Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.926837

55 (2015) 1488–1500
July

Taylor & Francis
Taylor & Francis Group

Sol–gel coated polypropylene hollow fiber-based liquid-phase microextraction of triazine herbicides in real water samples

Iqbal Hussain[a,b,*], Rabiatul Adawiyah Ismail[a], Mohd Marsin Sanagi[a,b,*], Wan Aini Wan Ibrahim[a]

[a]*Faculty of Science, Department of Chemistry, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia, Tel. +601115127396; Fax: +6075566162; email: iqbal.analyst@gmail.com (I. Hussain), Tel. +60197328842; email: rabia1210@gmail.com (R.A. Ismail), Tel. +6075534517; Fax: +6075566162; email: marsin@kimia.fs.utm.my (M.M. Sanagi), Tel. +60197173940; email: wanaini@kimia.fs.utm.my (W.A.W. Ibrahim)*
[b]*Ibnu Sina Institute for Fundamental Science Studies, Nanotechnology Research Alliance, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia*

Received 1 January 2014; Accepted 13 May 2014

ABSTRACT

A sol–gel coated hollow fiber-based liquid-phase microextraction (LPME) method was developed for the extraction of triazine herbicides. The polypropylene hollow fiber was coated with polydimethylsiloxane–divinylbenzene using sol–gel method and characterized. The developed method was compared with uncoated hollow fiber LPME method for the extraction of simazine, atrazine, and propazine prior to gas chromatography–mass spectrometry analysis. Optimized conditions for both coated and uncoated hollow fibers LPME methods were toluene as an acceptor phase, length of hollow fiber (1.5 cm), volume of acceptor phase (3.0 μL), stirring rate (1200 rpm), and no addition of salt (sodium chloride). The optimized volumes of donor phase for uncoated fiber and coated fiber were 4.0 and 4.5 mL, respectively, while the optimized extraction times were 30 min for uncoated hollow fiber and 10 min for coated hollow fiber. The developed sol–gel coated hollow fiber LPME method provided good enrichment factors (EFs) ranging from 100 to 139, good recoveries (75.27–104.47%), and good reproducibility (relative standard deviations [RSDs] < 0.83%). Meanwhile, uncoated hollow fiber LPME method showed lower EFs ranging from 80 to 90 and relatively low recoveries of 60.72–68.17%, whereas it has good reproducibility with RSDs < 0.94%. The proposed method was successfully applied to the analysis of real water samples and the analyte recoveries for spiked water samples was in the range of 42.54–78.75%.

Keywords: Sol–gel coated polypropylene hollow fiber; Triazine herbicides; Liquid-phase microextraction; Gas chromatography–mass spectrometry; Water samples

1. Introduction

Triazines are most widely used selective, pre- and post-emergent herbicides for controlling weeds in crop harvesting [1]. In spite of their crucial role, herbicides have some adverse effect to the environment, human beings, and ecosystem. Among various triazine herbicides: atrazine, propazine, and simazine were selected for the analysis because of their toxicity to the environment, high persistency in water, soil, and

*Corresponding authors.

organisms [2]. Moreover, the United State Environment Protection Agency reported that the constant use of these herbicides resulted in life threatening problems such as breast cancer and endocrine system disruption [3,4]. Therefore, the pre-concentration or extraction of these herbicides from environmental samples is necessary and the development of extraction and sample preparation methods is utmost important to determine the lowest concentration in the environmental samples.

Many conventional sample preparation methods such as liquid–liquid extraction [5–7], solid-phase extraction [8–11], supercritical-fluid extraction [12,13], and microwave-assisted extraction [14,15] for the extraction of above-mentioned herbicides have been developed but currently these modalities are not in trend as they are time consuming, consume high volume of organic solvents, and multistep. To overcome these limitations, various novel miniaturized microextraction methods such as solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) methods have been developed [16–29]. However, some drawbacks such as less stability of fibers, limited lifetime, reduced performance with time, and sample carry over require new dimension of research to improve these modalities. Different modes of LPME have been developed for the microextraction of triazine herbicides. These include single-drop microextraction [30], hollow fiber liquid-phase microextraction (HF-LPME) [25,31], and dispersive liquid–liquid microextraction (DLLME) [32,33]. Recently, Sanagi et al. [34] carried out the microextraction of these herbicides in water and sugarcane samples with DLLME based on solidification of floating organic droplet. However, the key issue of instability of hollow fiber at high-stirring speed and temperature in HF-LPME reduces the sensitivity, extraction efficiency, and reproducibility of the technique.

Newly developed sol–gel coating process on the commercially available fibers has been widely used to prepare SPME fiber and getting good reputation for the microextraction of various organophosphorous pesticides [35–37]. However, to the best of our knowledge, the use of sol–gel coated polypropylene (PP) hollow fibers for the analysis of triazine herbicides in aqueous samples has not been reported. In this study, sol–gel coated PP hollow fibers were developed for the HF-LPME of the target triazine herbicides from water samples prior to gas chromatography–mass spectrometry (GC–MS) analysis. The coating of sol–gel phase of polydimethylsiloxane/divinylbenzene (PDMS/DVB) on PP hollow fiber was characterized and the extraction efficiencies of the coated hollow fibers were compared with uncoated hollow fibers.

2. Experimental

2.1. Chemicals, reagents, and materials

Triazine herbicides atrazine (98.0%), cyanazine (96.3%) (internal standard), propazine (98%), and simazine (99.0%) were purchased from Dr Ehrenstorfer (Augsburg, Germany). HPLC grade methanol, hexane, and toluene were obtained from J.T Baker (Texas, USA). Nonane and sodium chloride (99.98%) were purchased from Fluka (St. Gallen, Switzerland). AR-grade acetone was obtained from Merck (Darmstadt, Germany). The Accurel Q3/2 PP hollow fiber membrane (600 μm i.d., 200 μm wall thicknesses, and 200 μm pore size) was purchased from Membrane (Wuppertal, Germany). Microsyringe (10 μL) of Hamilton (Bonaduz, Switzerland) was used for microextractions. Double-distilled deionized water of at least 18 MΩ was prepared by nano ultrapure water system (Barnstead, USA). The materials for sol–gel synthesis, methyltrimethoxysilane (MTMOS) 95%, hydroxyl-terminated polydimethylsiloxane (OH-TPDMS), trimethylmethoxysilane (TMMS) 99%, poly (methylhydroxysilane) (PMHS), and trifluoroacetic acid (TFA) 98% were purchased from Sigma–Aldrich (Seelze, Germany) and DVB was obtained from Fluka (St. Gallen, Switzerland).

