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Determination of explosives in environmental water samples by solid-phase microextraction–liquid chromatography

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Abstract

When explosives are present in natural aqueous media, their concentration is usually limited to trace levels. A preconcentration step able to remove matrix interferences and to enhance sensitivity is therefore necessary. In the present study, we evaluated solid-phase microextraction (SPME) technique for the recovery of nine explosives from aqueous samples using high-performance liquid chromatography with ultraviolet detection (HPLC-UV). Several parameters, including adsorption and desorption time, coating type, rate of stirring, salt addition, and pH, were optimized to obtain reproducible data with good accuracy. Carbowax coating was the only adsorbent found capable of adsorbing all explosives including nitramines. Method detection limits (MDL) were found to range from 1 to 10 μg/L, depending on the analyte. SPME/HPLC-UV coupling was then applied to the analysis of natural ocean and groundwater samples and compared to conventional solid-phase extraction (SPE/HPLC-UV). Excellent agreement was observed between both techniques, but with an analysis time around five times shorter, SPME/HPLC-UV was considered to be applicable for quantitative analysis of explosives.

Keywords: Water analysis; Explosives; Nitramines; Solid-phase microextraction; Solid-phase extraction

1. Introduction

The location of many active and formerly used defense sites adjacent to aquatic environments including ponds, lakes, rivers, estuaries and coastal ocean areas has resulted in the presence of unexploded ordnance (UXO) at underwater sites. Wartime activities, including dumping of ammunition and sinking of warships have also resulted in the undersea deposition of considerable amounts of UXO. Since most explosives are toxic [1–4], leaching from UXO is considered to be a potential source of contamination for surrounding water. Rapid and sensitive techniques for their environmental monitoring are thus needed.

Current methods for extracting explosives from water are liquid–liquid extraction (LLE) [5,6], salting out liquid–liquid extraction (SOE) [7,8], and solid-phase extraction (SPE) using bonded silica sorbents [5,8–11]. LLE and SOE are time consuming, require large volumes of solvents, and can lead to different extraction efficiencies depending on the analyte investigated. SPE is a robust method, which offers the advantage of a lower consumption of organic solvent. However, the numerous steps involved in SPE including conditioning, retention, rinse, and elution make the technique a very lengthy and time-consuming technique.

In this context, a rapid, simple, solvent-free and sensitive method that could be applied for the analyses of explosives in water would be very advantageous. Solid-phase microextraction (SPME) that was developed by Pawliszyn [12,13] is endowed with these qualities. Few studies were recently dedicated to the use of SPME coupled with gas chromatography for the analysis of organic explosives [14–16]. The reported techniques proved to be very sensitive, however

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they are hardly applicable to the detection of weakly volatile explosives such as the two cyclic nitramines RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro1,3,5,7-tetranitro-1,3,5,7-tetrazocine). Since these two nitramines are now present in numerous explosive compositions, we decided to investigate the potential use of SPME/HPLC to analyze explosives in aqueous samples. Furton et al. explored the use of SPME/GC-ECD and SPME/HPLC-UV for the recovery of explosives from aqueous solutions using Carbowax-coated fiber [17]. In the present study, we used several fibers (Carbowax/templated resin, polydimethylsiloxane/divinylbenzene, polyacrylate) and optimized the conditions for analysis of explosives in water by SPME/HPLC. An emphasis was given to the quantitative aspect of the analysis, and accuracy, precision, and limits of detection were determined. The method efficiency was then compared to that of SPE/HPLC for analyzing natural ocean water samples from Hawaii and groundwater samples from Massachusetts.

2. Experimental

2.1. Chemicals

A stock mixture containing HMX, RDX, 1,3,5-trinitrobenzene (1,3,5-TNB), 1,3-dinitrobenzene (1,3-DNB), tetryl, 3,4-dinitrotoluene (3,4-DNT), TNT, 4-amino-2,6-dinitroluene (4-ADNT) and 2,4-dinitrotoluene (2,4-DNT), each at a concentration of 10 mg/L was prepared in acetonitrile. Spiking standards were then prepared by diluting this mixture with acetonitrile. Explosives were purchased from either Chromatographic Specialities (Brockville, Ont.) or Supelco (Oakville, Ont.) in acetonitrile solution (1000 μg/mL). Acetonitrile (CH_3CN, HPLC grade) was from Fisher (Nepean, Ont.), and methanol (CH_3OH, HPLC grade) from J.T. Baker Chemicals (Phillipsburg, NJ). Deionized water was obtained with a Milli-Q^{UV} plus (Millipore) system.

