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PAPER

Polypyrrole nanowires network for convenient and highly efficient microextraction in packed syringe

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A novel method based on microextraction in packed syringe (MEPS), as a sample preparation technique in combination with gas chromatography-mass spectrometry (GC-MS) was developed using a polypyrrole (PPy) nanowires network as the extracting medium. The PPy nanowires network was prepared using a soft template technique and its characterization was studied by scanning electron microscopy (SEM). The use of micelles in this methodology has an important role in the shape of the growing polymer. The pyrrole monomer was introduced into cetyltrimethylammonium bromide (CTAB) micelles and this has led to the formation of nanowires with diameters ranging from 30 to 60 nm. The bulk PPy prepared without CTAB were all spherical particles with diameters of 100–400 nm. The PPy nanowires network was shown to have a 7–28 times higher extraction capability in comparision with bulk PPy. The developed method was applied to the analysis of some important triazine herbicides. Important parameters influencing the extraction and desorption processes were optimized and a 25 cycles of draw–eject of sample with a speed of 10 rpm gave a maximum peak area, when 2 mg of PPy nanowires network was packed in the syringe. After entrapment of the selected analytes, the desorption was performed using 150 μL of acetonitrile. Limits of detection (LODs) were in the range of 0.02 to 0.05 ng mL^{-1} using the time scheduled selected ion monitoring (SIM) mode. Intraday precision (RSD %) values for four replicates ranged from 7 to 10% and interday precision values obtained for three replicates measured on different days were in the range of 10–12% at a concentration level of 5 ng mL^{-1}. The linearity of the method was in the range of 0.5–500 ng mL^{-1}. The developed method was successfully applied to the analysis of water samples obtained from the Zayandeh-roud river and the matrix factor for the spiked real water samples was found to be in the range of 0.72–0.92.

Introduction

Conducting polymers (CPs), due to their multifunctional properties and promising technological applications, have attracted much attention as advanced materials[1,2] and have been used in the development of chemical stationary phases for the separation and extraction of polar and ionic compounds.[3,4] Among the various CPs studied, polypyrrole (PPy) and its derivatives have been widely used for the extraction and preconcentration of different types of compounds.[5] PPy is expected to show different extraction efficiencies towards compounds with different functionalities. When PPy is being used as a sorbent for extraction purposes, various mechanisms such as π–π interactions, polar functional group interactions, anion-exchange properties, and hydrogen bonding are involved in the isolation of aromatic hydrocarbons,[6] polar aromatic compounds,[7] anionic species[8] and alcohols,[9] respectively. This interesting polymer has shown to have different extraction selectivity towards acidic compounds as well.[4]

Lately, interest in micro- and nanostructures of CPs has grown remarkably since these structures of low scaled dimensions have highly usable properties that might lead to improved performance and versatile applications. A major reason for their superiority over conventional materials is the much larger exposed surface area. These nanostructures could be formed from one-dimensional structures like nanofibers, wires or rods up to complex three-dimensional microstructures. Other typical forms are hollow nanocapsules or nanotubes.

Several synthesis procedures have been developed for the preparation of conducting polymers-based micro- or nanostructured materials. The main approach relies on the use of different forms of hard templates like porous materials *e.g.* zeolites[10] and soft templates like micelles and interfaces.[11] In the soft template approach micelles are being used as the structure directing agents to determine the shape of the growing polymers.[12] As an example, the pyrrole monomers were introduced

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into cetyltrimethylammonium bromide (CTAB) micelles. These acted as nanoreactors during the oxidative polymerization.[13]

Conductive polymers-based nanoparticles (CPNs) are expected to have a significant impact on extraction efficiency due to the enhanced effective surface area. To our knowledge there are few publications in the literature on the use of CPNs especially PPy nanoparticles in extraction techniques.[14,15]

