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Development of a hollow fibre liquid phase microextraction method to monitor the sonochemical degradation of explosives in water

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Abstract

A novel method for the enrichment of nitroaromatic compounds present in water samples is presented here coupling hollow fibre liquid phase microextraction (LPME) with gas chromatography. A hydrophobic porous polypropylene hollow fibre was used as the interface between the donor water sample and microvolumes of the acceptor organic phase. Parameters such as extraction solvent, stirring rate, salt concentration and sampling time were studied and optimised. Overall, extraction of 11 nitroaromatics was achieved by exposing 3 μl of toluene for 20 min in a 5 ml stirred aqueous solution at room temperature. The developed protocol yielded a linear calibration graph in the concentration range 10–500 $\mu g\,l^{-1}$ and the limits of detection were calculated to range between 0.29 and 0.87 $\mu g\,l^{-1}$. Precision expressed in terms of relative standard deviation varied between 6.1 and 11.8%. The developed hollow fibre LPME method was subsequently used successfully to monitor the sonochemical degradation of an aqueous solution containing 100 $\mu g\,l^{-1}$ of each target analyte at an ultrasonic frequency of 80 kHz. Ultrasonic treatment was found capable of efficiently removing the 2-, 3- and 4-nitrotoluene isomers as well as the 2- and 4-amino dinitrotoluene isomers within 300 min of irradiation. The rest of the analytes were more recalcitrant and significant removal was not observed even after prolonged times of ultrasonic irradiation.
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Keywords: Liquid phase microextraction; Nitroaromatics; Extraction; Ultrasound

1. Introduction

Over the past few decades site investigations of past and present military installations in the USA and Europe confirmed the presence of nitroaromatic explosives and their metabolites caused by extensive manufacturing, storage or even leakage from unexploded ordnance. Explosives are moderately to weakly soluble in water and thus can migrate through subsurface soil to cause groundwater contamination [1]. Once they enter the environment, they are exposed to environmental and biological processes, yielding by-products of high reactivity and often greater polarity and water solubility, which may constitute an even greater environmental concern than the original compounds themselves [2]. The presence of these hazardous waste mixtures in sediments and aquifers presents a major challenge in terms of developing efficient and sensitive analytical methods as well as implementing effective and feasible remediation technologies.

Conventional liquid–liquid extraction (LLE) has been the main method for enrichment of nitroaromatic compounds from aqueous solutions [3]. Although LLE is widely used, it presents many disadvantages such as being a labour intensive and time-consuming method which requires the use of large amounts of high purity solvents. Driven by the need to overcome these drawbacks, new simple and rapid sample preparation techniques have been developed over the last two decades including solid-phase extraction [4] and solid phase microextraction (SPME) [5,6]. A recent trend in sample pre-treatment techniques involves the miniaturisation of the LLE extraction procedure by greatly reducing the solvent (acceptor) to aqueous (donor) phase ratio. A technique that evolved from this approach is single drop microextraction (SDME), where the extractant phase is a microdrop of a water-immiscible solvent suspended on the tip of a conventional microsyringe, immersed in a contaminated water sample [7,8]. Another way of miniaturising the LLE process is by using a membrane to separate the acceptor–donor

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phases. Hollow fibre liquid phase microextraction (LPME) evolved from this approach. According to this method, a porous polypropylene hollow fibre impregnated with an organic solvent is used as an interface between the donor and acceptor phase [9]. In one of the possible configurations, the fibre is connected at one of its ends to the needle tip of a microsyringe while the other end is left suspended in the sample solution [10]. This fibre configuration is considered to be an evolution of SDME due to the protective feature of the hollow fibre for the organic phase. Hollow fibre LPME has been successfully applied for the extraction of drugs from a variety of biological fluids or for the preconcentration of pollutants from several environmental matrices [11]. Overall, this recently introduced method proved to be an attractive alternative to other microextraction concepts having the advantages of being simple, inexpensive, sensitive, fast and virtually solvent-free. In addition, the disposable nature of the hollow fibre due to the low cost of analysis per sample eliminated the possibility of carry-over between analyses.