2.2. Instrumentation

Fourier transform infrared (FTIR) spectra of PDMS/DVB sol–gel coated hollow fiber were recorded with a Perkin Elmer Nicolet Avatar 370DTGS spectrometer (Ueberlingen, Germany) in the range of 4,000–400 cm^{-1}. Detection of –Si–functional group by Nuclear magnetic resonance (NMR) spectra was carried out using solid state NMR at a frequency of 9.39 MHz/Tesla. The surface morphology was determined by field-emission scanning electron microscopy (FE-SEM) model Number (JEOL JSM-6701F) equipped with energy dispersive X-ray (EDX) analyzer (JED-2300 series) Tokyo, Japan, The functional groups present on the surface were detected by EDX. A Zentrifugen Mikro 120 centrifuge machine (Hettich, Germany) and Heidolph type Reax 2000 vortex machine (Schwabach, Germany) were used. Ultraviolet radiator (365 nm) was purchased from ETS Vilber-Lourmat (France). The ultrasonic machine used was a Branson model No. 3510 (USA) and the stirring hot plate was a Favorit HS 0707V2 (Malaysia).

Triazine herbicides were analyzed using Agilent Technology GC–MS system (Palo Alto, CA, USA) consisting of MS detector (model 5973). The GC column of polysilphenylene-siloxane (HP-5) (30 m × 0.25 mm i.d., 0.25 μm film thickness) and helium was used as

carrier gas. The instrument was operated with 5973i software.

2.3. Gas chromatographic conditions

The standard sample (3.0 μL) of triazine herbicides was injected using split less injection. The flow rate of a carrier gas (helium) was 1.5 mL min^{-1} with vacuum compensation. A temperature program was used in selected ion monitoring mode: start at 100°C (held for 2 min) ramp at 25°C min^{-1} to 170°C (held for 2 min), ramp at 1°C min^{-1} to 180°C (held for 2 min) followed by ramp at 30°C min^{-1} to 280°C (held for 1 min). The solvent delay was held for 4 min to prevent the damage of the MS filament. The mass spectrometer was equipped with quadruple ion filter system and using electron impact ionization mode at 70 eV. Peak areas of the analyte peaks were used to demonstrate the effect of parameters on the extraction efficiency.

2.4. Preparation of sol–gel coated hollow fiber for LPME

For the preparation of sol–gel coated hollow fiber, the PP fiber was cut manually into 3.0 cm lengths and each piece was sealed at one end by a sealer machine. The fibers were washed with acetone to remove any contaminants and allowed to dryness then stored in a small vial before use. To activate the surface of the fiber, Fenton's reagents ($FeSO_4$ and H_2O_2) were mixed into the vial step by step to complete the Fenton's reaction. After completing this reaction, treated fiber containing vial was exposed to UV-ray for 1 h at 365 nm and then the fiber was dried at ambient temperature and ready for coating.

The PDMS/DVB sol phase was prepared by mixing of MTMOS (400 μL), OH-TPDMS (25 μL), DVB (50 μL), PMHS (25 μL), and 95% TFA (400 μL) in a test tube. The mixture was vortexed for 2 min and centrifuged at 12,000 rpm for 5 min to produce two layers and the sol solution (upper layer) was used for fiber coating. The fibers were dipped vertically into the sol solution for 2 min. After the coating process, the coating fibers were end-capped in 20% (v/v) methanol solution of TMMS for 1 min and then dried at room temperature for 1 day. The resulting coated fiber was characterized by FE-SEM and EDX analyses while the sol–gel solution was characterized by FTIR and NMR.

2.5. Sample preparation before HF-LPME

Stock solutions of simazine, atrazine, and propazine (1,000 μg mL^{-1}) were prepared with methanol in 10 mL volumetric flask, separately. A stock solution of NaCl (1,000 μg mL^{-1}) was also prepared with distilled water in 25 mL volumetric flask. The stock solutions were preserved at 4°C and used by dilution accordingly. Tap and lake water samples were collected from the analytical chemistry laboratory and the lake of Universiti Teknologi Malaysia, Johor Bahru, Malaysia, while the river water sample was from the Gelang Patah river, Johor Bahru, Malaysia. The collected water samples were filtered with nylon membrane filter (0.45 μm) to eliminate the impurities, followed by preservation at 4°C in dark brown glass bottles, pre-cleaned with acetone and covered with aluminum foil. The water samples were spiked with different concentrations of simazine (50 and 100 μg L^{-1}), atrazine (10 and 50 μg L^{-1}), and propazine (5 and 10 μg L^{-1}) for the extraction with sol–gel coated and uncoated hollow fiber under optimum conditions. The spiked samples were homogenized completely and allowed to stand overnight before the extraction. An aliquot of 2.0 mL of each sample was used for the HF-LPME and further analysis.

2.6. Sample preparation by HF-LPME

A 10 μL microsyringe was used to introduce the organic solvent (acceptor phase) into uncoated PP hollow fiber membrane. The length of hollow fiber was cut manually to desired length (1.0, 1.5, or 2.0 cm) prior to use. Uncoated hollow fiber was cleaned with acetone for 5 min with ultra-sonication to remove contaminants and then sealed at one edge by sealer machine. The PP hollow fiber was dipped in organic solvent (toluene) for 10 s to impregnate the pores of the fiber with organic solvent. The needle of a microsyringe containing organic solvent as acceptor phase (3.0 μL of toluene) was inserted through the septum of the sample vial and then the needle tip was inserted into the hollow fiber segment; this assembly was immersed in 4.0 mL of sample solution and put on a magnetic stirrer. The plunger was pushed slowly to dispense acceptor phase from microsyringe into the hollow fiber and the magnetic stirrer was switched on to start extraction. After extraction for prescribed time, the plunger of the microsyringe was withdrawn and the acceptor phase was transferred into a small vial for drying at room temperature. After the acceptor phase was completely evaporated, 2.5 μL (300 μg mL^{-1}) of internal standard (cyanazine) was mixed into the vial and diluted with 47.5 μL of methanol. An aliquot of the solution (0.1 μL) was injected into the GC/MS for separation and analysis. In order to prevent carryover effect, a new fresh hollow fiber was used for each extraction. Similar the sample preparation was performed with sol–gel coated PP hollow fiber except the cleaning step of coated hollow fiber was performed

using acetone to prevent any side effects to the sol coating.

3. Results and discussion

3.1. Characterization of sol–gel coated PP hollow fiber

3.1.1. FTIR spectral analysis

FTIR spectral analysis of PDMS–DVB was performed to determine the stretching vibrations of functional groups by NaCl pallet method over the range of 4,000–400 cm^{-1}as shown in Fig. 1. A broad medium intensity band at 3,413 cm^{-1} observed in the case of PDMS–DVB is ascribed to the stretching frequency of O–H functionality. This inference is attributed to residual hydroxyl groups that had not been removed completely in PDMS–DVB sol–gel even after the end-capping treatment. The O–H group allowed reaction with activated PP hollow fiber. The strong absorption band at 2,961 cm^{-1} is a characteristic of stretching vibrations of C–H modules of methyl substitution. Further, it is worth mentioning that the core observations for Si–O stretching vibrations were observed in the range of 1,019–1,094 cm^{-1}. It was also noted that the sharp bands at 2,164 and 909 cm^{-1} for Si–H, 1,459, 1,413, and 1,377 cm^{-1} for C=C conjugated systems and 1,795 cm^{-1} for C=O functional group are observed in the spectrum of PDMS–DVB sol–gel, whereas these bands are absent in the case of OH-TPDMS. The presence of Si–H group in the PDMS–DVB sol–gel originated from poly(methylhydroxysiloxane) (PMHS) which was used as surface deactivating agent, while the C=C groups was derived from conjugated benzenyl substitution in DVB structure. Meanwhile, the presence of C=O group is attributed to the acyl halide from TFA residual.