Microextraction in packed syringe could be regarded as a new approach for solid-phase extraction (SPE) in which low amounts of solid packing materials, low sample volumes and desorption solvent volumes are being used. In contrast to conventional SPE columns, the MEPS sorbent bed containing 1–2 mg of sorbent is integrated into a liquid handling syringe that allows for low dead volume sample manipulations either manually or in combination with autosamplers.[16,17] MEPS can be coupled on-line to high performance liquid chromatography (HPLC)[18,19] or GC[20,21] without any modification of the instrument. The aquatic sample is drawn through the sorbent by an autosampler. When the sample is passed through the sorbent by an autosampler, the compounds are trapped. The sorbent is then washed by water to remove the interfering species and the analytes are subsequently eluted with appropriate amounts of an organic solvent such as methanol or the HPLC mobile phase. A key factor in MEPS is that the volume of desorbing solvent is very much amenable to be injected directly into an LC or GC system. For this purpose GC systems have to be equipped with a programmed temperature vaporizing (PTV) system. MEPS coupled with a PTV technique could be employed to inject most of the analytes in a sample at once, and to promote labor-saving sample preparation. When working with split–splitless injector systems it is not possible to inject whole amounts of desorption solvent into the injection port. If these injection techniques are used it is necessary to employ MEPS in off-line combination with the GC systems.

In this work an attempt was made to synthesis a PPy nanowires network using a soft template method and to use these as a sorbent for MEPS in off-line combination with GC-MS. The developed method was applied to the microextraction of some selected triazine herbicides from water samples.

Experimental

Reagents and standards

Atrazine, ametryn and terbutryn were obtained from Merck (Darmstadt, Germany). The stock solution of these compounds was prepared in methanol at a concentration of 1000 μg mL^{-1} and was stored at 4 °C. Methanol, ethanol, acetone, *n*-hexane, acetonitrile, butyl acetate, dichloromethane, chloroform, hydrochloric acid (HCl), sodium hydroxide (NaOH), trimethylchlorosilane, citric acid hydrate (CI), ammonium persulfate (APS) and cetyltrimethylammonium bromide (CTAB) were supplied from Merck (Darmstadt, Germany). Pyrrole (98%) was obtained from Aldrich (Mississauga, Canada) and distilled before use.

Instrumentation

A gas chromatograph model Agilent 6820, with a split–splitless injection port and flame ionization detection (FID) system, was used to determine the optimized extraction conditions. A homemade glass inlet liner with 1 mm i.d. was deactivated by trimethylchlorosilane and used. Separation of analytes was carried out using a capillary column HP-1 MS (60 m × 0.25 mm i.d.) with 0.25 μm film thickness (Hewlett-Packard, Palo Alto, CA, USA). The carrier gas was helium (99.999%) at a flow rate of 1 mL min^{-1}. The gas chromatograph was operated in the splitless mode and the split valve was kept closed for 1 min. The column was held at 100 °C for 3 min, increased to 200 °C at a rate of 70 °C min^{-1}, then was kept at this temperature for 3 min and raised to 280 °C at 10 °C min^{-1} and was kept at this temperature for 10 min. The injector and detector temperatures were set at 250 and 290 °C respectively.

For quantitative determination, a Hewlett-Packard (HP, Palo Alto, USA) HP 6890 plus series GC equipped with a split–splitless injector and a HP 5973 mass-selective detector system were used. The MS was operated in the EI mode (70 eV). Helium (99.999%) was employed as the carrier gas and its flow rate was adjusted to 1 mL min^{-1}. The separation of triazines was performed on a 30 m × 0.25 μm HP-5 MS column (0.25 μm film thickness). The column was held at 100 °C for 3 min, increased to 200 °C at a rate of 20 °C min^{-1} and was kept at this temperature for 4 min then raised to 250 °C at 50 °C min^{-1} and was kept at this temperature for 1 min. The injector temperature was set at 250 °C. The GC-MS interface, ion source and quadrupole temperatures were set at 280, 230 and 150 °C, respectively. The detection method was programmed for SIM considering two or three characteristic ions for each compound.

In order to characterize the morphological properties of the prepared nanowires the SEM images were obtained by a TESCAN VEGA II XMU (Berno, Czech Republic).

