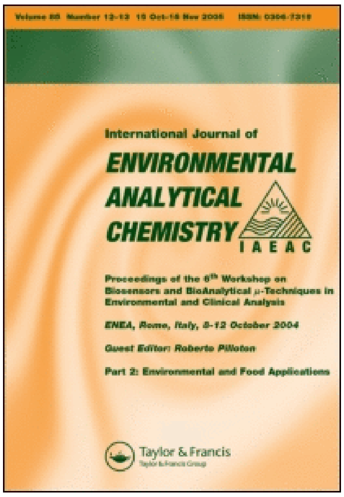

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Ebrahimzadeh, Homeira , Mehdinia, Ali , Yamini, Yadollah , Kasraee, Saeed and Gholizade, Amir(2010) 'Analysis of mono-nitrotoluenes in water samples by using nano-structured polypyrrol as a sorbent of solid-phase microextraction', International Journal of Environmental Analytical Chemistry, 90: 13, 963 — 975

To link to this Article: DOI: 10.1080/03067310903267349

URL: http://dx.doi.org/10.1080/03067310903267349

Intern. J. Environ. Anal. Chem.
Vol. 90, No. 13, 15 November 2010, 963–975

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(*Received 22 February 2009; final version received 2 August 2009*)

Nano-structured polypyrrole (PPY) was used as a coating of solid-phase microextraction (SPME) fibre to increase the extraction efficiency of headspace solid phase microextraction (HS-SPME) of mono-nitrotoluene (MNT) isomers in water samples. The nano-structured PPY was prepared electrochemically by template-free method in the presence of dodecylbenzene sulphonate (DBS) as dopant. Nano-fibrous structures of PPY with a diameter in the range of 38–129 nm were obtained. The porous surface structure of the film, revealed by scanning electron microscopy (SEM), provided high surface areas and allowed for high extraction efficiency of MNT isomers. The extraction procedure was optimised by selecting the appropriate extraction parameters including the time and temperature of adsorption, salt concentration and stirring rate. The calibration graphs obtained by HS-SPME using the proposed fibre followed by GC-FID analysis were linear in a concentration range of $0.1–500\,\mu g\,L^{-1}$ ($r > 0.999$) with detection limits below $0.012\,\mu g\,L^{-1}$ for three isomers. Repeatability of the method was less than 6% (RSD%, $n = 4$). Good recoveries (88–108%) were obtained for the extraction of mono-nitrotoluenes in real water samples.

Keywords: nano-structured polypyrrole; headspace solid phase microextraction; mono-nitrotoluenes; dodecylbenzene sulphonate

Abbreviations: HS-SPME, headspace solid phase microextraction; MNT, mono-nitrotoluene; DBS, dodecylbenzene sulphonate; CV, cyclic voltammetry; SDME, single drop microextraction; HSME, headspace microextraction

1. Introduction

The extraction selectivity and efficiency of solid-phase microextraction (SPME) mainly depend on the coating's properties and its interactions with the analytes [1]. Recently, efforts have been made to obtain high extraction efficiency for SPME, including the use of porous coatings for SPME characterised by high distribution constants. New extraction materials, such as sol–gel method based materials [2] and conducting polymers [3,4], have

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310903267349
http://www.informaworld.com

also been utilised, due to their porous extraction phases and multifunctional properties. Higher extraction selectivity than commercial SPME fibres has been achieved for some compounds. Since the amount of analyte extracted by solid porous coatings is proportional to the surface area of the extraction phase (Equation (1)), the sensitivity of a method can be improved by increasing the surface area of the extraction phase [1]:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = (D_s A/\delta)C_s \tag{1}$$

where n is the mass of analyte extracted over the sampling time t, A is the surface area of the extraction phase, D_s is the diffusion coefficient of the analyte in the sample matrix, and δ is the thickness of the boundary layer surrounding the extraction phase.

In the past decade, nano-structured materials have been the focus of scientific research [5,6] due to their unusual optical [7], chemical [8], photoelectrochemical [9] and electronic properties [10]. Effective area of the materials with structures in nano-scale greatly increases, which is a favourable feature in view of a possible application as an extracting phase of SPME. Porous nano-structured coating should significantly increase the available surface area of the fibre and therefore, increase its extraction capacity [11,12]. Limited studies on the application of nano-structured fibres in SPME are available. Carbon nanotubes [13,14], nano-structured lead dioxide [11], nano-structured titania [15] and nano-structured polyaniline (PANI) [16] are the coatings used in SPME, up to now.