3.1.2. Field-emission scanning electron microscopy

The morphology of sol–gel coated fibers was investigated using FE-SEM as shown in Fig. 2. The morphological comparison of original PP hollow fiber, Fenton's activated hollow fiber and PDMS–DVB sol–gel coated fibers were also studied. It was observed that the thickness of original hollow fiber decreased by 0.6 μm (from178.0 to 172 μm) during the activation of hollow fiber through Fenton's reaction due to the removal of corroded materials in presence of H_2O_2 and $FeSO_4$ (catalyst). However, the thickness increased by 2.0 μm (from 172.0 to 174.0 μm) after PDMS–DVB sol–gel coating. This is expected as the sol–gel reaction on the Fenton's activated hollow fiber was involved with coating process that increased the thickness of sol–gel coated hollow fiber.

Optimization of dipping time for coating on to the hollow fiber was also carried out in order to obtain the best surface morphologies and surface performance. It was confirmed that long dipping time (>10 min) resulted in the complete blockage of pores on the surface of hollow fiber. Meanwhile, dipping time of 2 min resulted in good morphologies of coated fiber and it was taken as the optimum dipping time and used for further experiments. The estimated pore size of the Fenton's activated hollow fiber was 0.25 μm which is higher than that of the original hollow fiber pore size (0.15 μm). The enlargement of the pores

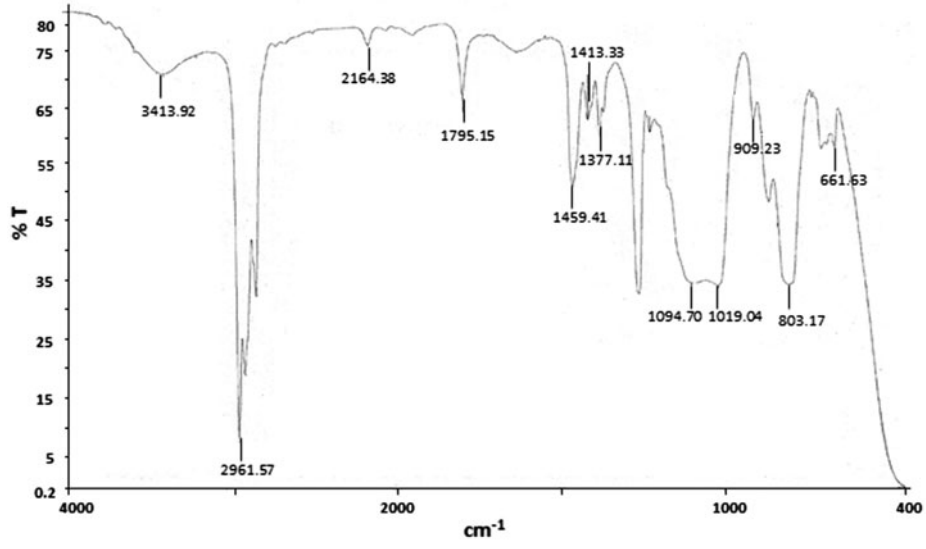

Fig. 1. FTIR spectrum of PDMS–DVB sol–gel sample.

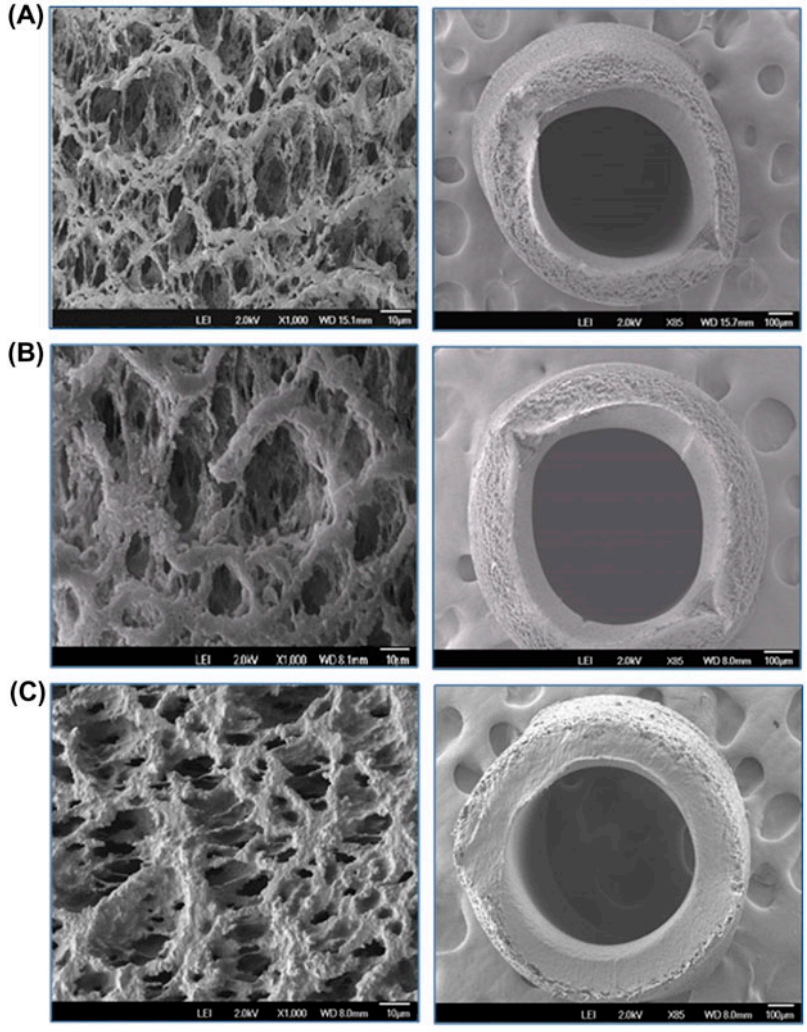

Fig. 2. FE-SEM micrographs of hollow fiber surface and cross cut section at 1,000 magnification and 85 magnifications, respectively, for (A) uncoated hollow fiber, (B) Fenton's reacted hollow fiber, and (C) PDMS–DVB sol–gel coated hollow fiber.

during the pretreatment process may be due to the hydroxylation and corrosion [38]. The estimated pore size of coated hollow fiber was found to be essentially uniform for triplicate FE-SEM analyses with a mean value of 1.75 μm. The coated fibers have enlarged pores due to the reaction that occurs between the sol–gel compound and hydroxyl groups on the surface of hollow fiber. Nevertheless, the size could not be taken as the exact size of the coated hollow fiber as there were more small pores within the large pores.