2.2. Sample collection

Four seawater samples were collected from a location near the Hawaiian Islands. The latter have been used to train military personnel for air and sea attacks, as well as for marine landings over a period extending from 1941 to 1990. Samples UXO-1 and UXO-3 were collected from WWII-ERA UXO disposal sites, sample UXO-5 was collected at a subsurface detonation site and sample UXO-7 came from a reference site with no ordnance field nearby. At each labeled site, water was collected about 0.5 m below the surface, in polyethylene 4-L bottles. Samples were immediately transferred into 1-L amber glass bottles containing 1.5 g of sodium bisulphate for acidification. At the end of the 6.5-h campaign, all samples were immediately placed on ice in a commercial cooler and processed for shipping. Upon arrival at BRI-CNRC (Montreal, Que.), samples were immediately stored at 4 °C, and analyzed 3 days later.

Two groundwater samples (E1 and E2) were collected from a military site in Massachusetts, USA. Containers used consisted of 1-L amber glass bottles. The samples (non-acidified) were then shipped the same day, on ice, in a commercial cooler. Analyses were performed immediately upon reception.

2.3. Sample extraction

Since explosives are polar analytes that exhibit high affinity toward aqueous solutions and low vapor pressures [18], immersion, rather than headspace SPME was selected as extraction mode. Aqueous samples (25 or 35 mL) were thus extracted by immersing completely a fused-silica fiber coated with the sorbent phase of interest (Supelco) in the solution that was stirred continuously with a Variomag magnetic stirrer (ColeParmer Instrument, Anjou, Que.). Three different fibers were tested for their ability to extract explosives: a 50-μm film of Carbowax/templated resin (CW/TPR); a 60-μm film of polydimethylsiloxane/divinylbenzene (PDMS/DVB); and a 85-μm film of polyacrylate (PA). Adsorption was conducted at room temperature and stirring rate, concentration of NaCl, fiber sorbent phase, and adsorption and desorption time were optimized.

For comparison with the SPME technique, water samples were also extracted using SPE with a Porapak Rdx Sep-Pak cartridge (500 mg) (Waters, Mississauga, Ont.) as described in the USEPA SW-846 method 3535A [9]. The cartridge was previously conditioned with 15 mL of acetonitrile followed by 30 mL of deionized water as recommended by the manufacturer. The aqueous sample (500 mL) was passed through the cartridge at a rate of 10 mL/min. After letting the cartridge dry under reduced pressure, potentially adsorbed contaminants were eluted with 5 mL of acetonitrile, and the sample was diluted with 5 mL of deionized water, before HPLC analysis.

2.4. HPLC-UV system

HPLC analyses were made with a Waters chromatographic system equipped with a Model 600 pump, a Model 717 Plus injector, a Model 996 Photodiode-Array Detector and a temperature control module. Separation was performed with a Discovery C18 column (25 cm, 4.6 mm, 5 μm) (Supelco) maintained at 35 °C. An isocratic mobile phase (50% methanol/water) was used at a flow of 1 mL/min for direct injection and 0.75 mL/min for SPME coupling. Chromatograms were extracted at a wavelength of 254 nm. For direct injection, 50 μL of sample was injected. For SPME/HPLC coupling, an interface (Rheodyne valve version) from Supelco was used. After placement, in the 60-μL SPME desorption chamber, the fiber was desorbed by static soaking in 50 μL of a 1:1 (v/v) H_2O:acetonitrile solution.