Due to the inherent multifunctional properties of polypyrrole, primarily π–π interactions, base acid interactions and interactions from polar groups and hydrogen bonding, polypyrrole coating can be used for SPME of a large range of analytes [17]. The physical properties of polypyrrole films such as morphology, porosity, mechanical property and thermal stability are influenced by the counter ions used. The nature and size of counter ions have a significant effect on the properties of polypyrrole. It has been shown that improved mechanical and thermal properties can be achieved for polypyrrole films when large aromatic counter anions (i.e. sulphonated aromatic ions) are incorporated into the films [18–20]. One of the developed methods for nano-structured polypyrrol fabrication includes templated free electropolymerisation in the presence of surfactants [21]. Dodecylbenzene sulphonate (DBS) is a suitable dopant for preparing more stable and robust polypyrrole SPME coating and in addition can be used as surfactant for preparing nano-structured PPY.

Nitroaromatic chemicals are used to synthesise a wide variety of industrial products. The nitrotoluenes are high production chemicals with over 30 million pounds of ortho-mononitrotoluene (*o*-MNT) and over 10 million pounds of para-mononitrotoluene (*p*-MNT) produced in the USA each year. These chemicals are in the EPA list of high production chemicals and there is potential for human exposure [22]. It is reported that *o*-MNT caused clear evidence for cancer in rats and mice; and *p*-MNT caused only equivocal evidence of carcinogenic activity in male rats; some evidence of carcinogenic activity in female rats; equivocal evidence of carcinogenic activity in male mice; and no evidence of carcinogenic activity in female mice [23]. There are a few reports regarding headspace analysis of MNTs in different matrices. Psillakis and Kalogerakis [24] used SPME and single-drop microextraction (SDME) for the analysis of nitroaromatic explosives in water samples. They achieved the limit of detection (LOD) of 0.03 and 0.08–0.11 $\mu g\,L^{-1}$ for MNTs by SPME and SDME, respectively. Perr *et al.* [25] used SPME-ion mobility spectrometry for the analysis of MNTs in the headspace of common explosives. The LOD values of 0.57 and 0.32 $ng\,L^{-1}$ were obtained for 2- and

4-nitrotoluene, respectively. Berg *et al.* [26] analysed nitroaromatic compounds in aqueous samples using SPME coupled to GC/MS. LODs of the method were 0.011 and 0.012 $\mu g\,L^{-1}$ for 2- and 4-nitrotoluene, respectively.

Different modified polypyrrole polymer was used as coating for SPME. Yu and Lia [27,28] used molecularly imprinted polypyrrole modified carbon nanotubes on stainless steel frit for selective micro solid phase pre-concentration. Djozan *et al.* [29] applied modified polypyrrole with tetrasulphonated nickel phthalocyanine as a fibre for SPME. In the present work, a simple method was proposed for synthesis of nano-structured polypyrrole coating using dodecylbenzene sulphonate dopant and the prepared coating was used for HS-SPME of the three MNTs isomers in aqueous samples. The extraction efficiency of nano-structured polypyrrole coating for microextraction of MNTs was compared to a micro-structured one using a HS-SPME device coupled with gas chromatography-flame ionisation detection (GC-FID).

2. Experimental

2.1 *Reagents and materials*

Reagent grade methanol, *p*-nitrotoluene, *m*-nitrotoluene, *o*-nitrotoluene (Merck, Darmstadt, Germany) were used without any further purification. Pyrrol (98%) (Aldrich, Milwaukee, WI, USA) was triply distilled until a colourless liquid was obtained and then stored under nitrogen before use. All of the required solutions were prepared using deionised water provided from a Milli-Q (Millipore, Bedford, MA, USA) purification system. Sodium chloride, sodium dodecylbenzene sulphonate (DBS) and lithium perchlorate were purchased from Merck.

The wastewater sample was obtained from the Research Center of Azad University (Tehran, Iran) and the well water sample was collected from the north region of Tehran (Iran).