3.1.3. EDX analysis

The elemental analysis of normal, activated, and sol–gel coated PP hollow fiber was carried out by EDX analyzer to observe the percentage of carbon (C), oxygen (O), iron (Fe), silicon (Si), and platinum (Pt) elements. The results are given in Table 1. It was observed that activated PP hollow fiber comprised 28.50% oxygen atom and 6.89% iron atom due to the activation in presence of Fenton's reagent while PDMS/DVB sol–gel coated hollow fiber comprised 9.60% silicon atoms. Moreover, carbon was present in good percentage in every form of PP hollow fiber as main constituent. The presence of platinum was also detected at very low percentage in each spectrogram because of the platinum coating on each sample before EDX analysis.

3.1.4. NMR analysis

In this study, ^{29}Si NMR technique was used to determine the chemical environment of silicon

Table 1
Elements present in different forms of hollow fibers

Elements (%)	Uncoated hollow fiber	Fenton's reacted hollow fiber	PDMS–DVB sol–gel coated hollow fiber
Carbon (C)	95.94	64.61	63.9
Oxygen (O)	0	28.5	26.16
Iron (Fe)	0	6.89	0.34
Silicon (Si)	0	0	9.6
Platinum (Pt)	Low percentage	Low percentage	Low percentage

bonding with carbon and hydrogen in PDMS/DVB sol–gel. The results were compared with the ^{29}Si NMR spectrum of PDMS as shown in Fig. 3. It was observed that the chemical shift obtained corresponded to the possible silicon species considering trimethylsilane (TMS) as standard reference in ^{29}Si NMR. In the spectrum of PDMS–DVB, three silicon resonances were observed for D2D2Vi siloxane, D2 units of siloxane,

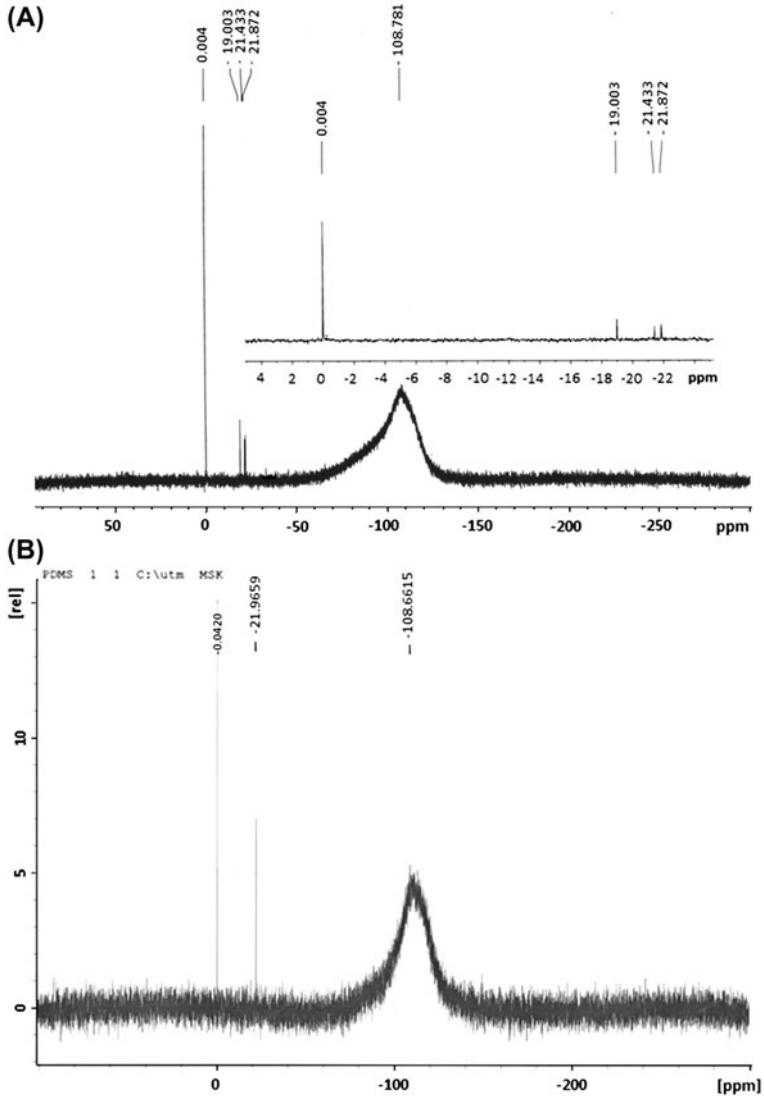

Fig. 3. NMR spectra of (A) PDMS–DVB sol–gel and (B) PDMS.

and D units with D4 at −19.003, −21.443, and −21.872 ppm, respectively, whereas in the case of PDMS compound siloxane D2 environment is observed at −21.966 ppm. However, the broad peaks found in both the spectra between −100 and −120 ppm were due to the glass effect from the sample or tube. Furthermore, some general siloxane groups such as –O–Si–$(Me)_3$, –$(O)_2$–Si–$(Me)_2$, –$(O)_3$–Si–Me, and Si–$(O)_4$– were found around ~6, ~−21, ~−67, and ~−106 ppm, respectively. This phenomenon is attributed to the decrease in intensity of the siloxane resonances in the range ~−100 to −120 ppm with the progressive disappearances of Q structures from Q_1 to Q_4 silicon environment. This describes the cross-linking phenomenon of silicon polymerization at this chemical shifts range.

3.2. Gas chromatography–mass spectrometry

Triazine herbicides (simazine, atrazine, and propazine) were resolved on GC–MS system with optimized chromatographic conditions. The order of elution of these herbicides was simazine, atrazine, and propazine with retention times of 10.65, 11.03, and 11.23 min, respectively (Fig. 4(A)). The calibration curves were linear for all herbicides in the concentration range from 0.10 to 5.0 μg mL^{-1} for simazine, from

