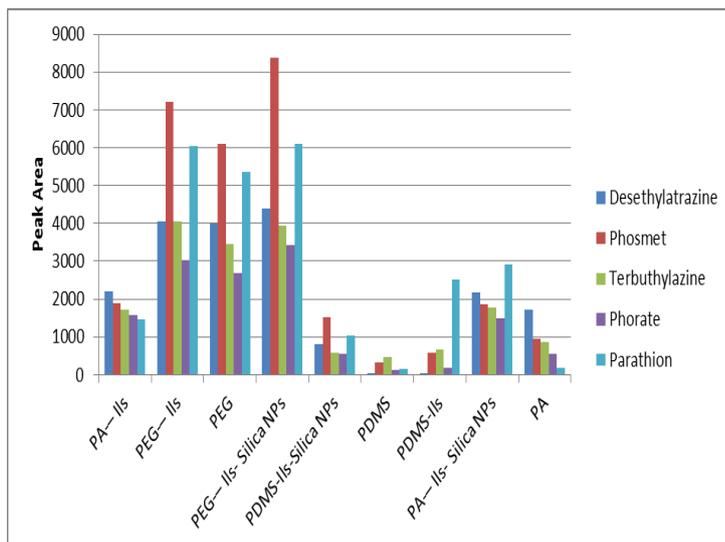


Fig. 3: Comparison of the extraction efficiency of five pesticides spiked in tomato solution by SPME with different fibres. The sample concentration was 500 ppb.

DISCUSSION

Camel Optimization of SPME procedure

To determine optimal conditions for separation and measurement of the amount of pesticides, we compared the area of the peak of the pesticide as studied in the chromatogram obtained by direct fiber injection with a SPME syringe in to the GC inlet. To achieve accurate and reliable results, each analysis was repeated three times. This optimization was performed by keeping other parameters constant at values obtained from the literature.

The best extraction temperature for the pesticides studied was 30 °C due to increasing diffusion coefficient of analytes in higher temperatures and 45 min was chosen as the duration of extraction as the best equilibration time.

Adding salt may lead to increased or decreased extraction efficiency where-as ionic strength of the solution may reduces water solubility of organic compounds and several folds increases partition coefficient of the analytes present in water. After optimization the salt concentration in the solution was selected as 15%. The finding is probably due to different physicochemical properties and polarity of the pesticides.

Stirring the solution can speed up the process of mass transfer between the fiber and the solution but much higher speeds can remove the analytes or absorbent layer. Optimization resulted in to stirring rate of 400 rpm as the optimal stirring rate.

When the analytes are in ionic, acidic or basic form the analytes are compounds that their decomposition or formation is affected by pH, it is necessary to adjust the pH value. Therefore effect of pH value on extraction of pesticides was studied in the range of 2-13 by adding hydrochloric acid or sodium hydroxide. Some pesticides such as terbuthylazine showed considerable signal loss at high pH values. This is while Phosmet and Phorate showed lower signal loss as pH value changes from the neutral state. So pH = 7 was chosen as the optimal pH value which caused the best extraction efficiency for majority of investigated pesticides.

By finishing the extraction process the fiber was directly injected into the GC inlet by SPME syringe. The inlet temperature and the time which SPME fiber remained in it were studied because of their remarkable effect on the final achieved signal. The results showed that the peak area of each individual pesticide was at its highest level at 250 °C and 4 min placing SPME fiber in the GC inlet.

Method validation

To assess method validation of this proposed method, specific values of each pesticide spiked into the tomato samples so that final concentration of each of them was between 50 to 1000ppb and the whole process was conducted on them in the optimum conditions. The coefficient of correlation was higher than 0.98 for all the pesticides measured. The values obtained for R², RSD, LDR, LOD and LOQ are summarized in [Table 2].