2.2 *Apparatus*

A Varian 3800 CP gas chromatography (GC) equipped with a flame ionisation detector and split/splitless injector was used for all analyses. A CP-Sil-5 fused silica capillary GC column (25 m × 0.32 mm i.d. and 0.52 μm film thickness) was used for separation of MNTs. Nitrogen (99.999%) was used as carrier gas at a flow rate of 2 $mL\,min^{-1}$. The injector and detector temperatures were set at 250°C and 300°C, respectively. The injection mode was splitless and 0.75 mm I.D. inlet liner was used for SPME applications. The column oven was initially held at 45°C for 1 min, programmed to 100°C at a rate of 10°C min^{-1}, hold for 5 min at 100°C and then programmed to 250°C at a rate of 20°C min^{-1}. The total analysis time was 19 min. A Heidolph MR 3001 K magnetic stirrer (Schwabach, Germany) was used to heat and stir the sample during the extraction procedure. Polytetrafluoroethylene (PTFE) coated stir bars (8 mm × 3 mm) were put in 13 mL vials just before runs. Surface characteristics of the prepared polypyrrole fibres were studied by scanning electron microscopy (SEM) using a Philips XL30 instrument (Eindhoven, The Netherlands). A SPME holder for manual sampling was purchased from Azar Electrode Co. (Urmia, Iran). Electropolymerisation was performed using a Metrohm 747 VA polarograph (Herisau, Switzerland) which was controlled by electrochemical software, VA Data Base 2.

2.3 *SPME fibre preparation*

Polypyrrole films were prepared electrochemically using a three-electrode system. Prior to the electrodeposition, the platinum wire (working electrode, 250 µm diameter) was dipped in acetone for 10 min in ultrasonic bath to remove the organic contaminants on the surface before rinsing in ultrapure water. A platinum strip with thickness of 0.1 cm was used as a counter electrode and an Ag|AgCl|KCl (sat) electrode was employed as a reference electrode. An aqueous solution of 0.15 M pyrrole/ 7×10^{-3} M NaDBS was prepared for depositing of the polypyrrole film on Pt wire. A cyclic voltammetry (CV) method was used to fabricate polypyrrole nano-structures. The potential was scanned between 0 and +0.8 V *vs*. Ag|AgCl|KCl (sat) with a scan rate of 50 mV s^{-1} and the number of scans was set at 50 cycles. According to the SEM study, the average thickness of the polypyrrole-DBS coating obtained under these conditions was 20 µm. Micro-structured polypyrrole was synthesised in 0.15 M pyrrole and 0.1 M lithium perchlorate electrolyte solution using cyclic voltammetry. The CV operation conditions and the average thickness of obtained coating were similar to the pyrrole-DBS preparation.

All the experiments were performed at room temperature (25 ± 1°C). The polypyrrole films formed on the surface of the Pt wire were subsequently washed with deionised water, then with methanol or acetone for 3 min and dried under nitrogen stream at room temperature. Finally, the fibres were connected to the stainless steal tubing of the SPME holder and conditioned at 280°C for 30 min in a GC injector port under nitrogen flow before being applied for the SPME experiments.

2.4 *SPME sampling conditions*

A stock standard solution of MNTs (1000 mg L^{-1}) was prepared in methanol. The standard solutions were stored at 4°C and brought to the ambient temperature just prior to use. The working standard solutions in the range of (0.01–800 µg L^{-1}) were prepared by proper dilution of the stock solution with water. After addition of 5 mL of the working solution into a 13 mL glass vial and a magnetic stirring bar, the vial was sealed. The nano-structured polypyrrole fibre was exposed to the headspace of solution by piercing the septum with the SPME needle assembly and then depressing the plunger. During the extraction, the vial was thermostated using a heated circulating water bath and the temperature was maintained at the desired value. After extracting for a defined time, the fibre was withdrawn into the needle and removed from the sample vial. The fibre was then immediately inserted into the injection port of the GC and the analytes were then thermally desorbed into the GC injection port at 250°C for 2 min. Fibre blanks were run between the analyses. The identification of compounds was made by comparison of the retention times of the GC peaks with those of the standard compounds.

3. Results and discussion

3.1 *Morphology characterization*

The surface morphology of the polypyrrole films was characterised by SEM. Figures 1a and 1b show the morphology of the micro- and nano-structured polypyrrole films prepared in the presence of perchlorate and DBS counter ions, respectively. Figure 1c is the morphology of nano-structured polypyrrole film in higher magnification (×30,000) than Figure 1b. As shown in Figure 1c, polypyrrole synthesised with DBS