Water treatment technologies are continuously improved, particularly in the field of advanced oxidation processes, to meet the more demanding water quality standards for groundwater decontamination and municipal/industrial wastewater discharge. In this respect, the use of high power ultrasound with frequencies in the range 20–1000 kHz has gained considerable attention in recent years as a promising remediation technology for hazardous pollutants elimination. Extreme temperatures of several thousand degrees and pressures of several hundred atmospheres can be developed locally within the bubbles during their collapse with these bubbles serving as hot spot "microreactors" in an otherwise cold liquid [12]. It is generally believed that there are three potential zones for chemical reactions in ultrasonically irradiated aqueous solutions, namely: the bubble itself, the interface between the bubble and the surrounding liquid, and the solution bulk. Compounds may degrade directly via pyrolytic reactions occurring inside the bubble and/or at the interfacial region or indirectly via radical reactions occurring at the interface and/or in the solution bulk. The latter involve the participation of OH radicals and possibly H atoms that are formed from the water dissociation within the bubble and migrate towards the interface and the solution bulk. Several studies report the sonochemical degradation of various pollutants commonly found in waters and wastewaters, including amongst others chlorinated hydrocarbons, aromatic compounds, pesticides, explosives, dyes and surfactants; these studies are summarised in a recent review by Adewuyi [13]. However, it is notable that very few studies report the use of ultrasound for the destruction of nitroaromatics in water. The sonochemical degradation at 20 kHz of 2,4,6-trinitrotoluene (TNT), 2-amino-4,6-dinitrotoluene (2-ADNT) and 4-amino-2,6-dinitrotoluene (4-ADNT) was investigated by Goskonda et al. [14], while Weavers et al. [15] demonstrated the synergistic effects of ultrasonic irradiation at 20 and 500 kHz and ozonation for the degradation of nitrobenzene (NB) and 4-nitrophenol. In further studies, Sierka [16] studied the beneficial synergy between ultrasound at 859 kHz and ozonation for the degradation of a mixture of TNT and 1,3,5-trinitro-1,3,5-triazine (RDX), while Hoffmann et al. [17] studied the sonochemical degradation of TNT at 20 and 500 kHz in the presence of various saturating gases (i.e. oxygen, argon and a mixture of oxygen and ozone).

The primary objective of this work is to develop and optimise an innovative analytical protocol for the extraction of nitroaromatic explosives from water samples based on the hollow fibre LPME methodology, thus providing a sensitive, cost-effective and easy-to-use tool for the environmental monitoring of such pollutants. The developed protocol is then used to follow concentration–time profiles of several explosives subject to ultrasonic irradiation in synthetic aqueous solutions. Although previous reports have dealt with the sonochemical degradation of single-component solutions containing some nitroaromatic explosives, this is the first report on the use of LPME to monitor the sonochemical degradation of low concentration multi-component solutions of these compounds.

2. Experimental

2.1. Chemicals and sample preparation

Target analytes were purchased from Supelco (Bellefonte, PA, USA) in the form of two separate 1 ml acetonitrile solutions (Mix A and Mix B). Mix A contained 2-ADNT, 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrotoluene (2,4-DNT), RDX, NB, 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), 1,3,5-trinitrobenzene (1,3,5-TNB), TNT, each at 100 $\mu g\,ml^{-1}$. Mix B contained 4-ADNT, 2,6-dinitrotoluene (2,6-DNT), 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), 4-nitrotoluene (4-NT) and N-methyl-*N*,2,4,6-tetranitroaniline (tetryl), each at 100 $\mu g\,ml^{-1}$. A toluene solution of 2,3-dinitrotoluene (2,3-DNT) (Riedel-de Haën Laborchemikalien, Seelze, Germany) was prepared and used as the internal standard solution. All solvents were pesticide-grade (Merck KgaA, Darmstadt, Germany). Deionized water was prepared on a water purification system (EASYpure RF, Barnstead/Thermolyne Dubuque, USA). Spiked aqueous solutions were prepared daily at the concentration levels of interest. For extraction, 5 ml of the corresponding spiked solution were placed in 7 ml clear glass vials (Supelco), equipped with a glass-coated flea micro spinbar (8 mm × 3 mm).

2.2. Hollow fibre LPME

A 10 μl Gastight syringe (Hamilton, Bonaduz, Switzerland), Model 1701RNR, with a blunt needle tip (length: 5.1 cm, o.d.: 0.071 cm, and i.d.: 0.015 cm), was used to introduce the acceptor phase, support the hollow fibre and act as the injection syringe. The Accurel Q 3/2 polypropylene

hollow fibre membrane (200 μm wall thickness, 600 μm i.d., and 0.2 μm pore size) purchased from Membrana (Wuppertal, Germany) was used for all LPME experiments. Each membrane unit was ultrasonically cleaned in acetone for several minutes. Once dried, it was cut manually into 1.3 cm segments which may approximately accommodate 3 μl of solvent. The length and consequently the volume capacity of the hollow fibres were adjusted to the size of the vials used in the present studies. Due to the low cost, a new fibre was used for each extraction.

The LPME procedure consisted of the following steps [18]: (i) 3 μl of the organic solvent (typically toluene) was manually withdrawn into the microsyringe followed by 3.4 μl of water; for all quantification experiments the organic phase consisted of a toluene solution of the internal standard; (ii) the hollow fibre segment was mounted onto the needle tip and the assembly was immersed for few seconds in the organic solvent for impregnation of the pores of the hollow fibre; while the fibre was immersed in the solvent solution the water in the microsyringe was injected carefully removing thus any excess of organic solvent from the inside; (iii) the fibre was then removed from the organic solvent and subsequently immersed into aqueous sample destined for analysis; the organic solvent was injected into the hollow fibre initiating extraction; (iv) after extracting for a given period of time (typically 20 min) the stirred aqueous solution (1000 rpm, unless otherwise stated within the text) at room temperature, 1.4 μl of the organic solvent was withdrawn into the microsyringe, the fibre segment was removed and the organic phase was then injected into the heated injection port of the GC–MS for further analysis.