Preparation of PPy nanowires networks

Under stirring, CTAB (0.91 g, 0.0025 mol), CI (0.85 g, 0.004 mol) and pyrrole (0.27 mL, 0.004 mol) were dissolved in 125 mL of deionized water at about 15 °C for 3 h. An aqueous solution of APS (10 mL, 0.004 mol; the molar ratio of APS to pyrrole, 1 : 1) was added to the above solution in one portion. The reaction was allowed to proceed for 4 h at about 15 °C under stirring. The resulting product was washed with double distilled water and methanol repeatedly. Finally, the product was dried in an oven at 40 °C for 24 h. The bulk PPy was prepared as discussed above without using CTAB.

The MEPS condition

For these studies 1 mL insulin injection syringes were used. An amount of 2 mg of PPy nanowires network was manually inserted inside the syringe between two polyethylene filters (SPE frits, 20 μm pore size). For this purpose the size of SPE frits was changed to match the used syringes. Prior to the first use, the sorbent was manually conditioned with 2 mL of methanol followed by 4 mL of water. After that, the spiked sample (7 mL) was drawn through the syringe forward and backward several times using a variable speed cycling motor which was attached to a circular plate (Fig. 1). It is important that samples are drawn with sufficient speed to decrease the extraction time and to obtain good percolation between the sample and solid support. In this

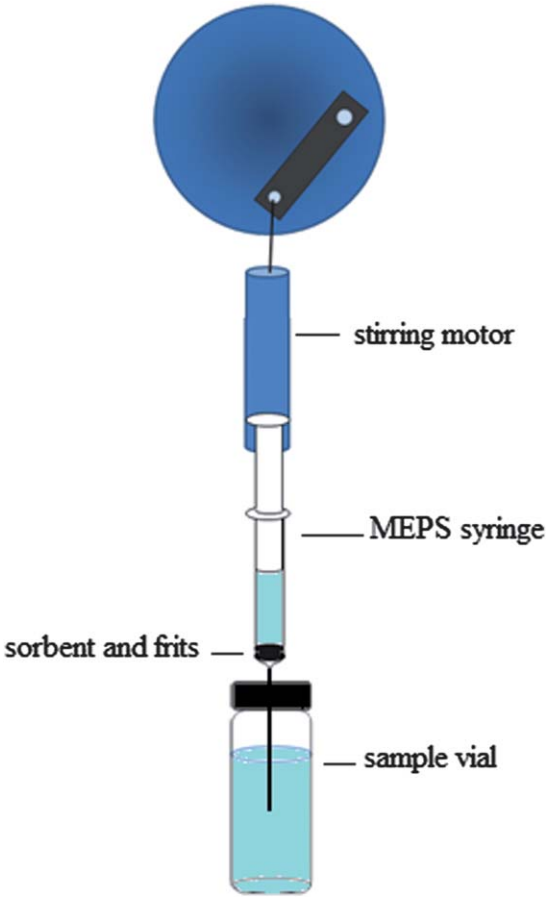

Fig. 1 Scheme of the extraction set up and MEPS syringe.

work the speed of the cycling motor was adjusted at 10 rpm (170 μL s^{-1}). After the extraction, the syringe was dried under nitrogen flow and the analytes were then desorbed with 200 μL acetonitrile. The desorption step was performed manually by solvent aspiration into the syringe. Afterward the desorbed analytes were transferred into a glass vial. Next, the desorbing solvent was evaporated under a N_2 flow until complete solvent drying. Finally 10 μL of acetonitrile was added to the desorption vial and then 2 μL of desorbed solution was injected into the injection port of the GC system. After each extraction the MEPS syringe was washed with approximately 200 μL of acetonitrile, 200 μL of methanol and 1 mL of water.