3. Results and discussion

3.1. Optimization of SPME/HPLC-UV analysis

3.1.1. Selection of desorption time

Experimental method optimization began with establishing an extraction profile as a function of desorption time. The coated fiber, CW/TPR, PDMS/DVB, or PA, was immersed for 30 min in the aqueous solution of explosives (0.75 g of NaCl and 250 μL of the stock explosives mix (10 mg/L) in 25 mL of deionized water) that was stirred at 500 rpm. The fiber was then placed in the SPME/HPLC interface with desorption times varying from 1 to 10 min. The results (not shown) indicated that desorption from CW/TPR and PDMS/DVB fibers was fast (less than 1 min for all explosives), while desorption from polyacrylate fiber was a little slower. For most analytes, HPLC peak areas obtained with PA fiber increased between 1 and 3 min of desorption time and remained roughly constant thereafter. A desorption time of 5 min was then used for all other SPME/HPLC experiments.

3.1.2. Effect of NaCl concentration on analyte extraction

The presence of salt can reduce the solubility of some analytes thereby favoring their extraction by the fiber. The effect of salt on explosives extraction by SPME has been reported by two research groups [17,19]. While one team did not notice any increase in extraction efficiency when salt was added [19], the other group found that the addition of either NaCl or Na_2SO_4 had positive effects on extraction [17]. The contradictory observations were likely due to the difference in the concentrations of salt investigated (0–3% (w/v) for the first group [19] and 0–25% (w/v) for the second one [17]). Since none of these reports included numerical data and natural marine samples contain around 3% of salt, we found it necessary to elucidate the effect of NaCl on explosives extraction from aqueous media. Four NaCl concentrations (3, 10, 20, and 30% (w/v)) were tested, using the three fibers mentioned above, and a desorption time of 5 min. The experimental conditions and the results are shown in Fig. 1. Except for 1,3,5-TNB, which was more favorably extracted from unsalted water, addition of NaCl enhanced the extraction of all energetic compounds. In the case of PDMS/DVB fiber, however, enhancement in HPLC peak areas was apparent only at salt concentrations exceeding 10% (w/v). These results show that the extraction efficiency depends on the concentration of salt in the medium. As a consequence, 30% (w/v) NaCl solutions were used throughout the present study to ensure maximal extraction of explosives.