2.3. GC–MS analysis

All analyses were carried-out using a Shimadzu GC-17A, Version 3, QP-5050A gas chromatograph-mass spectrometer. The split/splitless injector operated at 200 °C with the split closed for 1 min. Helium was used as a carrier gas at a flow-rate of 2.0 ml min^{-1}. Separation was performed on a 10 m × 0.25 mm 0.25 μm HP-5MS (equivalent to a 5% phenyl, 95% methylpolysiloxane) capillary column (Agilent Technologies). The column oven was initially held at 60 °C for 6 min, programmed to 130 °C at a rate of 5 °C min^{-1} and then to 250 °C at 20 °C min^{-1}. A 3 min solvent delay time was used. The interface temperature was set at 260 °C and the detector voltage was at 1.40 kV. The ionization mode was electron impact (70 eV). Data was acquired in the full-scan detection mode from 45 to 300 amu at rate of 0.5 scan s^{-1}.

2.4. Sonication experiments

An Ultrason 250 (LabPlant, UK) sonicator connected to a titanium-made horn, capable of operating either continuously or in a pulse mode at a fixed frequency of 80 kHz and a variable electric power output up to 150 W was used for the sonication experiments. Reactions were carried out in a cylindrical all-glass reaction vessel which was kept closed during ultrasonic irradiation and was immersed in a water bath. One hundred ninety-five millilitres of an aqueous solution containing 100 μg l^{-1} of each target analyte was subject to ultrasonic irradiation at a constant water bath temperature of 20 °C and an electric power output of 150 W. To avoid any photochemical reactions the vessel was covered with aluminium foil. Experiments were discontinued periodically to remove 5 ml samples that were analysed by means of hollow fibre LPME/GC–MS.

3. Results and discussion

3.1. Optimisation of hollow fibre LPME

The first aim of this study was to optimise hollow fibre LPME sampling conditions for the extraction of explosives from water samples. In this context several parameters (such as extraction solvent, agitation speed, ionic strength and extraction time) were monitored and controlled for optimum performance.

3.1.1. Extraction solvent

Selecting the most suitable organic solvent as the acceptor phase is an important step in hollow fibre LPME. There are several requirements for the organic solvent [11] and these include: (i) low values of solubility in water and volatility will prevent solvent dissolution into the aqueous phase and solvent evaporation during extraction; (ii) target analytes should be highly soluble to the organic solvent ensuring high distribution ratios between the acceptor and the donor phase; (iii) in cases were a GC instrument is used, the selected solvent must have an excellent chromatographic behaviour; (iv) the polarity of the acceptor organic phase should be similar to that of the polypropylene fibre so that it can be easily immobilised within the pores of the fibre. The latter greatly affects the performance of hollow fibre LPME since extraction occurs on the surface of the immobilised solvent. For the purpose of the present experiments, several water-immiscible solvents were tested (toluene, dichloromethane and hexane). Solvent selectivity was evaluated for 20 min extractions of 5 ml water samples spiked at 50 μg l^{-1} of each target analyte and stirred at 1000 rpm. Under the present experimental conditions dichloromethane failed to extract any of the target analytes and hexane resulted in the elution of small amounts of the three nitrotoluene isomers and 2,4-DNT. Toluene, on the other hand, gave the best results by combining the best extraction performance, low solvent loss during extraction and the ability to be easily immobilised in the pores of the hollow fibre within seconds. Toluene has been successfully used in the past for the liquid–liquid extraction [19] and single drop microextraction of nitroaromatic compounds in water samples [20]. As expected from these studies, investigation of nitrobenzene is restricted since this analyte co-elutes with toluene during GC–MS analysis. Furthermore, extraction of

nitramines (RDX and HMX) in toluene is limited and additional problems of thermal instability for HMX during gas chromatographic separation obstructed its detection [20,21]. Consequently, under the present experimental conditions investigation of NB, HMX and RDX was not possible.

3.1.2. Sample agitation

In another set of experiments the effect of sample agitation during extraction with toluene was investigated. In general, increasing the agitation rate of the aqueous sample enhances extraction, by aiding diffusion of analytes present in the donor phase through the interfacial layer of the hollow fibre and into the acceptor solution. In LPME, the hollow fibre protects the acceptor solution, and consequently high agitation speeds can be applied [11]. Optimisation was investigated by performing 20 min extractions on aqueous solutions containing 50 $\mu g\,l^{-1}$ of each target analyte at stir rates of 0, 300, 500, 700, 1000 and 1250 rpm. The results are shown in Fig. 1. As expected increasing the agitation rate (up to 1000 rpm) resulted in an increase of the peak areas for each target analyte. However, at 1250 rpm solvent dissolution was promoted reducing thus the volume of organic solvent injected in the analytical instrument and leading to reduced analytical signals for each analyte[19]. Thus, for all subsequent experiments a stirring rate of 1000 rpm was used.