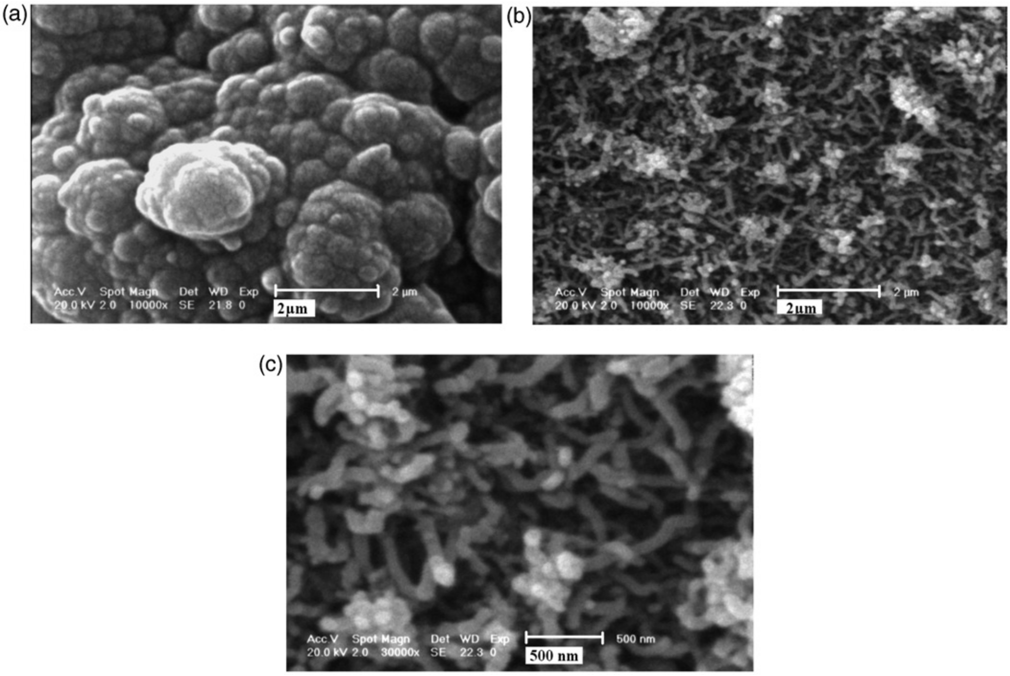

Figure 1. Scanning electron microscopy images of micro-structured polypyrrole at 10,000 magnifications (a) and nano-structured polypyrrole at 10,000 (b) and 30,000 (c) magnifications.

dopant possesses fibrous morphology including fibres with estimated diameter in the range of 38–129 nm (estimated by SEM software). Whereas, polypyrrole synthesised with perchlorate dopant possesses agglomerated globular morphology including globules with micro scale.

Pyrrole/DBS micelles might form during the synthesis of nano-structured polymer in the presence of DBS, due to the hydrophobicity of pyrrole and the hydrophilicity of sulphonate group of DBS. If DBS is assigned as a ‘head’ and pyrrole as a ‘tail’, the micelles with ‘head-tail’ structure can be formed. In general, spherical micelles are expected to form through aggregation process first [30] due to the lowest surface energy. They have a fluid surface due to the repulsive interaction of the ‘head’ group of the micelles. At the same time, a portion of the free pyrroles existing in the reaction solution can be diffused into the micelles. When the potential is applied, the electropolymerisation mainly takes place in the micelle/water interface. The surfactant molecules can surround the deposited polypyrrole particles and restrict their further growth. Consequently, the particles’ dimension is diminished [31,32].

3.2 *Comparison of extraction efficiency of micro- and nano-structured polypyrrole fibres*

In order to compare the extraction efficiency of micro- and nano-structured polypyrrole fibres, nano- (polypyrrole-DBS) and micro-structured (polypyrrole-ClO_4) PPY fibres were used for the HS-SPME extraction of the standard solutions of MNTs under the same conditions. Figure 2 shows that the extraction efficiency of MNTs by nano-structured

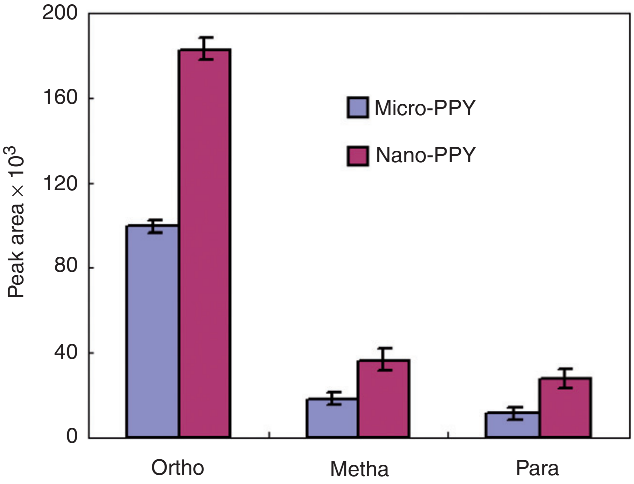

Figure 2. Comparison of the peak areas of MNTs obtained by nano- (Nano-PPY) and micro-structured (Micro-PPY) PPY fibres. Conditions: the MNTs concentration, 10 µg L^{-1}; sample temperature, 45°C; stirring speed, 400 rpm; extraction time, 15 min; without salt addition. The sampling was conducted in HS-mode.