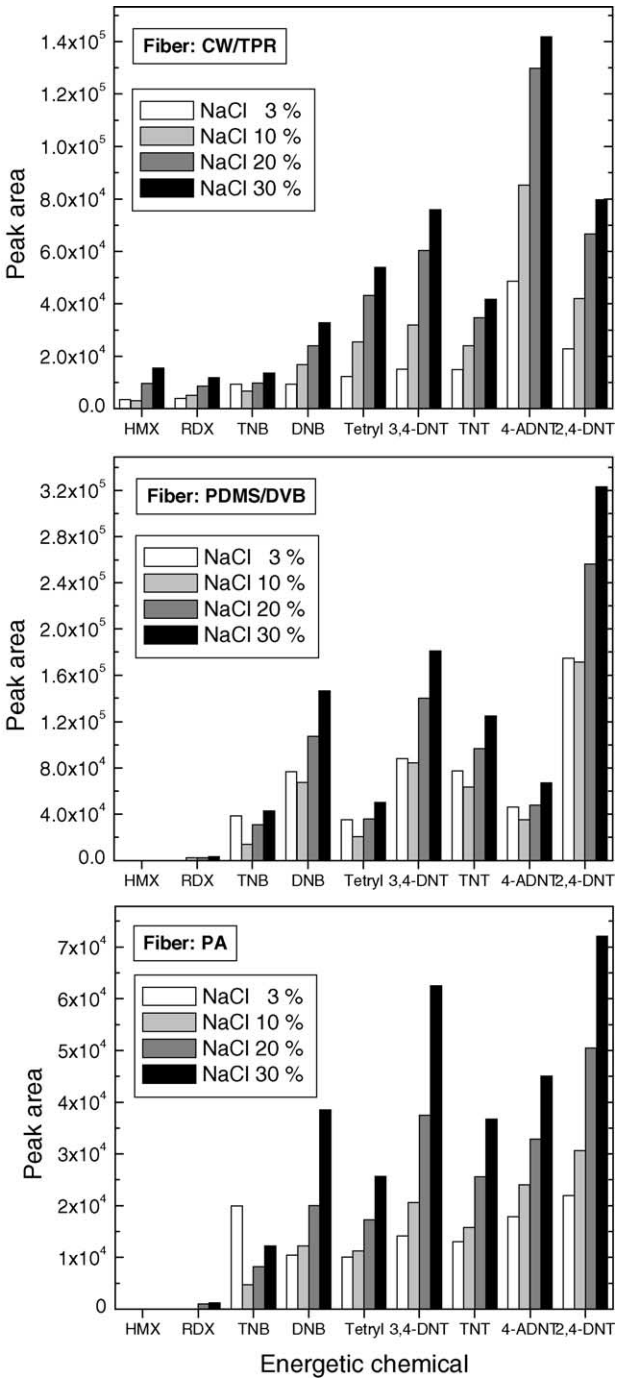

Fig. 1. Effect of medium salinity on the extraction of energetic compounds by SPME/HPLC. Extraction vials contained various amounts of NaCl (3, 10, 20, or 30% (w/v)), water (25 mL), energetic compounds (2.5 μg in 250 μL of acetonitrile). Fiber was immersed for 30 min in the solution stirred at 500 rpm (TNB = 1,3,5-TNB; DNB = 1,3-DNB).

3.1.3. Selection of stirring rate

Two different stirring rates (500 or 990 rpm) were tested with two of the three fibers investigated in this study (CW/TPR, PDMS/DVB) using the conditions given in Fig. 2. The stirring rate had only a small effect on the extraction efficiency with the Carbowax fiber (Fig. 2). In contrast, increasing the stirring rate with the PDMS/DVB fiber led to a consistent increase in the extracted amounts of the explosives, as demonstrated by HPLC response. These observations suggested that more time was needed for the analytes distribution between the aqueous phase and the PDMS-DVB fiber to reach thermodynamic equilibrium (discussed below). For both fibers, 4-ADNT was the most affected by changing

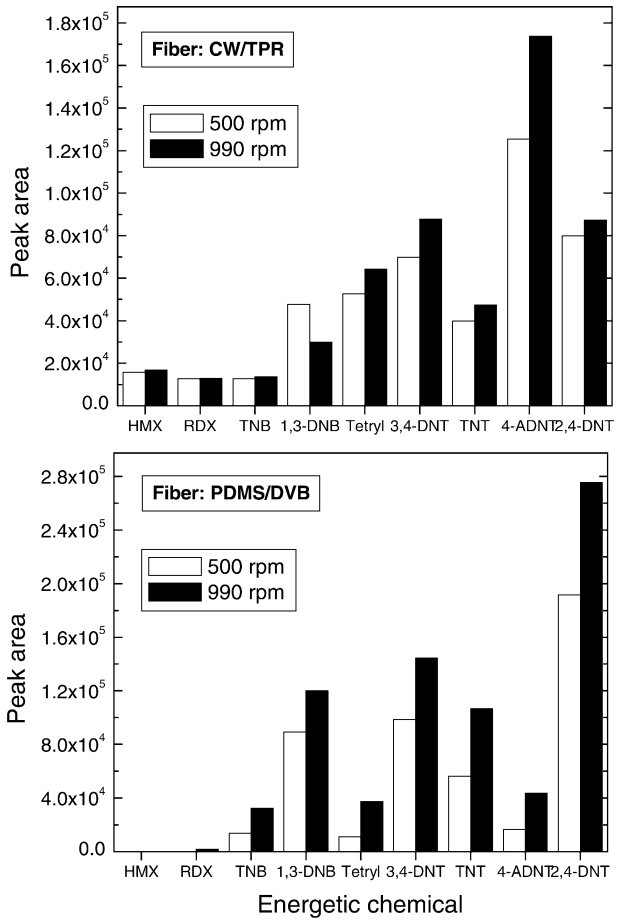

Fig. 2. Effect of stirring rate on the extraction of energetic compounds by SPME/HPLC using the CW/TPR and PDMS/DVB fibers. Extraction vials contained NaCl (30% (w/v)), water (35 mL), energetic compounds (3.5 μg in 350 μL of acetonitrile). Fiber was immersed for 30 min in the solution stirred at either 500 or 990 rpm.

the stirring rate from 500 to 990 rpm, indicating a slower adsorption process for this compound. In order to maintain analysis time as short as possible, the stirring rate was then maintained at 990 rpm.