Results and discussion

Preparation and characterization of PPy nanowires

Template synthesis is a chemical oxidative method which introduces structural directors into the chemical polymerization bath. These structural directors could contain soft templates such as surfactants, organic acids or polyelectrolytes that assist the self-assembly of nanostructures. When the soft-template method is considered, usually micelles or three-dimensional aggregations of micelles are the structure-directing agents. Depending on the specific conditions, *i.e.* constitution of the surfactant, its concentration, ionic strength, hydrodynamics and temperature, the polymer grows inside or outside the micelles thus replicating the morphology of the micelles. Most frequently spherical polymer particles are formed. But if the spherical micelles aggregate to form three-dimensionally organized cylindrical structures, then the conditions for formation of rods could be overcome. In the cases of soft templates it is necessary to remove the corresponding surfactant after termination of the polymerization reaction. Regarding the literature, the mechanism of formation for PPy nanowires network could be explained as follows: when pyrrole monomer is added into an aqueous solution containing CTAB and citric acid hydrate, it has been suggested that a kind of three-dimensional network is formed from the assembly or aggregation of pyrrole, CTAB, and citric acid before the oxidation polymerization of pyrrole occurs.[22] Based on these results, it can be concluded that when CTAB, citric acid, and pyrrole are added to water, micelles would be formed because of the long alkyl chain of CTAB.[23,24] Two micelles of CTAB might be connected by citric acid molecules to form one or more T junctions. When APS is added into the reaction solution, the three-dimensional networks of the soft templates can be elongated and form the three dimensional PPy nanowires network.[25]

Also, CI acts as a dopant for PPy in this procedure and it is not a prerequisite for wire formation, but the ability of the micelles to link together to form a micelle network is improved when the PPy is formed after addition of the oxidant ammonium peroxodisulphate (APS).[26] The surface characteristics of the prepared polypyrrole nanowires were investigated by the SEM technique. According to Fig. 2A, the formation of nanowires is confirmed and all of them are packed in rough porous structures. Also it is shown that the nanowires diameters are in the range of 30–60 nm and there are some observable T junctions as discussed earlier. The SEM image of bulk PPy (CTAB was not used in preparation of this polymer) is illustrated in Fig. 2B. Clearly, the PPy prepared without CTAB are all spherical particles with diameters of 100–400 nm, indicating that these particles are linked and packed together.

Extraction capability of the prepared PPy nanowires network

Features such as high surface area and π-functional groups of the conductive polymer together with polar functional groups of CI, are definitely important characteristics of the fabricated PPy nanowires network, which make it a suitable candidate for extraction purposes. In order to investigate the extraction capability of the prepared PPy nanowires, the MEPS syringes were prepared using two different kinds of PPy. As shown in Fig. 3 the PPy nanowires network exhibits 7 to 28 times higher extraction capability in comparison with that of the bulk PPy. This enhancement in extraction capability is probably due to the increase in surface area and hydrophilicity of the PPy nanowires network.[26]

MEPS optimization

MEPS is usually coupled on-line with most separation techniques. However it can be used off-line with some analytical systems such as matrix assisted laser ablation desorption ionization-time of flight (MALDI-TOF) and direct infusion MS.[16] For on-line coupling of MEPS with GC the employment of

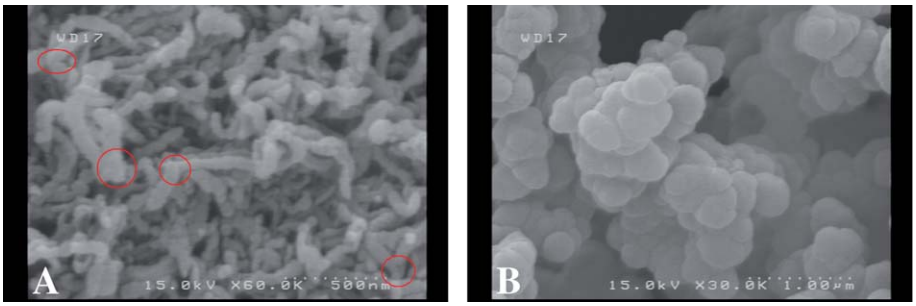

Fig. 2 SEM image of prepared (A) PPy nanowires network, T junctions are cycled on the SEM image, (B) bulk PPy.