Table 1. The peak areas of different compounds extracted by nano- and micro-structured polypyrrole.

	Peak area (× 10^3)		
Fibre type	*o*-MNT	*m*-MNT	*p*-MNT
Nano-PPY	180	40	30
Micro-PPY	100	20	10

polypyrrole fibres is higher than micro-structured one. Table 1 shows the peak areas of different compounds extracted by nano- and micro-structured polypyrrole.

As expected, the higher surface area and extraction capacity of the nano-structured polypyrrole compared to the micro-structured polypyrrole resulted in a higher extraction yield. On the other hand, the differences in the extraction efficiencies between micro- and nano-structured polypyrrole could also be a result of the different polarity of the particles in the surface area.

3.3 *Optimisation of SPME procedure*

Various extraction parameters including extraction time, adsorption temperature, stirring rate and ionic strength that affect the efficiency for the HS-SPME of MNTs by nano-structured fibre were optimised.

During the SPME sampling, the analytes should achieve an equilibrium distribution between the sample matrix and the fibre coating. The equilibration time should be

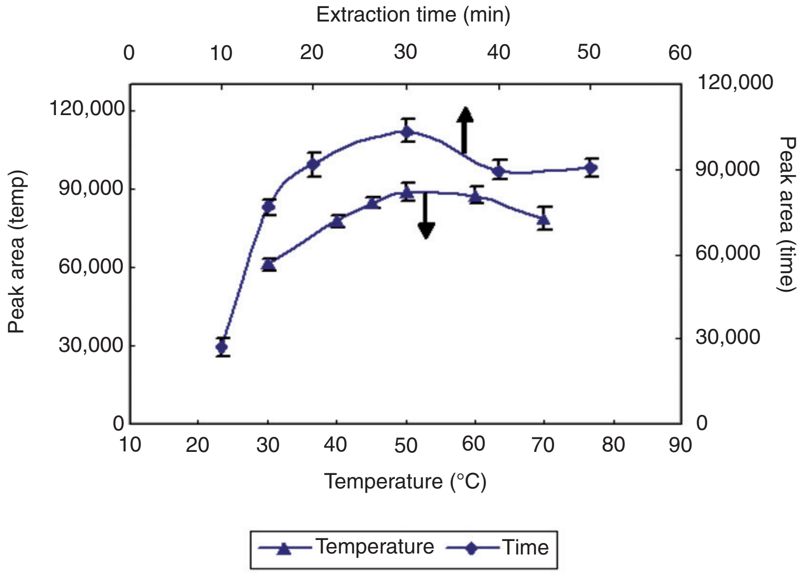

Figure 3. Effects of extraction time and temperature on the HS-SPME efficiency of the *o*-MNT with nano-structured PPY. Conditions: the MNTs concentration, 10 μg L^{-1}; stirring speed, 400 rpm; without salt addition. The sampling was conducted in HS-mode.

separately determined for each analyte, since it depends on partition coefficient of the analytes [33]. To find the best extraction time, the fibre was exposed to the headspace of the spiked samples containing 10 μg L^{-1} of MNTs for 10, 15, 20, 30, 40 and 50 min in 50°C. The adsorption time profile for *o*-MNT, as a model compound, is shown in Figure 3. It can be observed that the peak area increases as a function of time and the maximum peak area is obtained at 30 min but the peak area is decreased after 30 min for *o*-MNT.

It can be related to this fact that *o*-MNT is the most volatile MNT between the three MNTs and it could be lost during the long period of extraction time. It should be noted that the same profile was observed for *m*-MNT and *p*-MNT until 30 min and then reached a plateau when equilibrium was established. Thus, 30 min was selected as the extraction time in the subsequent experiment.

In order to study the effect of temperature on the extraction process, the procedure was followed at varying temperatures in the range 30–70°C for 15 min. Figure 3 illustrates that an increase in the extraction efficiency was observed when the temperature of the sample solution increased from 30 to 50°C. When the extraction temperature exceeded 50°C, a significant decrease in the sensitivity was observed for the extraction and determination of the MNTs. Thus, a working temperature of 50°C was selected for further experiments. High temperatures are supposed to release more analytes into the headspace, allowing better extraction due to the enhanced mass transfer kinetics. On the other hand, it can be related to this fact that *o*-MNT is the most volatile one between the three MNTs and it could be lost during the long extraction time. Since adsorption is generally an exothermic process, the extraction by the fibre coating decreases at higher temperatures. Figure 4 reveals that the chromatographic peak areas of the analyte increased up to 1000 rpm and then remained more or less constant. Therefore, for further experiments, a stirring rate of 1000 rpm was chosen.