3.1.4. Effect of adsorption time

SPME sampling under equilibrium conditions is preferred for quantitative analysis, as extractions performed under non-equilibrium situation will inevitably sustain poor precision. The amount of analyte adsorbed by the fiber is a function of the distribution constant between the fiber and the solution, the thickness of the adsorbing phase, and the analyte's diffusion coefficient. Because these parameters differ from one analyte to the other and from one fiber to the other, the equilibration time should be measured for each analyte/fiber couple. Adsorption profiles were determined as a function of time for the three fibers, CW/TPR, PDMS/DVB, and PA, using the conditions given in Fig. 3. Results showed that the three fibers used for HPLC analysis did not all behave similarly (Fig. 3). With the Carbowax coating, equilibration was attained after around 30 min for all the analytes investigated

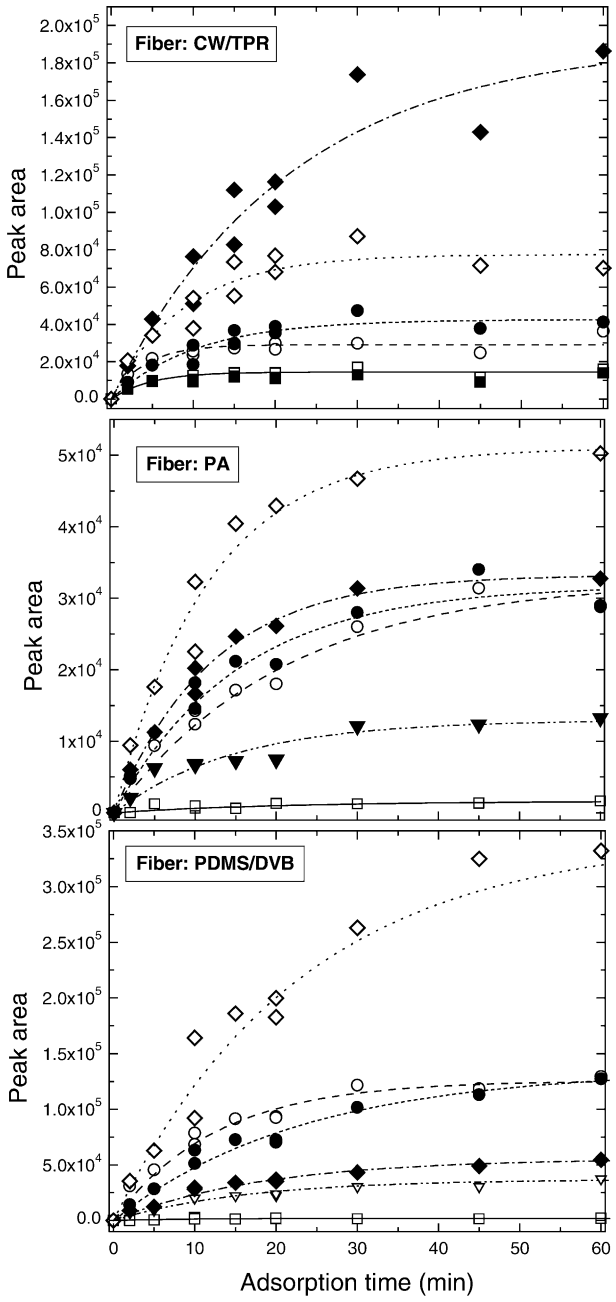

Fig. 3. Adsorption time profiles for RDX (□), HMX (■), 1,3,5-TNB (▼), 1,3-DNB (○), TNT (●), 2,4-DNT (◊), 4-ADNT (♦) by SPME/HPLC using CW/TPR, PDMS/DVB and PA fibers. Extraction vials contained NaCl (30%), water (35 mL), energetic compounds (3.5 μg in 350 μL of acetonitrile). Fiber was immersed for various periods of time in the solution stirred at 990 rpm.