Table 2: Specific values of each pesticide spiked into the tomato

Analyte	% RSD	R ²	LDR	LOD	LOQ
Phosmet	1.2	0.989	60-1000	20	60
Parathion	2.5	0.998	150-1000	50	150
Phorate	4.6	0.987	270-1000	90	270
Desethylatrazine	2.3	0.985	120-1000	40	120
Terbuthylazine	3.8	0.996	240-1000	80	240

CONCLUSION

Regarding the importance of pesticide residues in agricultural products, a new SPME fiber coated by sol-gel technology based on ionic liquids, on a copper porous substrate using silica NPs was fabricated. Different parameters in extraction of pesticides from real sample solution containing the pesticides such as extraction time and temperature, stirring rate, pH, ionic strength, desorption temperature and time were optimized.

Extraction of pesticides from tomato samples using fibers showed that the PSG-ILs-silica NPs fiber has the highest efficiency in the extraction and determination of pesticides in real samples. This new method was successfully able to extract different pesticides from tomato samples with high reliability and reproducibility.

CONFLICT OF INTEREST

There is no conflict of interest.

ACKNOWLEDGEMENTS

The authors wish to thank Islamic Azad University, Science and Research Branch for financial support of the project.

FINANCIAL DISCLOSURE

None

REFERENCES

- [1] Wahib SMA, Ibrahim WAW, Sanagi MM. [2016] New methyltrimethoxysilane-(3-mercaptopropyl)-trimethoxysilane coated hollow fiber-solid phase microextraction for hexanal and heptanal analysis. Malaysian Journal of Analytical Sciences. 20 (1): 51-63
- [2] Abdura'uf LB, Chai MK, Tan GH. [2012] Applications of Solid-Phase Micro extraction for the Analysis of Pesticide Residues in Fruits and Vegetables: A Review, J AOAC Int., 95(5):1272-90.
- [3] Andraščíková M, Hrouzková S. [2015] Recent achievements and applications of solid - phase micro