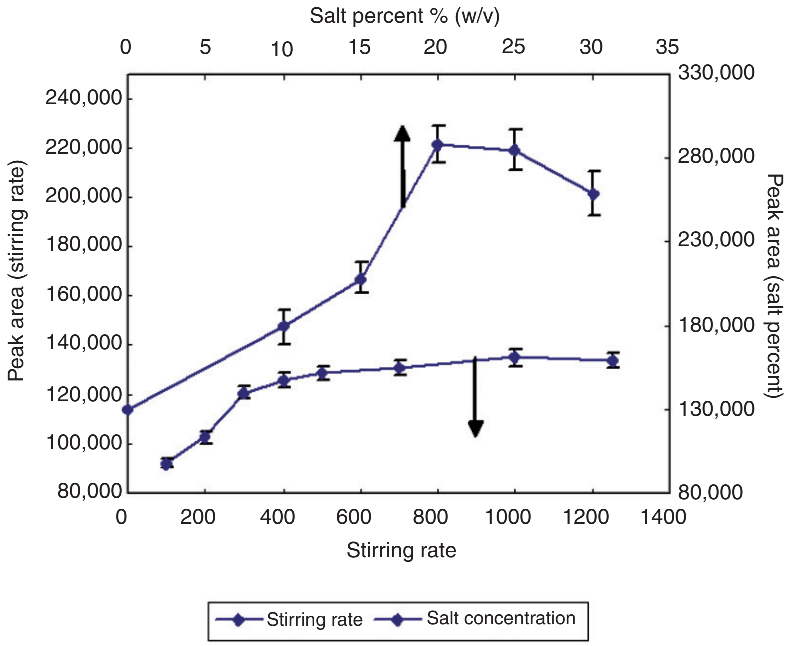

Figure 4. Effects of stirring rate and salt concentration on the HS-SPME efficiency of the *p*-MNT with nano-structured PPY. Conditions: the MNTs concentration, 10 µg L^{-1}; sample temperature, 50°C; stirring speed, 1000 rpm; extraction time, 30 min. The sampling was conducted in HS-mode.

The suitability of the HS-SPME technique for the extraction of compounds depends on the transfer of the analyte from the sample into the gaseous phase and, therefore, into the fibre. Figure 4 shows the effect of addition of NaCl in the range of 0–30%(w/v) on the HS-SPME of *o*-MNT. It was observed that the chromatographic signal increased as the amount of NaCl increased, reaching a maximum value and then decreased with further increase in salt concentration. Initially, the analyte recovery is enhanced due to '*salting-out*' effect, whereby the water molecules form the hydration spheres around the ionic salts molecules, and there is a reduction in the concentration of water available to dissolve the analyte molecules [34,35]. This behaviour is found especially for the analytes with low hydrophobicity. On the other hand, increasing ionic strength may cause the analyte molecules to participate in the electrostatic interactions with the salt ions in the solution, thereby reducing their ability to move into the fibre coating [36]. Accordingly, NaCl (20%w/v) was added into the solutions and samples in the subsequent experiments.

To investigate the desorption temperature, the extraction from a solution with 10 µg L^{-1} concentration of MNTs was performed at optimum conditions. The injector temperatures were adjusted in the range of 200–300°C. It was observed that above 250°C; the peak area was not increased, significantly (data not shown here). Therefore, 250°C was selected as a desorption temperature. To avoid carry-over effect, the desorption time should be sufficient for quantitative desorption of the extracted analytes from the surface of the nano-structured polypyrrole coated SPME fibre. Various desorption times (1, 2, 3, 4, and 5 min) at 250°C were also tested to investigate the effect of desorption time on the chromatographic peak areas of the analytes. It was found that the peak areas of the analytes slightly increased as the desorption time increased from 1 to 2 min and then remained unchanged with further increase of the desorption time to 5 min. Therefore, in the subsequent experiments, the desorption time was set at 2 min.

3.4 *Analytical performance characteristics*

Under optimum conditions, each solution was analysed five times. The standard solutions were filtered to test the influence of the filtering process on the probable adsorption of MNTs onto the filter paper. It was observed that the filtration process did not have any influence on the MNTs concentrations.