except for 4-ADNT. With the PDMS/DVB fiber, equilibration was reached after about 60 min for all the explosives. With the polyacrylate fiber, equilibration times varied from 5 min for RDX to 1 h for other explosives. The longer times required to achieve adsorption equilibrium with PDMS/DVB coating has previously been reported for other types of analytes [20]. The presence of a porous polymeric material such as DVB not only provided larger surface area, but also lengthened

the distance the analyte had to diffuse through. An adsorption time of 60 min was then used for the PDMS/DVB fiber, whereas 30 min were estimated to be sufficient to approach equilibrium conditions with CW/TPR and PA fibers.

3.1.5. Selection of fiber coating

The adsorption time profiles presented in Fig. 3 constitute a substantial basis for comparing the efficiency of each of the three fibers to extract explosives. PA fiber gave the lowest HPLC response for all explosives. Large errors varying from 10 to 25% were obtained with this coating (results not shown) when analyzing in triplicate an aqueous solution containing 100 μg/L of each analyte. In addition, the stationary phase of the PA fiber decomposed under the conditions used, as demonstrated by the sudden pressure increase and consequent leaking of eluent from the injector during HPLC analysis. PA coating was thus no longer employed for SPME/HPLC analysis. While PDMS/DVB did give higher peak areas than CW/TRR for most nitroaromatic compounds, it did not allow the detection of nitramines such as RDX or HMX. To make sure that no analyte was missed, both CW/TPR and PDMS/DVB coatings were used and compared in subsequent experiments.

3.1.6. Effect of acetonitrile on analyte recovery

Because analytes were introduced in the aqueous media from CH_3CN stock solution, this solvent was present at a concentration of 1% (v/v) in all the samples mentioned above. By increasing the solubility of the analyte in the aqueous solution, acetonitrile is expected to act negatively on the extraction efficiency of the SPME method, unless its effect is limited by the addition of salt in the medium. Therefore, in order to decide whether samples and standards could be prepared with a constant volume of acetonitrile, or whether all samples should be free of acetonitrile, the effect of the solvent was evaluated. Samples each containing 30% (w/v) of NaCl, 0.7 μg of each analyte, 35 mL of water and a volume of acetonitrile of either 0, 35 or 350 μL (corresponding to 0, 0.1 or 1% (v/v), respectively) were prepared and analyzed using the optimized experimental conditions described above. No correlation was observed between the HPLC responses and the concentration of acetonitrile. Besides a higher recovery was observed in the presence of acetonitrile for several analytes. Since the presence of acetonitrile did not decrease the extraction effectiveness of the method, calibration curves were established with the same amount of acetonitrile (1% (v/v)) in each standard.

3.1.7. Effect of pH on the extraction efficiency

It is a common practice to acidify natural samples shortly after collection in order to limit both abiotic and biotic degradation of organic contaminants. However, changing pH will change the ionization form of certain analytes and thereby affect their water-solubility and extractability. Among the analytes investigated in this study, 4-ADNT is the only compound the structure of which is expected to vary with pH. Although its pK_a has not been reported, it is expected to be below 2.5, which corresponds to the pK_a value of 3-nitroaniline [21]. At pH 2 to 3, a significant fraction of the amino groups of 4-ADNT could therefore be protonated, thus resulting in a higher water solubility and a lower extractability under acidic conditions.