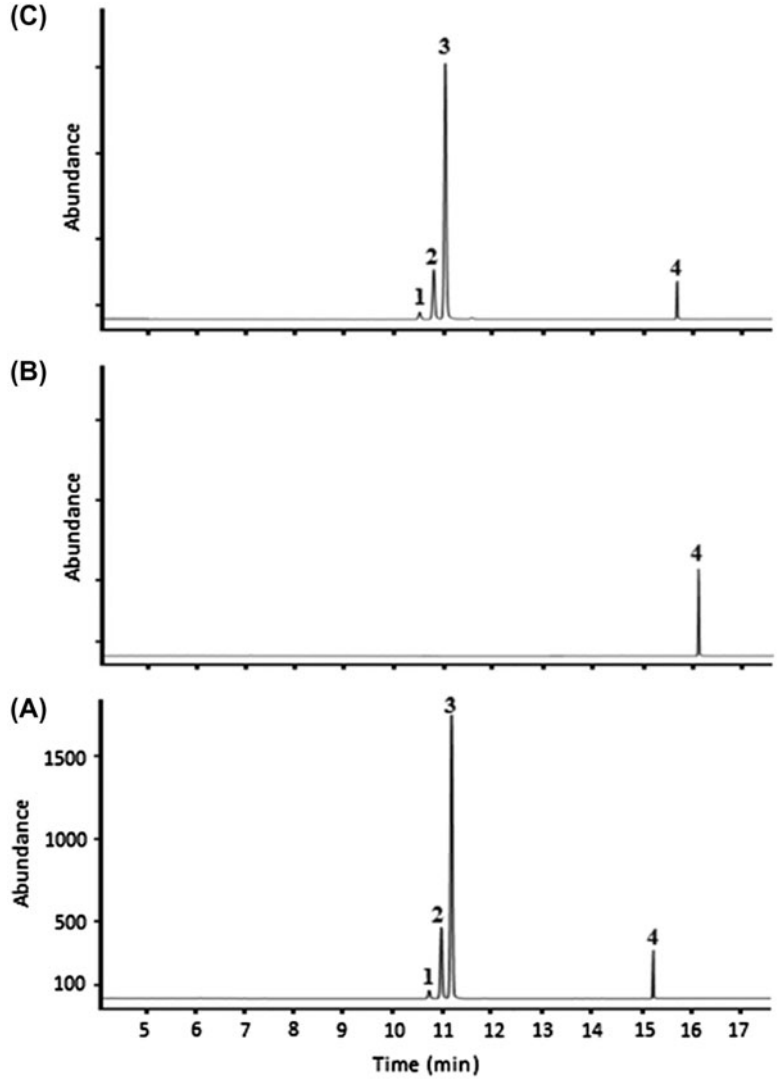

Fig. 4. GC/MS chromatograms under optimized chromatographic conditions as described in the text. (A) Standards of triazines herbicides, (B) real sample (C) spiked samples. Peaks identification: 1 – simazine, 2 – atrazine, 3 – propazine, and 4 – Internal standard (IS).

Table 2
Optimized parameters and conditions for coated hollow fiber LPME

Optimizing parameters and conditions		Response factor (p[A]/p[I.S])		
		Analytes		
Parameters	Conditions	Simazine	Atrazine	Propazine
Acceptor phase (organic solvents)	*n*-Nonane	0.079	0.816	0.102
	n-Hexane	0.362	6.185	3.759
	Toluene	0.451	8.941	4.583
Length of hollow fiber (cm)	1.0	0.337	4.227	2.322
	1.5	1.408	8.044	5.249
	2.0	1.283	4.613	2.149
Volume of acceptor phase (μL)	1.0	1.323	8.366	5.463
	2.0	1.784	8.900	5.873
	3.0	1.819	8.925	5.900
Volume of donor phase (mL)	3.0	0.797	7.912	4.701
	3.5	1.130	7.983	4.730
	4.0	1.386	8.177	4.777
	4.5	1.781	8.389	5.872
Stirring rate (rpm)	840	1.836	9.003	5.982
	960	1.849	9.190	6.000
	1,080	1.895	9.229	6.191
	1,200	1.921	9.336	6.231
Extraction time (min)	10	2.210	9.853	6.723
	20	1.928	9.340	6.401
	30	1.884	8.907	5.921
	40	1.870	8.789	5.507
Salting-out effect (addition of salt) (% w/v)	0.0	2.200	9.874	6.720
	5.0	2.161	9.603	6.200
	10	1.893	8.036	5.088
	15	1.653	7.147	4.332
	20	1.176	6.487	4.007

0.05 to 1.0 μg mL^{-1} for atrazine, and from 0.01 to 0.50 μg mL^{-1} for propazine with coefficients of determination (r^2) of 0.9950, 0.9908, and 0.9984, respectively. The limits of detection (LODs) for simazine, atrazine, and propazine were 0.030, 0.010 and 0.005 μg mL^{-1}, respectively.

3.3. Optimization of HF-LPME

In order to obtain high-extraction efficiency and extraction recoveries of target analytes, several controlling parameters were optimized namely organic solvent as acceptor phase, length of hollow fiber, volume of donor and acceptor phase, stirring rate, extraction time, and salting-out effect. The values in terms of response factors for all optimized conditions are discussed as follows.

3.3.1. Selection of organic solvent

For the selection of organic solvent as acceptor phase, the organic solvent should be easily immobilized in the pores of the PP hollow fiber and the polarity of the solvent should be matched with the analytes [39]. A few organic solvents: *n*-nonane, *n*-hexane, and toluene were studied and the results are given in Table 2. It was observed that *n*-nonane gave the lowest extraction efficiency for the analytes because it has relatively high log $K_{o/w,}$ high-boiling point and lower volatility; therefore, it can easily diffuse out from the PP hollow fiber into the donor phase. Meanwhile, *n*-hexane has low-boiling point and lower log $K_{o/w}$ as compared to *n*-nonane; thus resulted in better extraction. It was found that toluene could extract the triazines better than both *n*-nonane and *n*-hexane due to its relatively lower log $K_{o/w}$ and acceptable boiling point that resisted evaporation for longer time. Therefore, toluene was selected as the optimum organic solvent as acceptor phase for the target analytes.

3.3.2. Length of hollow fiber

The length of hollow fiber is an important key parameter for attaining good performance and

efficiency of PP hollow fibers. In order to study the effect of length of hollow fiber, different lengths (1.0, 1.5, and 2.0 cm) were applied. According to the results (Table 2), the highest peak response was obtained for 1.5 cm fiber. This may be due to completely fill up of the hollow fiber's pores with acceptor phase (3 μL). Meanwhile, the 1.0 cm length of hollow fiber was too short to be filled up by 3 μL of acceptor phase. On the other hand, 2.0 cm length of hollow fiber was too long and the pores could not be filled completely. Therefore, 1.5 cm was selected as the optimum length for complete extraction.

3.3.3. Volume of acceptor phase and volume of donor phase

The sensitivity for the extraction efficiency of this method was also studied with different volumes of acceptor phase ranging from 1.0 to 3.0 μL. The results clearly indicated that the response factor increased with the increase in acceptor phase volume up to 3.0 μL. It may be due to the complete filling of the pores with 3.0 μL of acceptor phase for optimum extraction. Meanwhile, acceptor phase volumes of more than 3.0 μL caused acceptor phase outflow from the hollow fiber and resulting in the rapid diffusion of excess organic solvent to donor phase during extraction. Therefore, 3.0 μL of acceptor phase was selected as the optimized volume and used in further experiments.

The effect of volume of the donor phase on the enrichment factor (EF) and extraction efficiency was also examined. Different volumes of donor phase ranging from 3.0 to 4.5 mL were studied. The results (Table 2) showed that the response increased with the increasing volume of the donor phase up to 4.5 mL that was the maximum volume of the bottle used. Thus, 4.5 mL was chosen as the optimum donor phase volume and used in subsequent experiments.

3.3.4. Stirring speed

Stirring speed is one of the most important parameters for the optimization of LPME method because stirring helps to enhance the diffusion of analytes through the interfacial layer of the hollow fiber. Moreover, stirring of the donor solution can also reduce the time to reach thermodynamic equilibrium by accelerating the extraction kinetics and resulting in increase of the extraction efficiency [40]. To evaluate the effect of stirring speed, sample solution was continuously agitated at different stirring speeds (840, 960, 1,080, and 1,200 rpm) and the results are given in Table 2. It can be seen that response factors increased with the increase of stirring speed. Agitation rates of >1,200 rpm were not studied because of the instability of sample bottle that tends to rattle and splash its content. Therefore, 1,200 rpm was chosen as the optimum stirring speed and used in subsequently experiments.