LODs, dynamic linear ranges (DLRs), correlation coefficients (*r*) and relative standard deviations (RSDs) for three isomers of MNTs were obtained (Table 2). Eleven concentrations in the concentration range of 0.01–800 $\mu g\,L^{-1}$ were examined and the calibration curves were linear in the range of 0.1–500 $\mu g\,L^{-1}$ for the MNTs. The values of correlation coefficient were obtained as 0.999, showing an acceptable linearity. The RSD values for the analytes (repeatability for one fibre) ranged between 4.0 and 6.0%, while fibre-to-fibre RSDs varied in the range of 11.2 to 15.1%. The LODs for *o*-MNT, *m*-MNT and *p*-MNT were 0.017, 0.01, and 0.012 $\mu g\,L^{-1}$, respectively, at a signal-to-noise ratio (S/N) of 3. At least 50 extractions can be conducted with maintained performance using the proposed polypyrrole fibre.

This method revealed suitable reproducibility with RSD values in the range of 4.1–6.0%. Also fibre-to-fibre RSDs varied in the range 11.2–15%. Table 3 compares LODs and RSDs for the extraction and determination of MNTs in water samples by applying headspace microextraction (HSME) [37], single drop microextraction (SDME)

Table 2. LODs, correlation coefficients (R^2), DLR and RSDs values for the extraction and determination of MNTs in the aqueous samples by the proposed method.

Analyte	LOD ($\mu g\,L^{-1}$)	R^2	RSD % One fibre	RSD % Fibre-to-fibre	DLR ($\mu g\,L^{-1}$)
o-nitrotoluene	0.017	0.999	4.1	11.2	0.1–500
m-nitrotoluene	0.010	0.999	4.5	13.1	0.1–500
p-nitrotoluene	0.012	0.996	6.0	15.1	0.1–500

Table 3. Comparison of LODs, RSDs and correlation coefficient (*r*) of different extraction methods of mono-nitrotoluenes.

Method	Matrix	LOD ($\mu g\,L^{-1}$)	RSD (%)	*r*	Reference
SPME-GC-FID (Nano-polypyrrole fibre)	Well water	0.01	7.6–10.3	0.999	Proposed method
SPME-GC-MS (PDMS-DVB fibre)	Groundwater	0.03	5.9–6.0	0.992–0.994	[24]
HSME-GC-MS	Groundwater	0.08–0.11	9.3–9.7	0.985–0.986	[37]
SDME-GC-FID	Well water	0.02–0.06	2.6–6.6	0.998–0.999	[38]

Table 4. MNTs concentration found in waste- and well water samples, relative recovery and RSD values.

	Analyte											
	o-nitrotoluene				*m*-nitrotoluene				*p*-nitrotoluene			
Sample	C_{added} ($\mu g\,L^{-1}$)	C_{found} ($\mu g\,L^{-1}$)	RSD %	Rec[b] %	C_{added} ($\mu g\,L^{-1}$)	C_{found} ($\mu g\,L^{-1}$)	RSD %	Rec %	C_{added} ($\mu g\,L^{-1}$)	C_{found} ($\mu g\,L^{-1}$)	RSD %	Rec %
Wastewater	–	180.0[a]	11.6	–	–	10.0	9.2	–	–	80.0	10.3	–
	100.0	289.0	11.3	103.2	10.0	18.7	9.8	93.5	80.0	143	11.1	89.3
Well water	–	–	–	–	–	–	–	–	–	–	–	–
	4.0	4.3	9	108.1	4.0	3.61	7.6	93.3	4	3.4	10.3	88.2

Notes: [a] Mean value of four replicate measurements.
[b] Relative recovery.