- extraction in pesticide residues analysis in food. *Acta Chimica Slovaca*, 8 (2):178–190
- [4] Barata C, Solayan A, Porte C. [2004] Role of B-esterases in assessing toxicity of organophosphorus [chlorpyrifos, malathion] and carbamate [carbofuran] pesticides to *Daphnia magna*. *Aquat Toxicol.*, 66(2):125-39.
- [5] Kalhor H, Hashemipour S, Yafian MR. [2016] Ultrasound-Assisted Emulsification-Micro extraction/Ion Mobility Spectrometry Combination: Application for Analysis of Organophosphorus Pesticide Residues in Rice Samples. *Food Analytical Methods*, 9 (11), 3006–3014
- [6] Di S, Shi S, Xu P, Diao J, Zhou Z. [2015] Comparison of Different Extraction Methods for Analysis of 10 Organochlorine Pesticides: Application of MAE-SPE Method in Soil from Beijing. *Bull Environ Contam Toxicol.*, 95(1):67-72.
- [7] Gong L, Shi F, Jiang S, Zhao Y, Guo C. [2015] Determination of nine pesticide residues in vegetables by matrix solid-phase dispersion-ultra performance liquid chromatography-tandem mass spectrometry. *Chinese Journal of Chromatography*, 33(4): 408-412.
- [8] Keithmaleesatti S, Varanusupakul P, Siriwong W, Thirakhupt K, Robson M, Kitana N. [2009] Contamination of Organochlorine Pesticides in Nest Soil, Egg, and Blood of the Snail-eating Turtle (*Malayemys macrocephala*) from the Chao Phraya River Basin, Thailand. *International Scholarly and Scientific Research & Innovation* 3(4): 193-198.
- [9] Cruz S, Lino C, Silveira MI. [2003] Evaluation of organochlorine pesticide residues in human serum from an urban and two rural populations in Portugal. *Sci Total Environ.*, 317(1-3):23-35.
- [10] Mishra S, Saini MK, Alam S, Thakur LK, Raza SK. [2015] Method Validation and Uncertainty measurement for Determination of 25 Pesticides by GC-ECD and MSD in Banana using modified QuEChERS Technique. *Int. Res. J. Environment Sci.*, 4(3), 21-27.
- [11] Di Muccio A, Fidente P, Barbini DA, Dommarco R, Seccia S, Morrìca P. [2006] Application of solid-phase extraction and liquid chromatography-mass spectrometry to the determination of neonicotinoid pesticide residues in fruit and vegetables. *Journal of Chromatography A*, 1108(1):1-6.
- [12] Lambropoulou DA, Albanis TA. [2007] Methods of sample preparation for determination of pesticide residues in food matrices by chromatography-mass spectrometry-based techniques: a review. *Analytical and Bioanalytical Chemistry*. 389(6): 1663–1683.
- [13] Schenck FJ, Lehotay SJ, Vega V. [2002] Comparison of solid-phase extraction sorbents for cleanup in pesticide residue analysis of fresh fruits and vegetables. *Journal of Separation Science*, 25(14): 883–890.
- [14] Pawliszyn J. [1997] *Solid Phase Micro extraction: Theory and Practice*: Edt: Pawliszyn J, ISBN: 978-0-471-19034-9, Wiley, Germany.
- [15] Anastassiades M, Lehotay SJ, Stajnbaher D, Schenck FJ. [2003] Fast and easy multi residue method employing acetonitrile extraction/partitioning and dispersive solid-phase extraction for the determination of pesticide residues in produce. *J AOAC Int*. 86(2):412-31.
- [16] Arthur CL, Pawliszyn J. [1990] Solid phase micro extraction with thermal desorption using fused silica optical fibers. *Analytical Chemistry*, 62 (19): 2145–2148.
- [17] Pawliszyn J. [2000] Theory of solid-phase micro extraction. *J Chromatogr Sci*, 38(7):270-278.
- [18] Bousahel R, Bouland S, Moussaoui KM, Baudu M, Montiel A. [2002] Determination of chlorinated pesticides in water by SPME/GC. *Water Research*. 36 (7):1909-1911.
- [19] Kataoka H, Lord HL, Pawliszyn J. [2000] Applications of solid-phase micro extraction in food analysis, *Journal of Chromatography A*. 880 (1-2): 35-62.
- [20] Wercinski SA. [1999] *Solid Phase Micro extraction: A PRACTICAL GUIDE*: CRC Press.
- [21] Vas G, Vekey K. [2004] Solid-phase micro extraction: a powerful sample preparation tool prior to mass spectrometric analysis. *J Mass Spectrom.*, 39(3):233-254.
- [22] Zhang Z, Yang MJ, Pawliszyn J. [1994] Solid-Phase Micro extraction. A Solvent-Free Alternative for Sample Preparation. *Anal. Chem.*, 66 (17):844A–853A.
- [23] Abdulla'uf LB, Hamed WA, Tan GH. [2012] SPME Fibers for the Analysis of Pesticide Residues in Fruits and Vegetables: A Review. *Critical Reviews in Analytical Chemistry*. 42 (2): 152-161.
- [24] Yang Z, Liu Y, Liu D, Zhou Z. [2012] Determination of organophosphorus pesticides in soil by dispersive liquid-liquid micro extraction and gas chromatography. *J Chromatogr Sci*. 50(1):15-20.
- [25] Risticvic S, Niri VH, Vuckovic D, Pawliszyn J. [2009] Recent developments in solid-phase micro extraction. *Analytical and Bioanalytical Chemistry*. 393(3):781-795.
- [26] Budziak D, Martendal E, Carasek E. [2008] New poly [ethylene glycol] solid-phase micro extraction fiber employing zirconium oxide electrolytically deposited onto a NiTi alloy as substrate for sol-gel reactions. *J Chromatogr A*. 1198-1199:54-58.
- [27] Djozan D, Ebrahimi B, Mahkam M, Farajzadeh MA. [2010] Evaluation of a new method for chemical coating of aluminum wire with molecularly imprinted polymer layer. Application for the fabrication of triazines selective solid-phase micro extraction fiber. *Analytica Chimica Acta*. 674 (1): 40-48.
- [28] Djozan D, Assadi Y, Karim-Nezhad G. [2002] Modified copper wire as solid-phase micro extraction fiber, selective extraction of some amines. *Chromatographia*. 56(9-10): 611–616.
- [29] Bagheri H, Sistani H, Ayazi Z. [2011] Novel unbreakable solid-phase micro extraction fiber by electro deposition of silica sol-gel on gold. *J Sep Sci*. 34(22):3246-52.
- [30] Aberoomand Azar P, Mohammadiazar S, Saber Tehrani M, Norooz Haghi J. [2013] Nanoparticle-Incorporated PDMS Film as an Improved Performance SPME Fiber for Analysis of Volatile Components of Eucalyptus Leaf. *Journal of Chemistry*. Doi: 10.1155/2013/347927
- [31] Jiang R, Zhu F, Luan T, Tong Y, Liu H, Ouyang G, Pawliszyn J. [2009] Carbon nanotube-coated solid-phase microextraction metal fiber based on sol-gel technique. *Journal of Chromatography A*. 1216 (22): 4641-4647.
- [32] Rastkari N, Ahmadvaniha R, Yunesian M. [2009] Single-walled carbon nanotubes as an effective adsorbent in solid-phase micro extraction of low level methyl tert-butyl ether, ethyl tert-butyl ether and methyl tert-amyl ether from human urine. *J Chromatogr B Analyt Technol Biomed Life Sci*. 877(14-15):1568-74.
- [33] Bagheri H, Roostaie A. [2012] Aniline-silica nano composite as a novel solid phase micro extraction fiber coating. *J Chromatogr A*. 1238:22-9.
- [34] Chong SL, Wang D, Hayes JD, Wilhite BW, Malik A. [1997] Sol-gel coating technology for the preparation of solid-phase micro extraction fibers of enhanced thermal stability. *Anal Chem*. 69 (19):3889–3898
- [35] Yang M, Zeng ZR, Qiu WL, Wang YL. [2002] Preparation and investigation of polymethyl phenylvinyl siloxane-coated solid-phase micro extraction fibers using sol-gel technology. *Chromatographia*. 56 (1-2): 73–80.
- [36] Liu JF, Li N, Jiang GB, Liu JM, Jönsson JÅ, Wen MJ. [2005] Disposable ionic liquid coating for headspace solid-phase micro extraction of benzene, toluene, ethylbenzene, and xylenes in paints followed by gas chromatography-flame ionization detection. *Journal of Chromatography A*. 1066 (1-2): 27-32.
- [37] Zhao F, Meng Y, Anderson JL. [2008] Polymeric ionic liquids as selective coatings for the extraction of esters using solid-phase microextraction. *Journal of Chromatography A*. 1208 (1-2): 1-9.
- [38] Liu JF, Jiang GB, Jönsson JÅ. [2005] Application of ionic liquids in analytical chemistry. *TrAC Trends in Analytical Chemistry*. 24(1):20-27.
- [39] Germani R, Mancini MV, Spreti N, Profio PD, Savelli GN. [2011] Cu(II) Extraction in Ionic Liquids and Chlorinated