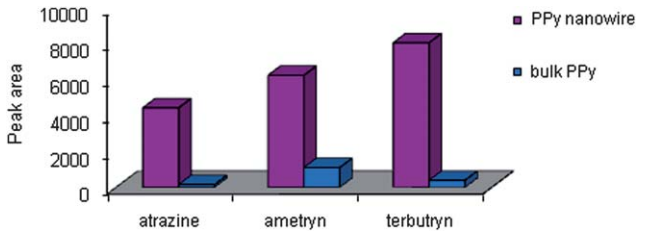

Fig. 3 Comparison of extraction capability of PPy nanowires network with that of bulk PPy. Extractions were performed using 7 mL of sample containing analytes at a level of 1 μg mL^{-1}, with 50 cycles of draw–eject. Desorption was performed using 200 μL of acetonitrile.

a PVT is necessary but when a split–splitless injector is used the off-line combination of MEPS with GC is preferred.

After the successful extraction of triazine analytes using MEPS it was necessary to optimize the MEPS conditions in order to obtain the highest extraction recovery while preventing carry over. To do so, some important influential parameters such as desorption solvent, volume of desorption solvent, the amount of sorbent in the packing, pH effect and the pump cycles were investigated.

Desorption condition

Both desorbing solvent and its volume were investigated, to ensure effective elution of the analytes from the sorbent. The optimum desorbing solvent, at its lowest possible volume, should be able to displace the target analytes from the sorbent. If the retention is based on hydrophobic interactions only, non-polar solvents would be able to disrupt the forces that bind the analytes to the sorbent. Different organic solvents with various functionality and polarity were used to investigate the optimum desorption conditions. The extractions were performed using 7 mL of aqueous sample spiked with the target analytes at a concentration level of 1 μg mL^{-1}, with 50 pump cycles at 10 rpm. The volume of applied desorption solvent was 200 μL. The results show that butyl acetate led to the highest desorption efficiency, but due to its low volatility acetonitrile was chose as the desorption solvent for further experiments. In this study the effect of desorbing solvent volume was investigated. The analytes response increased as elution volume increased up to 150 μL and remained constant after this value. Therefore a desorbing volume of 150 μL was selected for further experiments.

Influence of draw–eject cycles on the extraction efficiency

In MEPS the sample can be drawn through the needle into the syringe, once or several times (draw–eject). The multiple extraction cycles can be performed by draw–ejecting a certain fraction of sample in the same vial or by drawing a certain volume of sample and subsequently discarding it to waste (extract–discard). In this study the influence of the number of extraction cycles (draw–eject) on the extraction efficiency was evaluated. According to the literatures[20,27] multiple draw–eject of the sample in the same vial was preferred to extract each analyte from 7 mL of water samples. As shown in Fig. 4, the maximum extraction yield for all analytes was achieved using 50 pump cycles. After this point the analytes response is rather constant and no enhancement in response was observed. Furthermore, for investigating the efficiency of the extract–discard mode, this procedure was applied to the extraction of 7 mL of sample with an analyte concentration of 1 μg mL^{-1} by drawing 1 mL of sample and discarding it into another vial. Therefore in order to

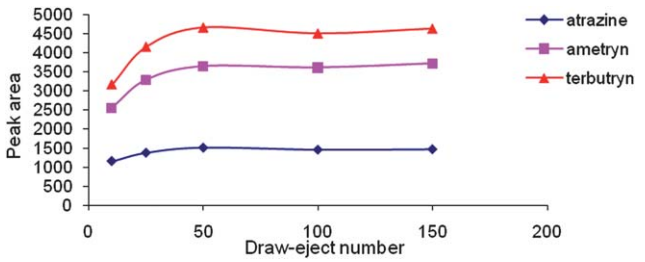

Fig. 4 Effect of draw–eject number of sample through the sorbent on the extraction efficiency. Extractions were performed using 7 mL of sample containing analytes at a level of 1 μg mL^{-1}. Desorption was performed using 150 μL of acetonitrile.