3.3.5. Extraction time

In LPME, the extraction time is an important parameter because the mass transfer of an analyte between donor and acceptor phase is a time-dependent process and the equilibrium is attained in a specific time period. Different extraction times in the range of 10–40 min were investigated. The results clearly showed that the response factor decreased with extraction time (Table 2). It may be due to the fast transfer of the analytes from donor phase to acceptor phase using the sol–gel coated hollow fibers. The results concluded that 10 min extraction time was enough to achieve the equilibrium for higher extraction efficiency and recovery of the analytes.

3.3.6. Ionic strength or salting-out effect

The addition of salt (NaCl) increases the ionic strength of the sample solution and this may enhance the extraction efficiency although it depends on the nature of the analyte. In order to evaluate the possibility of salting-out effect, extraction efficiency was studied by increasing sodium chloride concentration from 0 to 20% w/v. The effects of different concentrations of NaCl are given in Table 2 and Fig. 5. The results confirmed that the ionic strength had no effect on extraction efficiency for these analytes. Therefore,

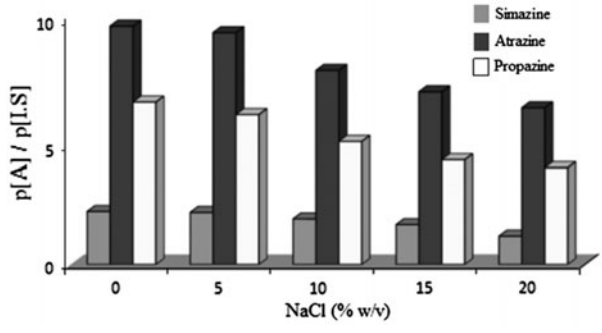

Fig. 5. Effect of salt (NaCl) addition in the extraction efficiency (response factor). Extraction conditions: toluene as extraction solvent, 1.5 cm hollow fiber, 4.5 mL of donor, 3 μL of acceptor phase, 840 rpm stirring rate, 10 min extraction time.

Table 3
Method validations for sol–gel coated and uncoated hollow fibers-based LPME of triazine herbicides

Analytes	Concentration range (μg L^{-1})	Coefficient of determination (r^2)	RSD (%)	LOD (μg L^{-1})	Recovery (%)	Enrichment factor (EF)
Uncoated hollow fiber						
Simazine	100–1,250	0.9950	0.44	36.2	60.72	80
Atrazine	50–250	0.9998	0.94	14.6	66.42	88
Propazine	10–100	0.9984	0.31	5.88	68.17	90
Coated hollow fiber						
Simazine	50–250	0.9991	0.83	6.49	75.27	100
Atrazine	10–100	0.9989	0.76	0.75	104.47	139
Propazine	05–75	0.9984	0.23	0.41	94.64	126

further experiments were carried out without the addition of any salt.

Similar optimized conditions were obtained with good extraction efficiency for uncoated PP hollow fiber-based LPME except for donor phase volume and extraction time of 4.0 mL and 30 min, respectively.

3.4. Method validation

To validate the applicability of the proposed coated HF-LPME method, the quantitative analytical parameters namely linearity range, coefficient of determination (r^2), LOD, relative standard deviation (RSD), and EF of each triazine herbicide for both PP sol–gel coated fiber and uncoated PP hollow fiber were determined using the optimized LPME conditions. The coefficient of determinations (r^2) was greater than 0.9950, with different linearity ranges for each analyte for both coated and uncoated hollow fiber (Table 3). The LOD was calculated at a signal-to-noise ratio $S/N = 3$. Low LOD values were obtained for sol–gel coated hollow fiber (0.41–6.49 μg L^{-1}) and more appreciable as compared to the LOD values for uncoated hollow fiber (5.88–36.2 μg L^{-1}). The RSDs for five replicate experiments varied from 0.31 to 0.94% for the uncoated hollow fiber and 0.22–0.83% for the sol–gel coated hollow fiber-based LPME. Moreover,

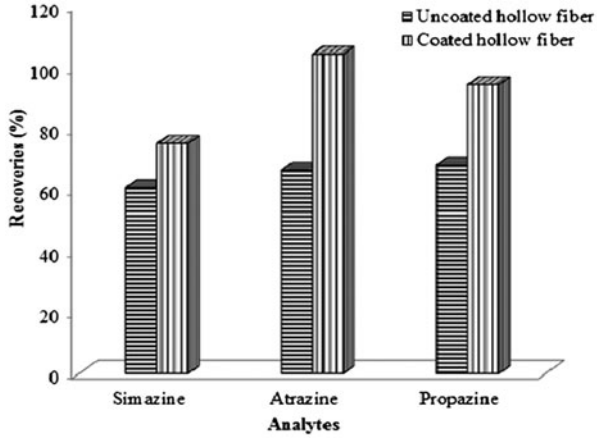

Fig. 6. Comparison of percentage recoveries of triazine herbicides for uncoated and coated hollow fiber LPME.

the values of EF achieved for sol–gel coated HF-LPME were higher (100–126) as compared with EF values for uncoated HF-LPME (80–90). These results confirmed that the proposed method has a high sensitivity and repeatability.

Based on the results discussed above, comparison between uncoated and coated hollow fiber LPME for the recoveries of the analytes was made. The analyte recovery for coated hollow fiber was considerably

Table 4
Analyte recoveries for spiked lake water, river water, and tap water samples using uncoated and coated hollow fibers

Analytes	Spiked level (μg L^{-1})	Recoveries (%) with uncoated hollow fiber LPME			Recoveries (%) with coated hollow fiber LPME		
		Lake water sample	River water sample	Tap water sample	Lake water sample	River water sample	Tap water sample
Simazine	100	32.15	34.50	54.96	47.79	42.54	63.90
Atrazine	75	45.70	41.57	59.44	58.77	55.33	78.75
Propazine	25	50.85	44.59	60.86	57.11	47.01	67.93

Table 5
Comparison of response factor data using Kolmogorov and *t*-test and coated hollow fiber LPME

	Simazine (μg L^{-1})								Atrazine (μg L^{-1})								Propazine (μg L^{-1})							
	100		250		750		50		100		250		25		50		100							
Parameter	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated						
Response factor	0.0266	0.04664	0.0359	0.06185	0.0659	0.1125	0.033	0.059	0.0402	0.0702	0.0616	0.1036	0.0121	0.0225	0.0188	0.0364	0.0322	0.0643						
Improvement (coated/uncoated)	1.75		1.72		1.7		1.96		1.74		1.68		1.85		1.93		1.99							
p-values (Kolmogorov)	0.972	0.991	0.974	0.992	0.952	0.879	0.961	0.993	0.996	0.99	0.984	0.904	0.930	0.984	0.904	0.927	0.910	0.927						
p-values (*t*-test)	$1.04\,E^{-5}$	1.03 E^{-6}	$2.10\,E^{-5}$	1.24 E^{-5}	$1.21\,E^{-4}$	1.00 E^{-3}	$2.10\,E^{-5}$	1.50 E^{-7}	$1.37\,E^{-5}$	1.11 E^{-4}	$1.02\,E^{-6}$	1.31 E^{-5}	$2.00\,E^{-6}$	1.25 E^{-5}	$1.08\,E^{-7}$	2.35 E^{-5}	$1.193\,E^{-5}$	1.24 E^{-4}						

high (up to 104.47%) as compared to those of uncoated hollow fiber (up to 68.17%) (Fig. 6). This means that analytes were extracted more efficiently by the coated hollow fiber as compared with the uncoated hollow fiber. It was probably because the coated fiber possessed better means for extracting analytes. Besides the analytes extraction via diffusion through pores of fiber, the analytes could also be extracted via adsorption–desorption process afforded by PDMS coating on the coated fiber. This consequently increased the EF for sol–gel coated fiber LPME as given in table.