3.1.3. Ionic strength

In order to examine the effect of ionic strength of the sample matrix upon extraction, a series of experiments were carried where the aqueous samples contained different amounts of NaCl. In general, depending on the nature of the contaminants, addition of salt to the sample solution can decrease their solubility and consequently increase their hydrophobicity [22]. This is due to the salting-out effect where fewer water molecules are available for dissolving the analyte molecules, preferably forming hydration spheres around the salt ions [23]. In hollow fibre LPME, the effect of salt addition in the donor solution prior to extraction has been investigated and the results showed that depending on the target analytes, an increase in the ionic strength of the aqueous solution may enhance, not influence or even limit extraction of analytes [11]. For the purpose of the present studies aqueous solutions containing 50 $\mu g\,l^{-1}$ of each target analyte and NaCl concentrations varying between 0 and 30% (w/v) were subject to 20 min hollow fibre LPME. The effect of NaCl addition is depicted in Fig. 2. It appears that the presence of salt either limits or causes insignificant changes on extraction efficiency. Since no significant increase in enrichment was achieved after adding salt in the sample matrix, it was decided not to alter the salt content of the sample solutions for all subsequent extractions. Similar results were obtained when single drop microextraction was used to preconcentrate nitroaromatics from water samples [20]. The authors concluded, that next to the salting-out effect, the presence of salt caused a second effect, adverse for the extraction, where the physical properties of the aqueous-organic solvent extraction film were changed, impeding thus diffusion of analytes into the toluene microdrop.

3.1.4. Sampling period

In a separate set of experiments the variation of the analytical signal for each analyte was studied as a function of

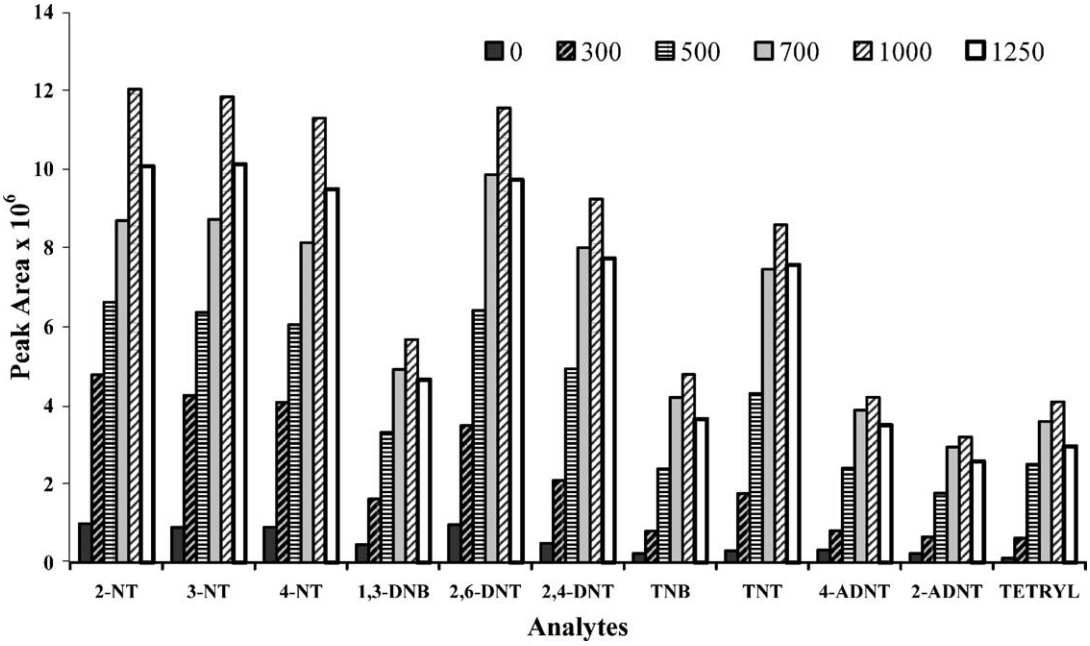

Fig. 1. The effect of stirring speed on the extraction efficiency of nitroaromatic compounds when using hollow fibre LPME with toluene as solvent. Other extraction conditions: analyte concentration 50 $\mu g\,l^{-1}$; sampling time 20 min; NaCl concentration 0% (w/v).