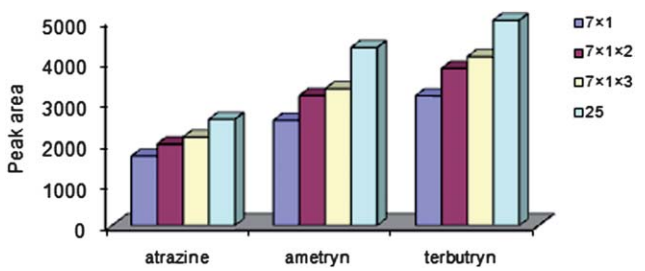

Fig. 5 Comparison of draw–eject in the same vial with the extract–discard method.

draw the whole sample (7 mL) it was necessary to repeat this cycle 7 times (7 × 1). For the extraction of whole sample *n* times a 7 × 1 × *n* protocol must be used. As shown in Fig. 5 the responses for all the analytes were enhanced by increasing the whole sample extraction repetition (increasing *n*). The extract–discard mode in comparison with the draw–eject mode in the same vial using 25 cycles, led to an insufficient improvement in the extraction efficiency. Thus, considering the simplicity of draw–eject in the same vial and the applicability of the cycling motor for extractions, draw–eject in the same vial with 25 cycles was selected for further extractions.

Effect of sample pH

The pH of the sample is an important factor, which may affect the trazines extraction recovery from water samples. To increase the extraction recovery of triazine herbicides by the developed procedure, it is necessary to adjust the sample pH to an optimum value. It has been shown that some pesticides such as simazine, atrazin, diazinon and fenthion can be extracted by acid–base interactions on the conducting polymers.[7] In addition, it was demonstrated that the acidic property of PPy is stronger than its basic property.[28] Therefore, it is expected that PPy could extract the basic forms of pesticides more efficiently than the acidic forms. The effects of pH on the extraction of triazines from water samples were evaluated by varying the pH values in the range of 1.5 to 12. As shown in Fig. 6, the extraction efficiency of PPy nanowires network for the selected triazines in water increased significantly when the sample pH was raised from 1.5 to 7, and then a decrease was observed. Therefore, a pH of 7 was found to be the most suitable value. These results can be easily described when considering the acid–base equilibrium of the triazines and PPy in solutions with different pH values. The capability of PPy to extract the selected triazine analytes depends on the inter-molecular interactions between PPy and analytes including acid–base, π–π, dipole–dipole, and ion exchange. Because the prepared PPy is positively charged[29] in its oxidized form (a weak acid) and triazines have a positive charge at low pH solutions, the electrostatic repulsion between the PPy network and pesticides leads to lower extraction efficiency at low pH sample solutions. With an increase in sample pH, the positive charge of the analytes is reduced while the basic forms of the analytes are increased, and the attractive inter-molecular interactions between analytes and PPy become more dominant, therefore, the extraction efficiency is increased.

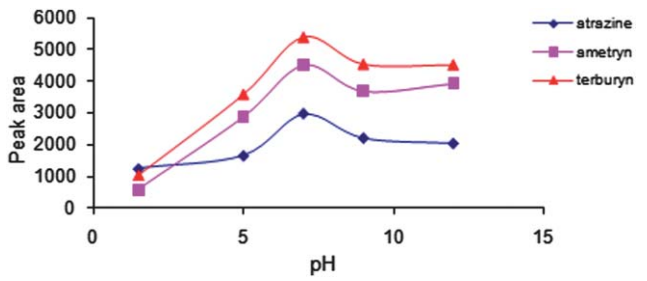

Fig. 6 Effect of pH on the extraction efficiency. Extractions were performed using 7 mL of sample containing analytes at a level of 1 μg mL^{-1}, with 25 cycles of draw–eject. Desorption was performed using 150 μL of acetonitrile.