3.5. Application of coated HF-LPME to real water samples

The proposed extraction method was applied to the analysis of three triazine herbicides in real water samples namely lake water, river water, and tap water under the optimized conditions of coated and uncoated hollow fibers-LPME. The results showed that none of the analytes was detected in the real water samples (Fig. 4(B)). In order to validate the accuracy of this established method, the water samples were spiked with standards of the target analytes at different concentrations (100, 75, and 25 μg L^{-1}) for simazine, atrazine, and propazine, respectively. The results for uncoated and coated fibers are given in Table 4 and a chromatogram for coated hollow fiber LPME is shown in Fig. 4(C). The analyte recoveries obtained were in the range of 32.15–60.86% for uncoated hollow fiber LPME. It was also observed that the recovery of spiked analytes for tap water sample was higher than those of lake water and river water samples. This suggested that there were significant sample matrix effects in extractions of analytes from lake and river water as compared with tap water. Meanwhile, the analyte recoveries obtained for coated hollow fiber LPME (42.54–78.75%) were higher than those of using for uncoated hollow fiber LPME. This can be attributed to the extraction of analytes by adsorption besides, the usual diffusion process. These results show one of the advantages for coated hollow fiber where higher analyte recovery is possible for real samples without any pre-treatment.

3.6. Comparisons of response factor of analytes for coated and uncoated hollow fiber-based LPME

Statistical hypothesis tests namely *t*-test and Kolmogorov–Smirnov test [41] were used to determine the possibility that the two methods used; uncoated

and coated hollow fiber LPME were significantly different. In order to compare both coated and uncoated hollow fiber LPME, methods with various concentrations of simazine (100, 250 and 750 μg L^{-1}), atrazine (50, 100, and 250 μg L^{-1}), and propazine (25, 50 and 100 μg L^{-1}) were used. The peaks area, the response factor (peak area for coated fiber LPME divided by peak area for uncoated fiber LPME), and *p*-values were recorded (Table 5). It was observed that the response factor for coated hollow fiber LPME was approximately two times higher than that for uncoated hollow fiber LPME. A plausible reason for the improved extraction performance of the coated fiber is that besides allowing usual diffusion process across pores, the coated hollow fiber also functions to extract analytes by adsorption process across coated sol–gel PDMS. The Kolmogorov–Smirnov test for each data obtained was normal distribution, as shown by *p*-values which were larger than $\alpha = 0.05$, thus the null hypothesis (H_O) cannot be rejected. Thus, it can be concluded that the data for uncoated hollow fiber and coated hollow fiber followed normal distribution. Since the normal distribution assumption was satisfied, the independent *t*-test for mean comparison can be used. The independent *t*-test obtained for each data gave results of *p*-values for mean values that were less than $\alpha = 0.05$, and thus it must reject the null hypothesis. Moreover, ratio of coated over uncoated hollow fiber in improvements in term of response factor for both methods was >1.68, which showed that the coated hollow fiber can extract significantly better than the uncoated hollow fiber.

4. Conclusion

Newly developed PDMS/DVB sol–gel coated PP hollow fiber has been successfully applied for the LPME of three triazine herbicides in water samples. A comparison of the extraction efficiency between sol–gel coated hollow fiber and uncoated hollow fiber-based LPME indicate the good reputation of coated hollow fiber with appreciable recovery, reproducibility, high-EF, coefficient of determination, limit of detection, and RSD. The improved performance of the sol–gel coated PP hollow fiber can attributed to the extraction of analytes by adsorption–desorption besides the diffusion process. The statistical Kolmogorov–Smirnov test and *t*-test also explained good comparison of the results and showed better results of the extraction with coated hollow fiber in terms of ability to extract the analytes using LPME method. Briefly, the advantages of sol–gel coated hollow fiber for LPME allow its potential application as a sample preparation and cleanup technique for the analysis of pesticides in real environmental water samples.

Acknowledgments

The authors would like to thank Universiti Teknologi Malaysia for facilitations and the Ministry of Higher Education Malaysia (MOHE) for financial supports through Research Grant Vote Numbers R.J130000.7809.4F177.

References

[1] S. Frias, M.A. Rodrìguez, J.E. Conde, J.P. Pérez-Trujillo, Optimisation of a solid-phase microextraction procedure for the determination of triazines in water with gas chromatography–mass spectrometry detection, J. Chromatogr. A 2003 (1007) 127–135.
[2] G.W.A. Milne, Handbook of Pesticides, CRC Press, Boca Raton, FL, 1995.
[3] USEPA, Office of Pesticide Programs, Health Effect Division, Washington, DC (2008). Available 22 May 2011 from: http://www.epa.gov/pesticides/cumulative/triazines/newdocket.htm.
[4] I. Ali, H.Y. Aboul-enein, Leaching of triazine pesticides in loamy soil and their determination by reversed phase HPLC, Int. J. Environ. Anal. Chem. 81 (4) (2001) 315–322.
[5] M. Battista, A. di Corcia, M. Marchetti, High-performance liquid chromatographic method for determining triazine herbicide residues in soil, J. Chromatogr. A 454 (1988) 233–242.
[6] R.A. McLaughlin, V. Michael Barringer, J.F. Brady, R.A. Yokley, M.L. Homer, E.M. Janis, C.B. Orvin, The Triazine Herbicides, Elsevier, San Diego, CA 2008, p. 243.
[7] G. Durand, V. Bouvot, D. Barceló, Determination of trace levels of herbicides in estuarine waters by gas and liquid chromatographic techniques, J. Chromatogr. A 607 (1992) 319–327.
[8] R. Carabias-Martínez, E. Rodríguez-Gonzalo, J. Domínguez-Álvarez, J. Hernández-Méndez, Determination of triazine herbicides in natural waters by solid-phase extraction and non-aqueous capillary zone electrophoresis, J. Chromatogr. A 869 (2000) 451–461.
[9] W.T. Ma, K.K. Fu, Z.W. Cai, G.B. Jiang, Gas chromatography/mass spectrometry applied for the analysis of triazine herbicides in environmental waters, Chemosphere 52 (2003) 1627–1632.
[10] A. Balinova, Solid-phase extraction followed by high-performance liquid chromatographic analysis for monitoring herbicides in drinking water, J. Chromatogr. A 643 (1993) 203–207.
[11] I. Ali, V.K. Gupta, H.Y. Aboul-Enein, A. Hussain, Hyphenation in sample preparation: Advancement from the micro to the nano world, J. Sep. Sci. 31 (2008) 2040–2053.
[12] S. Papilloud, W. Haerdi, Supercritical fluid extraction of triazine herbicides: A powerful selective analytical method, Chromatographia 40 (1995) 705–711.