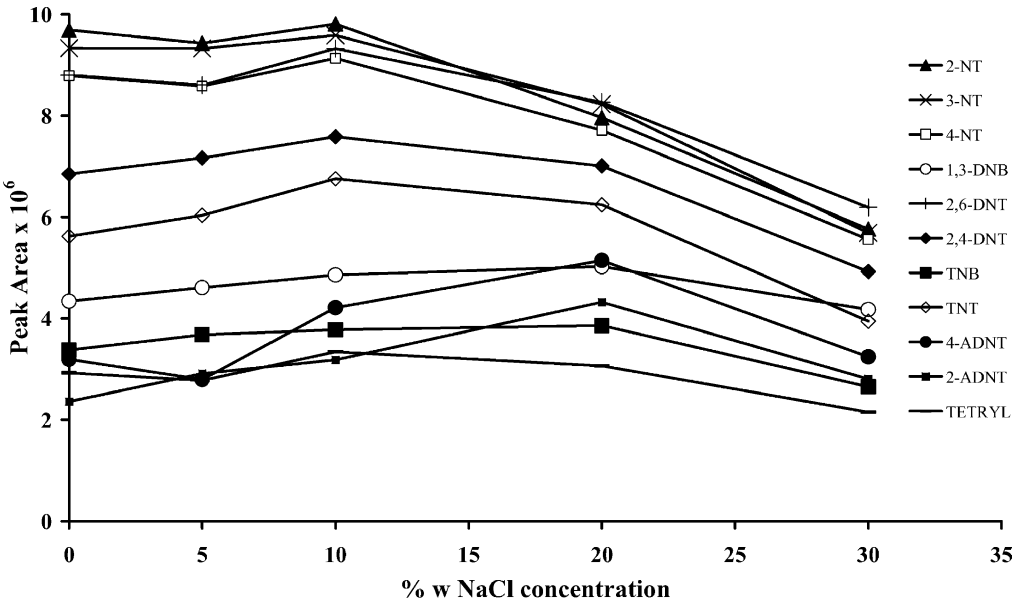

Fig. 2. The effect of salt on the extraction efficiency of nitroaromatic compounds when using hollow fibre LPME with toluene as solvent. Other extraction conditions: analyte concentration 50 $\mu g\,l^{-1}$; stirring rate 1000 rpm; sampling time 20 min.

sampling period. In general, mass-transfer is a time-dependant process and its rate is reduced the closer the system reaches to equilibrium conditions. Whether extraction is exhaustive or works as a preconcentration technique, equilibrium is only attained after exposing the acceptor solution to the aqueous sample for a "long" period of time [11]. For the purpose of the present studies, a series of standard aqueous solutions (50 $\mu g\,l^{-1}$) were prepared and extracted by varying the exposure of toluene to the sample from 5 to 30 min. Longer sampling periods were avoided since they typically resulted in significant solvent dissolution. Fig. 3 reveals that extraction efficiency increases with increasing exposure times. However, equilibrium could not be reached for any of those analytes within this time span. For quantitative analysis it is not necessary to attain equilibrium if constant extracting conditions are maintained [2]. For the purpose of the present studies, sampling period was set at 20 min matching thus the chromatography run time and maximising sample throughput.

Overall, the optimised experimental conditions found here were: 3 μl of toluene, 5 ml of water samples, 1000 rpm stirring rate and 20 min sampling time.

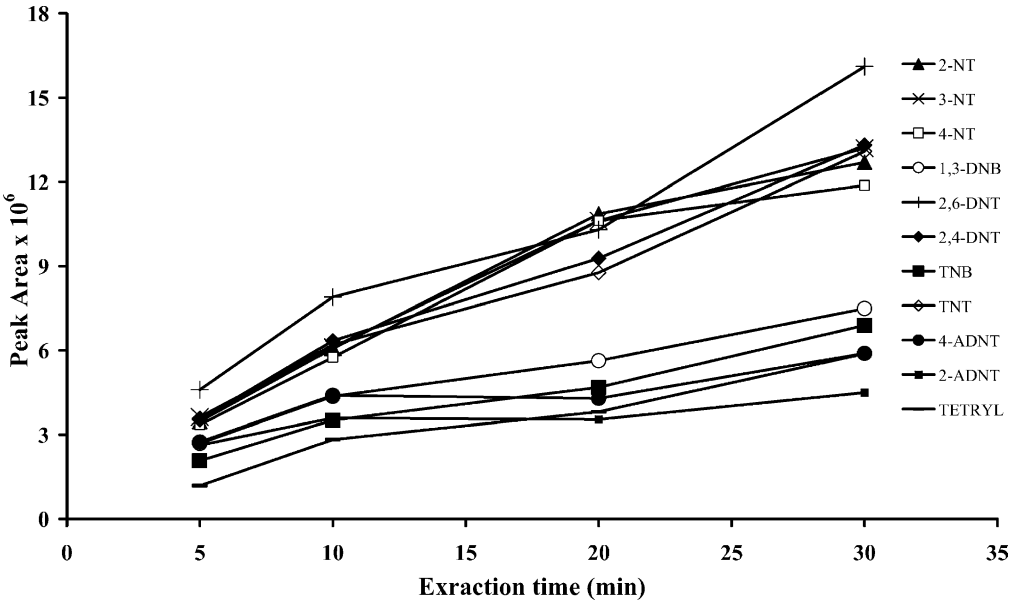

Fig. 3. The effect of sampling time on the extraction efficiency of nitroaromatic compounds when using hollow fibre LPME with toluene as solvent. Other extraction conditions: analyte concentration 50 $\mu g\,l^{-1}$; stirring rate 1000 rpm; NaCl concentration 0% (w/v).