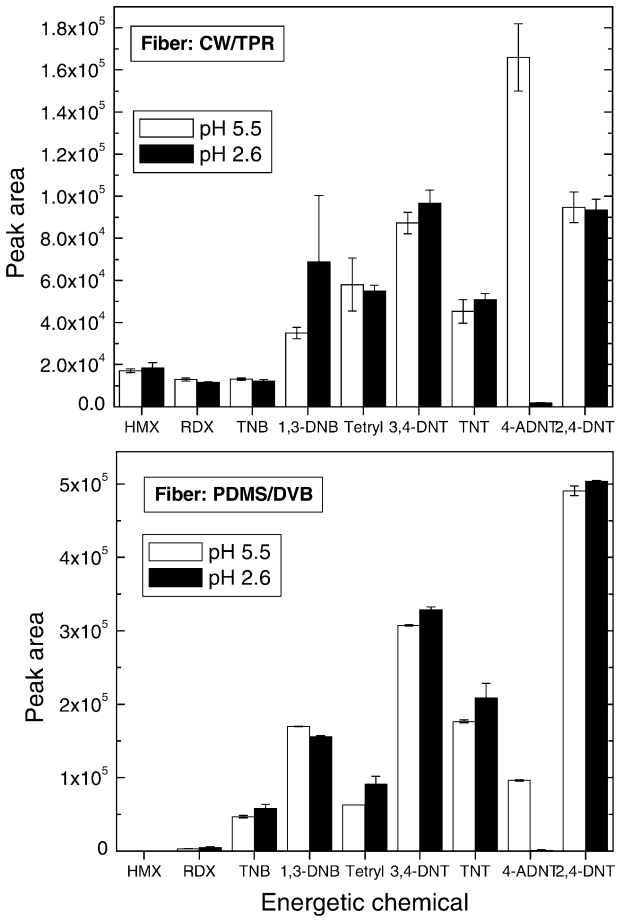

Fig. 4. Effect of medium pH on the extraction of energetic compounds by SPME/HPLC using the CW/TPR and PDMS/DVB fibers. Extraction vials contained 30% of NaCl, water (35 mL), energetic compounds (3.5 μg in 350 μL of acetonitrile). Fiber was immersed for 30 min in the solution stirred at 990 rpm. Error bars represent the standard deviation of duplicate experiments.

On the other hand, the stability of fibers under acidic conditions could be a source of bias in the determination of analytes. While PDMS/DVB fiber was reported by the manufacturer to be stable between pH 2 and 11, no information was provided on CW/TPR coating regarding its stability with pH. An experiment was consequently devised to investigate the effect of pH on the extraction efficiency of CW/TPR and PDMS/DVB fibers. A solution containing 100 μg/L of each of the nine analytes was acidified to pH 2.6 by adding 0.013 g of $NaHSO_4$ and results of SPME/HPLC were compared to those obtained with the non-acidified solution (pH 5.5) (Fig. 4). Negligible amounts of 4-ADNT were extracted at pH 2.6 for both types of coatings. This result indicated that the amine was present in the form of its

more soluble ammonium salt at pH 2.6 thus suggesting that the actual pK_a value of 4-ADNT might be higher than 2.5. The extractability of all other tested explosives did not vary with pH. Alkaline pH values were not considered because they are known to induce abiotic degradation of numerous explosives such as TNT [22], RDX and HMX [23].

3.2. Evaluation of SPME/HPLC method performance

3.2.1. Preparation of SPME calibration curves

The optimized conditions established above were then used to prepare calibration curves for the nine analytes spiked at 2, 5, 10, 20, 50, 100, and 200 μg/L using CW/TPR or PDMS/DVB fibers. The calibration curves resulting from duplicate analyses and the corresponding equations are shown in Fig. 5 and Table 1, respectively. Typical SPME/HPLC chromatograms of explosives in aqueous solutions are shown in Fig. 6.

Neither RDX nor HMX could be extracted by PDMS/DVB fiber, as already mentioned in the literature [15]. A good linearity was observed with the CW/TPR fiber for all the studied analytes except 1,3-DNB. The scattered results obtained with this chemical are likely due to an inconsistent interference that was observed at the same retention time. On the contrary, PDMS/DVB fiber led to a non-linear behavior with departure from linearity starting at concentrations as low as 10 μg/L. As a result, a polynomial equation rather than a linear fitting was adopted. As shown by r^2 coefficients (Table 1), excellent correlation was achieved between fitted expressions and experimental measurements.