[13] J.W. Pensabene, W. Fiddler, D.J. Donoghue, Supercritical fluid extraction of atrazine and other triazine herbicides from fortified and incurred eggs, J. Agric. Food Chem. 48 (2000) 1668–1672.
[14] J. Cheng, M. Liu, X. Zhang, L. Ding, Y. Yu, X. Wang, Determination of triazine herbicides in sheep liver by microwave-assisted extraction and high performance liquid chromatography, Anal. Chim. Acta 590 (2007) 34–39.
[15] G. Shen, H.K. Lee, Determination of triazines in soil by microwave-assisted extraction followed by solid-phase microextraction and gas chromatography–mass spectrometry, J. Chromatogr. A 985 (2003) 167–174.
[16] I.J. Barnabas, J.R. Dean, I.A. Fowlis, S.P. Owen, Automated determination of s-triazine herbicides using solid-phase microextraction, J. Chromatogr. A 705 (1995) 305–312.
[17] 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 2004 (1047) 189–194.
[18] D. Djozan, B. Ebrahimi, Preparation of new solid phase micro extraction fiber on the basis of atrazine-molecular imprinted polymer: Application for GC and GC/MS screening of triazine herbicides in water, rice and onion, Anal. Chim. Acta 616 (2008) 152–159.
[19] C. Aguilar, S. Penalver, E. Pocurull, F. Borrull, R.M. Marce, Solid-phase microextraction and gas chromatography with mass spectrometric detection for the determination of pesticides in aqueous samples, J. Chromatogr. A 795 (1998) 105–115.
[20] F. Hernandez, J. Beltran, F.J. Lopez, J.V. Gaspar, Use of solid-phase microextraction for the quantitative determination of herbicides in soil and water samples, Anal. Chem. 72 (2000) 2313–2322.
[21] S. Huang, H. Huang, Y. Sung, Analysis of triazine in water samples by solid-phase microextraction coupled with high-performance liquid chromatography, Talanta 64 (2004) 887–893.
[22] T. Kumazawa, X. Lee, K. Kondo, K. Sato, H. Seno, K. Watanabe-Suzuki, Determination of triazine herbicides in human body fluids by solid-phase microextraction and capillary gas chromatography, Chromatographia 52 (2000) 195–199.
[23] F. Perreau, J. Einhorn, Determination of frequently detected herbicides in water by solid-phase microextraction and gas chromatography coupled to ion trap tandem mass spectrometry, Anal. Bioanal. Chem. 386 (2006) 1449–1456.
[24] C. Rocha, E.A. Pappas, C. Huang, Determination of trace triazine and chloroacetamide herbicides in tile-fed drainage ditch water using solid-phase microextraction coupled with GC–MS, Environ. Pollut. 152 (2008) 239–244.
[25] G. Shen, H.K. Lee, Hollow fiber-protected liquid-phase microextraction of triazine herbicides, Anal. Chem. 74 (2002) 648–654.
[26] L. Zhao, H.K. Lee, Liquid-phase microextraction combined with hollow fiber as a sample preparation technique prior to gas chromatography/mass spectrometry, Anal. Chem. 74 (2002) 2486–2492.
[27] K.K. Sirkar, Membranes, phase interfaces, and separations: Novel techniques and membranes—An overview, Ind. Eng. Chem. Res. 47 (2008) 5250–5266.
[28] M.M. Sanagi, H.H. See, W.A. Wan Ibrahim, A.A. Naim, Determination of pesticides in water by cone-shaped membrane protected liquid phase microextraction prior to micro-liquid chromatography, J. Chromatogr. A 1152 (2007) 215–219.
[29] H.H. See, M.M. Sanagi, W.A. Wan Ibrahim, A.A. Naim, Determination of triazine herbicides using membrane-protected carbon nanotubes solid phase membrane tip extraction prior to micro-liquid chromatography, J. Chromatogr. A 1217 (2010) 1767–1772.
[30] C. Ye, Q. Zhou, X. Wang, Improved single-drop microextraction for high sensitive analysis, J. Chromatogr. A 1139 (2007) 7–13.
[31] K.E. Rasmussen, S. Pedersen-Bjergaard, Developments in hollow fibre-based, liquid-phase microextraction, TrAC Trends Anal. Chem. 23 (2004) 1–10.
[32] D. Nagaraju, S. Huang, Determination of triazine herbicides in aqueous samples by dispersive liquid–liquid microextraction with gas chromatography–ion trap mass spectrometry, J. Chromatogr. A 1161 (2007) 89–97.
[33] C. Wang, S. Ji, Q. Wu, C. Wu, Z. Wang, Determination of triazine herbicides in environmental samples by dispersive liquid–liquid microextraction coupled with high performance liquid chromatography, J. Chromatogr. Sci. 49 (2011) 689–694.
[34] M.M. Sanagi, H.H. Abbas, W.A. Wan Ibrahim, H.Y. Aboul-Enien, Dispersive liquid–liquid microextraction method based on solidification of floating organic droplet for the determination of triazine herbicides in water and sugarcane samples, Food Chem. 133 (2012) 557–562.
[35] W.A. Wan Ibrahim, H. Farhani, M.M. Sanagi, H.Y. Aboul-Enein, Solid phase microextraction using new sol–gel hybrid polydimethylsiloxane-2-hydroxymethyl-18-crown-6-coated fiber for determination of organophosphorous pesticides, J. Chromatogr. A 1217 (2010) 4890–4897.
[36] K. Alhooshani, T. Kim, A. Kabir, A. Malik, Sol–gel approach to *in situ* creation of high pH-resistant surface-bonded organic–inorganic hybrid zirconia coating for capillary microextraction (in-tube SPME), J. Chromatogr. A 2005 (1062) 1–14.
[37] S.S. Segro, A. Malik, Solvent-resistant sol–gel polydimethyldiphenylsiloxane coating for on-line hyphenation of capillary microextraction with high-performance liquid chromatography, J. Chromatogr. A 1205 (2008) 26–35.
[38] N. Grassie, G. Scott, Polymer Degradation and Stabilization, Cambridge University Press, New York, NY, 1985, pp. 79–103.
[39] R. Christian, W. Thomas, Solvents and Solvent Effects in Organic Chemistry, Wiley, Weinheim, 2011, pp. 145–160.
[40] T.S. Ho, T. Vasskog, T. Anderssen, E. Jensen, K.E. Rasmussen, S. Pedersen-Bjergaard, 25,000-fold pre-concentration in a single step with liquid-phase microextraction, Anal. Chim. Acta 592 (2007) 1–8.
[41] E.L. Lehmann, Testing Statistical Hypothesis, 5th ed., Wiley, New York, NY, 1970, pp. 70–84.