Table 1
Main method parameters for the extraction of nitroaromatic compounds from water samples using hollow fibre LPME

Analyte	Correlation coefficient (r^2) ($n = 6$)	Limits of detection (LOD, $\mu g\,l^{-1}$)	Relative standard deviations[a] (%)
2-NT	0.9999	0.30	6.1
3-NT	0.9999	0.32	7.7
4-NT	0.9999	0.29	8.4
1,3-DNB	0.9997	0.40	9.3
2,6-DNT	0.9995	0.38	8.9
2,4-DNT	0.9995	0.45	8.1
TNB	0.9976	0.57	10.2
TNT	0.9994	0.45	10.8
4-ADNT	0.9987	0.53	8.0
2-ADNT	0.9986	0.64	9.5
Tetryl	0.9982	0.87	11.8

Optimised extraction conditions: 3 μl toluene, 5 ml water samples, 1000 rpm stirring rate and 20 min sampling time.
[a] Value for five replicate analyses; spiking level $50\,\mu g\,l^{-1}$.

3.2. Evaluation of method's performance

The linearity of the hollow fibre LPME/GC–MS procedure was evaluated over the concentration range 10–500 $\mu g\,l^{-1}$. For all quantification experiments, the organic phase consisted of a toluene solution of the internal standard. Overall, linearity was very good along the whole evaluated range with the correlation coefficients (r^2) ranging between 0.9976 and 0.9999 (Table 1). The r^2 values obtained here were similar or better than the ones reported in the literature when using the SPME [24,25] or the single drop microextraction [20] approaches.

The reproducibility of the method was determined by performing the extraction of five water samples spiked at the same concentration ($50\,\mu g\,l^{-1}$). The relative standard deviations (Table 1) ranged from 6.1 to 11.8% with a mean value of about 9% and they are comparable to those usually obtained with hollow fibre LPME [11] as well as in other microextraction procedures developed for nitroaromatic compounds [20,21,24,25].

The limits of detection (LODs) were calculated from the calibration curves that defined linearity by considering the value of the Winefordner and Long criterion according which the LOD for each target analyte is three times the standard error of the independent term of the regression divided by the value of the slope of the calibration curve [26]. As can been seen in Table 1, the LODs were in the low $\mu g\,l^{-1}$ level ranging from 0.29 to 0.87 $\mu g\,l^{-1}$, well below the drinking water standards and health advisory numbers published by the Environmental Protection Agency for increased cancer risk of 10^{-4} ($100\,\mu g\,l^{-1}$ for TNT; $5\,\mu g\,l^{-1}$ for DNB, 2,4-DNT and 2,6-DNT) [20,27].

The developed method was also applied for the determination of nitroaromatics by spiking samples of tap and surface water at $50\,\mu g\,l^{-1}$ (Table 2). Standard deviations and mean values were compared with those obtained for ultrapure water spiked at $50\,\mu g\,l^{-1}$ using the Student two-tailed *t*-test (95% probability). No significant differences were obtained for values within the statistical allowances. It was concluded that matrix effects do not interfere in the quantitation process and that the proposed method may be applied to real water samples.

Overall, the performance of the method suggests that hollow fibre LPME is a fast, sensitive and efficient analytical tool providing an attractive alternative to conventional [3] and more recently introduced sample preparation methods [20,21,24,25].

3.3. Monitoring the fate of nitroaromatic compounds in water subject to ultrasonic irradiation

The efficacy of hollow fibre LPME to monitor the sonochemical degradation of nitroaromatic compounds in water sample solutions was then investigated. An aqueous solution containing $100\,\mu g\,l^{-1}$ of each target analyte was subject to continuous ultrasonic irradiation for 300 min at a constant electric power output of 150 W, a frequency of 80 kHz and a constant water bath temperature of 20 °C. Fig. 4 compares the two total ion chromatograms obtained at time zero and after sonicating the aqueous sample solution for 300 min. The normalised concentration-time profiles of contaminants

Table 2
Mean concentrations and standard deviations of nitroaromatics measured in tap and surface waters spiked at $50\,\mu g\,l^{-1}$ determined by hollow fibre LPME followed by GC–MS

Analyte	Mean water sample concentration ($\mu g\,l^{-1}$) ± standard deviation[a]	
	Tap water	Surface water
2-NT	47 ± 3.2	45 ± 2.9
3-NT	46 ± 3.9	45 ± 3.5
4-NT	46 ± 3.7	43 ± 3.9
1,3-DNB	50 ± 4.9	49 ± 4.8
2,6-DNT	46 ± 4.0	49 ± 4.5
2,4-DNT	46 ± 3.9	49 ± 4.1
TNB	51 ± 5.1	48 ± 4.9
TNT	44 ± 4.9	43 ± 4.8
4-ADNT	45 ± 3.9	45 ± 3.8
2-ADNT	44 ± 4.1	44 ± 4.4
Tetryl	43 ± 5.6	44 ± 5.8

[a] Mean values for three replicate analyses.