Sorbent amounts

To achieve acceptable recovery for extraction of target substances from water samples, the amounts of sorbent material needed to be optimized. MEPS syringes with different amounts of sorbents (2–10 mg) were prepared and applied for extraction of triazine analytes. According to the results an enhancement for the analytes responses was observed when the amount of PPy nanowires network increased up to 2 mg, but after this point curves tend to reach a plateau value. This effect is due to the increase of effective surface area and subsequently more available sites on the sorbent for entrapment of analytes. Considering these results and also the acceptable extraction efficiency achieved using 2 mg of the PPy nanowires network, this amount of sorbent was chose for the rest of the experiments.

Method validation

Based on the method development observed above, the following conditions were selected for the determination of triazines in water: acetonitrile as desorption solvent, elution volume of 150 μL, pH = 7, draw–eject number of 25 times in the same vial and 2 mg of PPy nanowires network. Double distilled water spiked with the selected triazines was used to evaluate the precision of the measurements, the limits of detection and the dynamic range of the method. The linearity of the method was studied by preparing the calibration curves for each analyte. The tested concentration range was from 0.5 ng mL^{-1} to 1000 ng mL^{-1}. The obtained calibration graphs for all analytes were linear in the concentration range of 0.5 to 500 ng mL^{-1}. The regression coefficient for the analytes was satisfactory ($R^2 > 0.9976$). LODs, based on a signal-to-noise ratio of 3/1, were in the range of 0.02 to 0.05 ng mL^{-1}, using the SIM mode (Table 1).

Recoveries were determined by comparing the response obtained by MEPS of 7 mL of sample at 20 ng mL^{-1} *versus* the response of a direct injection of 2 μL of a standard solution of 100 μg mL^{-1}. As Table 1 shows, the results ranged from 55 to 98%.

The method reproducibility was examined by determining the intraday and interday precisions. The intraday precision was evaluated by performing four consecutive extractions from the aqueous solution. The intraday precision showed RSD % ranging from 7 to 10% at 5 ng mL^{-1}. The interday precision was similarly calculated but using values from three extractions performed on different days. The interday precision showed RSD % ranging from 10 to 12% at 5 ng mL^{-1}. The potential for carryover of triazines was investigated by desorption of the washed MEPS syringe after extraction of a spiked sample solution at a level of 5 ng mL^{-1}. There were no observable peaks at the corresponding retention times for each of the selected triazines.

The developed method was compared to other relevant reports[30,31] and data are shown in Table 2. As illustrated, this method possess lower LODs and a wider linear range (LDR) but comparable precision.

Table 1 Some analytical data obtained for MEPS of triazines using the PPy nanowires network and GC-MS

Compound	Retention time (min)	LOD (ng mL^{-1})	LDR (ng mL^{-1})	R^2	Intraday RSD (%)	Interday RSD (%)	AR[a](%)	Matrix factor
Atrazine	8.11	0.04	0.5–500	0.9985	7	12	55	0.92
Ametryn	9.22	0.05	0.5–500	0.9988	7	10	98	0.85
Terbutryn	9.50	0.02	0.5–500	0.9976	10	11	96	0.72

[a] AR: Absolute recovery.

Table 2 Comparison of present work with some articles in the literature

Method	LOD (ng mL^{-1})	RSD (%)	LDR (ng mL^{-1})	Extraction time (min)	Sample volume (mL)	Ref.
MEPS-GC-MS	0.02–0.05	7–10	0.5–500	2.5	7	Present work
SPE-GC-MS	0.2–0.4	2.3–6	0.2–20	25	100	30
SME[a]-GC-MS	0.02–0.4	5.6–10.9	0.1–100, 1–100	15	1	31

[a] Immersed solvent microextraction.