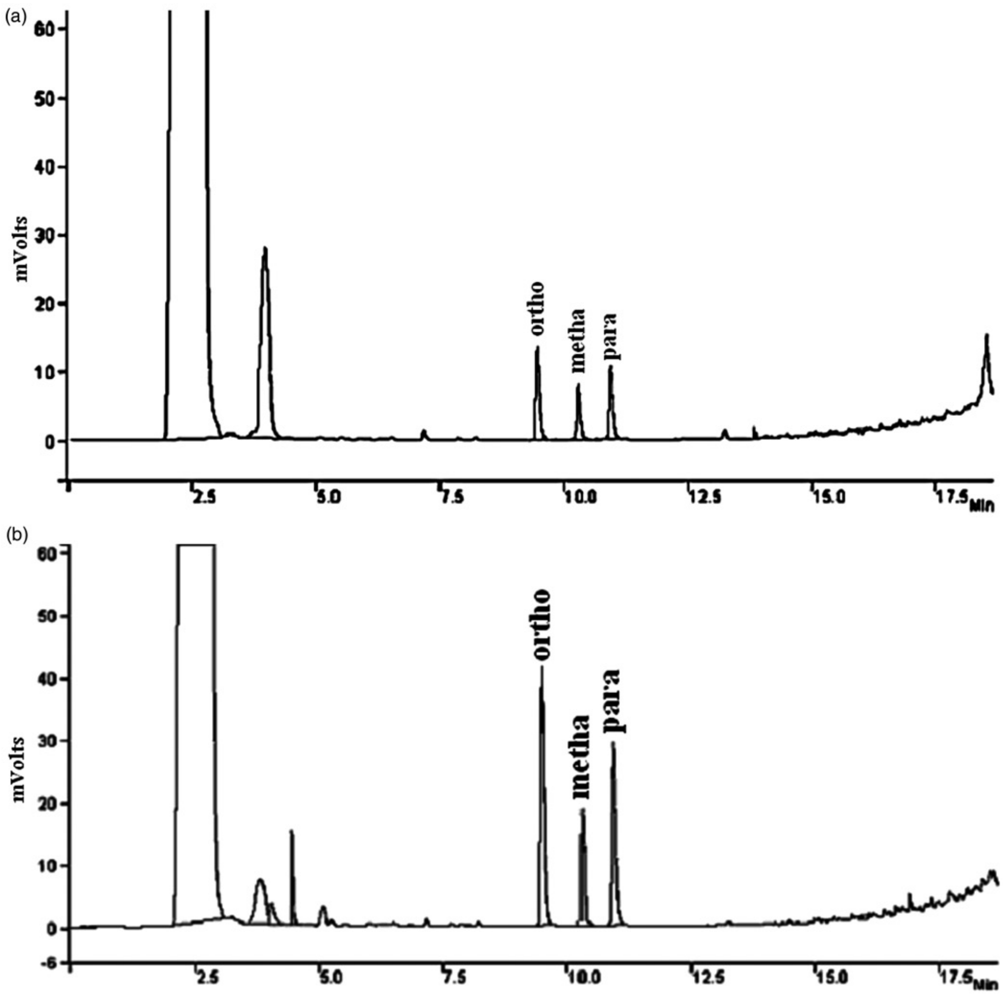

Figure 5. HS-SPME-GC–FID chromatograms of the non-spiked (a) and spiked wastewater with 100, 10 and 80 µg L^{-1} for *o*-MNT and *m*-MNT and *p*-MNT, respectively (b). Peaks: *o*-MNT (1), *m*-MNT (2) and *p*-MNT (3).

[38] and SPME methods [25]. It clearly shows that SPME with nano-structured polypyrrole fibre yields lower detection limits and better correlation coefficients (r) for the tested analytes.

3.5 *Application to real samples*

The waste- and well water samples were filtered before use and collected in amber glass bottles. Then the water samples were transported and stored at 4°C to await analysis for MNTs (without any pre-treatment). The applicability of the extraction method to the real samples was examined by extraction and determination of MNTs from the water samples.

The proposed method was successfully applied to determine MNTs in both waste- and well water samples. The results obtained from five repeated measurements are shown in Table 4. The results of well water sample analysis showed that it was free from MNT contamination, but low contents of *o*-MNT (180 $\mu g\,L^{-1}$), *m*-MNT (10 $\mu g\,L^{-1}$) and *p*-MNT (80 $\mu g\,L^{-1}$) were detected in the wastewater sample. The accuracy of the proposed method was tested by spiking the water samples with known amounts of the samples followed by applying the method to extract and determine the MNTs. The results demonstrated that real sample matrices had little effect on the efficiency of the proposed HS-SPME method. Therefore, the proposed fibre is suitable for the analysis of trace levels of MNTs in real water samples. Figures 5a and 5b show a typical gas chromatogram obtained for the non-spiked and spiked (with 100 $\mu g\,L^{-1}$ of *o*-MNT, 10 $\mu g\,L^{-1}$ of *m*-MNT and 80 $\mu g\,L^{-1}$ of *p*-MNT) wastewater, respectively.

4. Concluding remarks

Nano-structured polypyrrole film was electrochemically synthesised and used as a SPME fibre for GC-FID determination of trace MNTs in aqueous solutions. The nano-porous structure of polypyrrole was verified by scanning electron microscope. The nano-structured coating provided a high surface area that allowed for higher extraction efficiency than the micro-structured coating. Fast extraction equilibrium and desorption time, high mechanical stability, strong adhesion of the coating to the substrate and relatively low cost are some of the advantages of prepared nano-structured polypyrrole fibre. The proposed fibre was successfully applied to the analysis of MNTs in real water samples.

Acknowledgement

Financial support from the Research Affairs Department of Shahid Beheshti University is gratefully acknowledged.

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