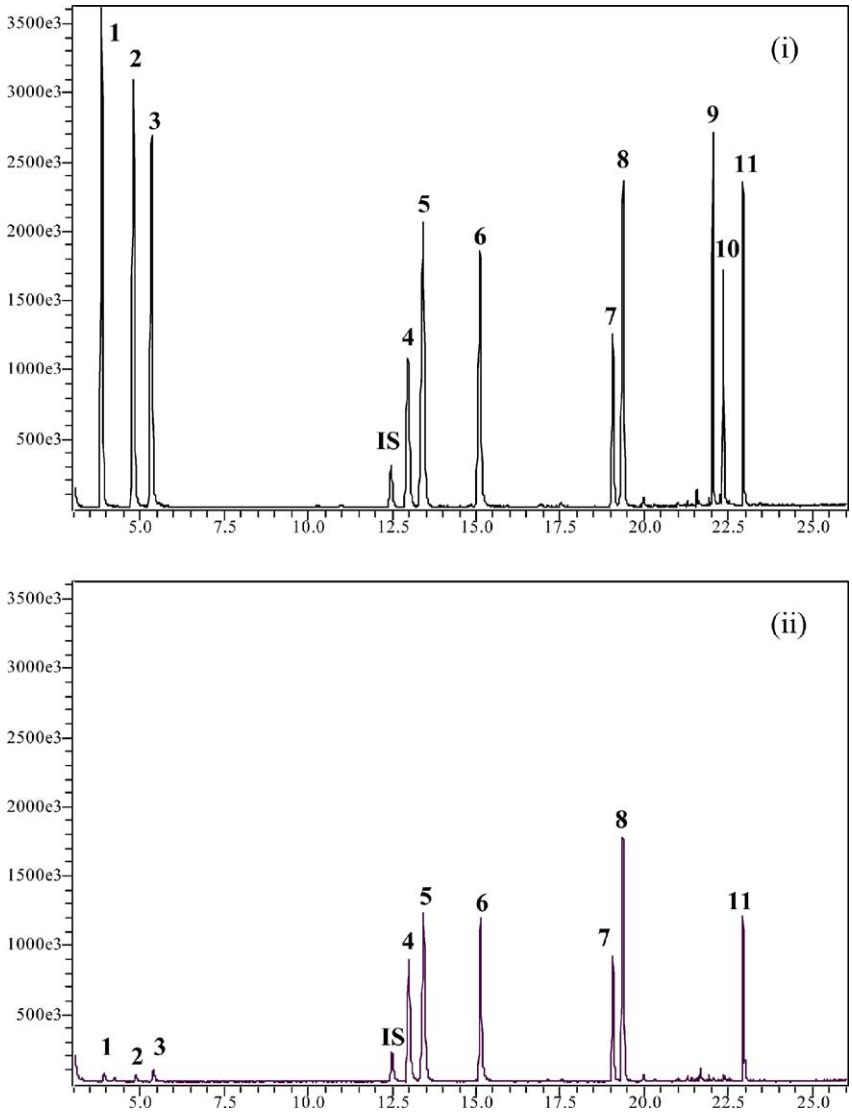

Fig. 4. Comparison of total ion chromatograms obtained with hollow fibre LPME/GC–MS at (i) time zero and (ii) after sonicating the aqueous sample solution for 300 min; (1) 2-NT, (2) 3-NT, (3) 4-NT, (4) 1,3-DNB, (5) 2,6-DNT, (6) 2,4-DNT, (7) TNB, (8) TNT, (9) 4-ADNT, (10) 2-ADNT, (11) Tetryl and (IS) internal standard. Other experimental conditions: 80 kHz ultrasound frequency, 150 W electric power output, 20 °C water bath temperature, 195 ml aqueous sample spiked at 100 $\mu g\,l^{-1}$ of each target analyte.

during sonochemical degradation are given in Fig. 5. As can been seen the relative reactivity of the investigated compounds can fall into two categories: the nitrotoluenes (2-NT, 3-NT and 4-NT) as well as the amino dinitrotoluenes (2-ADNT and 4-ADNT) isomers are all readily susceptible to sonochemical degradation and at the conditions under consideration nearly complete removal is achieved within 300 min of irradiation. Conversely, the rest of the analytes (1,3-DNB, 2,4-DNT, 2,6-DNT, TNB, TNT and tetryl) are more recalcitrant and significant removal is not observed even after 300 min of ultrasonic irradiation.