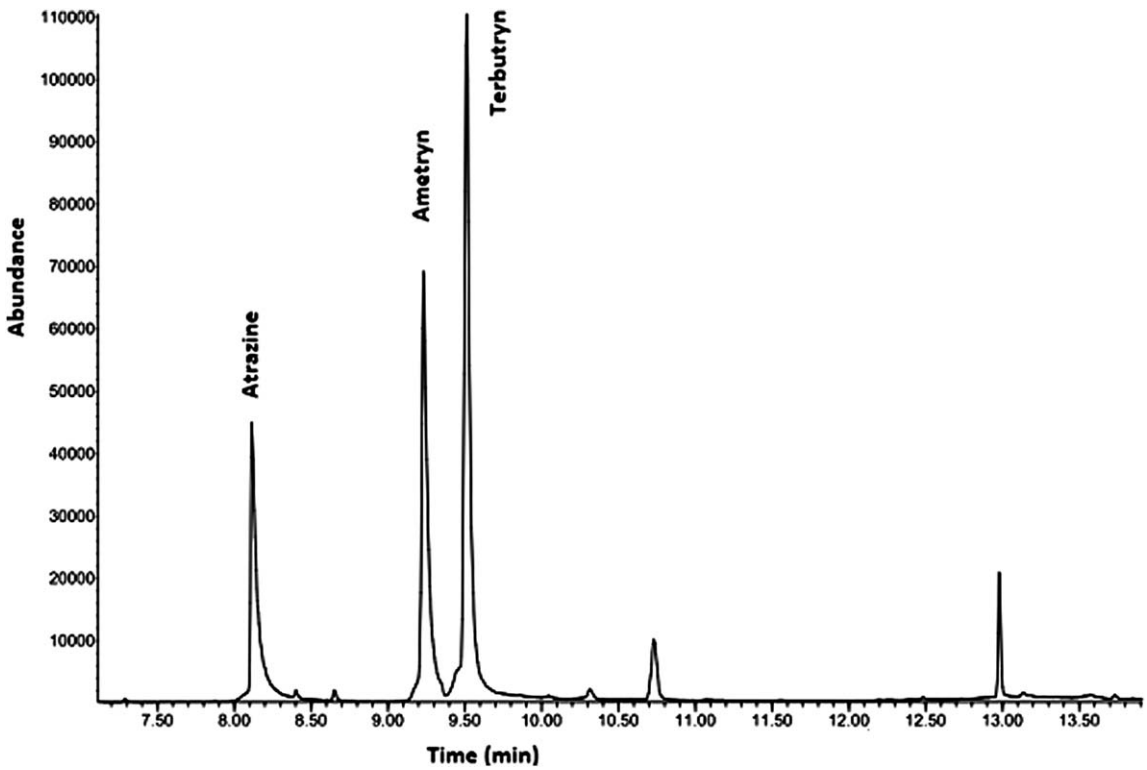

Fig. 7 Mass chromatogram obtained after extraction of triazines from spiked Zayandeh-roud river water samples (5 ng mL^{-1}).

Matrix effect and real water sample analysis

To evaluate the applicability of the developed method for real samples, a water sample obtained from the Zayandeh-roud river (Isfahan-Iran) was analyzed. In order to identify the matrix effect, the water sample was spiked with 5 ng mL^{-1} of each analyte and analyzed (Fig. 7). Finally, a matrix factor was calculated from the peak areas (PA) of the analytes in the spiked and original sample as:

$$\text{Matrix factor} = [\text{PA}_{\text{spiked river}} - \text{PA}_{\text{non-spiked river}}]/[\text{PA}_{\text{spiked pure water}}]$$

The matrix factors listed in Table 1 are an indication of the matrix influence on the analyte response in comparison with the spiked pure water. The determination of all analytes was slightly affected by the river water matrix.

Conclusion

The PPy nanowires network fabricated by a soft template method has been shown to be applicable as a sorbent for extracting trace amounts of triazines from aqueous samples. The nanowires network structure provides increased specific surface area and higher hydrophilicity while loading capacity is increased. The analytical performance parameters including the recoveries, reproducibility and robustness make the developed MEPS technique very much suited for analysis of pollutants and pesticides in real water samples. As shown, the matrix has no significant effect as far as the river water sample is concerned. Furthermore, employing such a miniaturized extraction scale meets the demands of reduced solvent consumption and deposition of waste.

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