- Solvents: Temperature Effect, Green and Sustainable Chemistry. 10.4236/gsc.2011.14024
- [40] Sarafraz-Yazdi A, Vatani H. [2013] A solid phase micro extraction coating based on ionic liquid sol-gel technique for determination of benzene, toluene, ethylbenzene and o-xylene in water samples using gas chromatography flame ionization detector. *J Chromatogr A*. 1300:104-11.
- [41] He Y, Pohl J, Engel R, Rothman L, Thomas M. [2009] Preparation of ionic liquid based solid-phase micro extraction fiber and its application to forensic determination of methamphetamine and amphetamine in human urine. *J Chromatogr A*. 1216(24):4824-30.
- [42] Zarzycki J. [1997] Past and present of sol-gel science and technology. *Journal of Sol-Gel Science and Technology*. 8(1-3): 17-22
- [43] Collinson MM. [2002] Recent trends in analytical applications of organically modified silicate materials. *TrAC Trends in Analytical Chemistry*. 10.1016/S0165-9936(01)00125-X
- [44] Ruivo A, Ventura MG, Gomes da Silva MDR, Laia CAT. [2013] Synthesis of gold nanoparticles in sol-gel glass porogens containing [bmim] [BF₄] ionic liquid. *Journal of Sol-Gel Science and Technology*. 68 (2): 234-244.