Goskonda et al. [14], who studied the sonochemical degradation of single-component solutions of TNT, 2-ADNT and 4-ADNT at 20 kHz of ultrasound frequency, 40 ml of liquid volume, pulsed mode of sonication and an initial substrate concentration of 86, 92 and 55 $mg\,l^{-1}$ for TNT, 2-ADNT and 4-ADNT, respectively, reported that only ca. 26, 19 and 18% removal occurred for TNT, 2-ADNT and 4-ADNT, respectively, after 300 min of irradiation. Nonetheless, the respective values of substrate removal increased to 74, 68 and 63% after 1920 min of irradiation. In their studies, 2-ADNT and 4-ADNT were of similar reactivity and this is consistent with the results obtained in our study. Hoffmann et al. [17] reported that the sonochemical degradation of TNT in aqueous solutions saturated with oxygen proceeded slowly through first order kinetics with respect to substrate concentration with the reaction rate constants being 1×10^{-3} and $1.2 \times 10^{-3}\,min^{-1}$ at 20 and 500 kHz, respectively. These values increased to 3.3×10^{-3} and $5.1 \times 10^{-3}\,min^{-1}$, respectively, when the solution was saturated with a 99:1 (v/v) mixture of O_2:O_3. They suggested that the enhanced efficiency of irradiation at

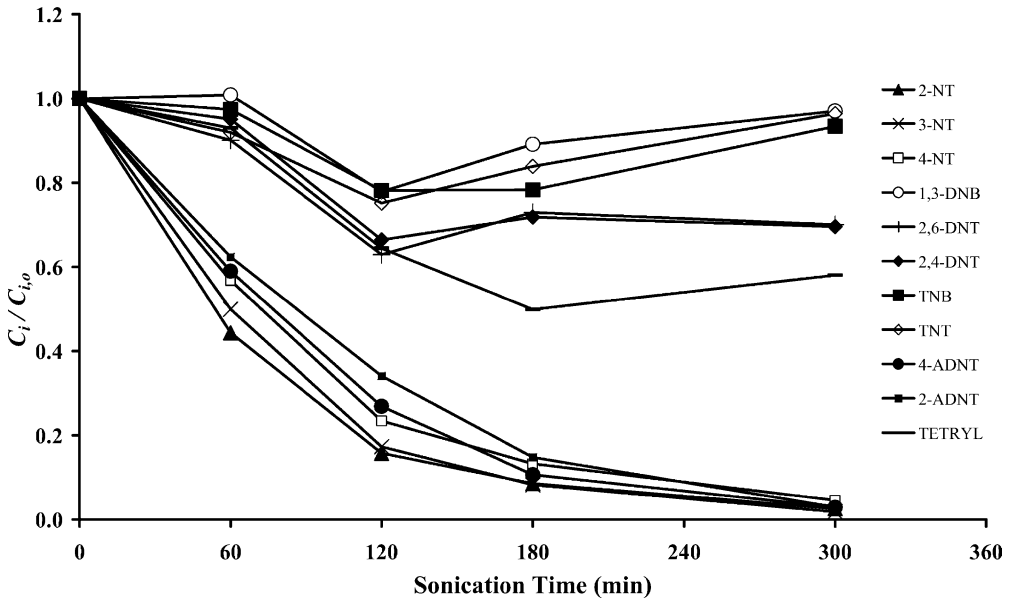

Fig. 5. Normalised concentration-time profiles during sonication (80 kHz ultrasound frequency, 150 W electric power output, 20 °C water bath temperature) of a 195 ml aqueous solution containing 100 $\mu g\,l^{-1}$ of each target analyte.

500 kHz over that at 20 kHz was due to a higher rate of OH radical production. Conversely, Sierka [16] reported that TNT could not be degraded sonochemically at 859 kHz ultrasound frequency and 50 W power output unless ultrasonic irradiation was coupled with ozonation. At the conditions employed in our study, TNT was found to be stable against sonochemical degradation; to confirm this, an additional run was carried out where a solution containing 100 $\mu g\,l^{-1}$ of TNT alone was irradiated for 120 min; at the conditions in question (80 kHz frequency, 150 W power output, 20 °C temperature) TNT remained practically unchanged.

4. Conclusions

Overall, during the present studies, a protocol comprising hollow fibre LPME coupled with GC–MS has been developed to quantify trace levels of nitroaromatic compounds in water. The overall cost, sample preparation time as well as consumption of toxic organic solvents were minimised without affecting the sensitivity of the method. The analytical method was then used to monitor concentration profiles of nitroaromatic compounds in aqueous solutions subject to low frequency ultrasonic irradiation. At the ultrasonic frequency employed in this study, sonochemical treatment was found capable of effectively destructing the nitrotoluene and amino dinitrotoluene isomers originally present in the reaction mixture.

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