3.2.2. Accuracy, repeatability and detection limits for SPME

The method detection limits (MDL) were calculated for the nine analytes according to published guidelines [24], as three times the standard deviation for a measurement value not higher than 10 times the MDL. Similarly, the method quantification limits can be estimated as 10 times the standard deviation. The accuracy (% recovery) and precision (% RSD) of the SPME/HPLC-UV method were evaluated for each analyte by analyzing a standard of known concentration (2 or 20 μg/L) seven times, on different days, and quantifying it using the calibration curves established above. The results for the detection limits, precision, and accuracy of quantification are given in Table 2. Depending on the analytes, detection limits ranged between 1 and 10 μg/L for both coatings. For RDX, HMX, 1,3,5-TNB, 1,3-DNB, and tetryl, the present detection limits are higher than those determined by Furton et al. using SPME/HPLC [17]. The higher MDL measured in this study may be attributable to the method used for evaluating the detection limits since Furton et al. used the signal to noise ratio method.

The precision observed with both CW/TPR and PDMS/DVB coatings, as determined by the relative standard deviation, ranged from 9 to 27%, and from 5 to 31%, respectively (Table 2). When comparing the measured concentrations of all analytes to the nominal concentrations in the check standard, recoveries ranging from 67 to 122% for the Carbowax fiber and from 72 to 148% for the PDMS fiber were obtained. The two lowest recoveries were observed with tetryl and 1,3-DNB. It is likely that tetryl known to be unstable in non-acidified aqueous solutions [25], has decomposed, while 1,3-DNB analysis was complicated by the presence of an unknown interference, as mentioned previously. These results represent a significant improvement on method accuracy and reliability, when comparing to earlier SPME methods [14]. In general, the two investigated fibers showed equivalent efficiency towards the extraction of explosives from water, but the CW/TPR fiber allowed the detection of nitramines like RDX and HMX when PDMS coating did not allow it.

3.2.3. Comparison to solid-phase extraction (SPE)

Because the SPE method is commonly used for routine analysis of explosives in water, its accuracy, precision and detection or quantification limits were also determined and compared to that of SPME, using detection by HPLC-UV (Table 2).

We found that the SPE detection limits for the extraction of 500-mL samples preconcentrated to a final volume of 5 mL were in the hundreds of nanograms per liter range (0.12 μg/L

Table 1
Analysis of calibration standards by SPME/HPLC-UV

Analyte	Fiber: CW/TPR		Fiber: PDMS/DVB	
	Linear equation	Corrrelation coefficient[a] r^2	Polynomial equation	Corrrelation coefficient[a] r^2
HMX	$y = 169x$	0.9995 ($n = 5$)	N.A.[b]	N.A.
RDX	$y = 136x$	0.9949 ($n = 5$)	N.A.	N.A.
1,3,5-TNB	$y = 130x$	0.9963 ($n = 6$)	$y = -913 + 130x - 1.2x^2$	0.9991 ($n = 6$)
1,3-DNB	$y = 535x$	0.9552 ($n = 6$)	$y = 4789 + 1820x - 1.7x^2$	0.9996 ($n = 7$)
Tetryl	$y = 603x$	0.9993 ($n = 6$)	$y = -219 + 799x - 1.7x^2$	0.9998 ($n = 6$)
3,4-DNT	$y = 960x$	0.9963 ($n = 7$)	$y = -848 + 3551x - 4.7x^2$	1.0000 ($n = 7$)
TNT	$y = 506x$	0.9949 ($n = 7$)	$y = 2176 + 2024x - 2.8x^2$	1.0000 ($n = 7$)
4-ADNT	$y = 1713x$	0.9994 ($n = 7$)	$y = 380 + 1180x - 2.2x^2$	0.9999 ($n = 7$)
2,4-DNT	$y = 955x$	0.9996 ($n = 7$)	$y = 130 + 5792x - 8.9x^2$	1.0000 ($n = 7$)

[a] Correlation coefficients were determined from the linear or polynomial regression analysis of five to seven (n) standards, using Microcal™ Origin 6.0 software.
[b] Not applicable.

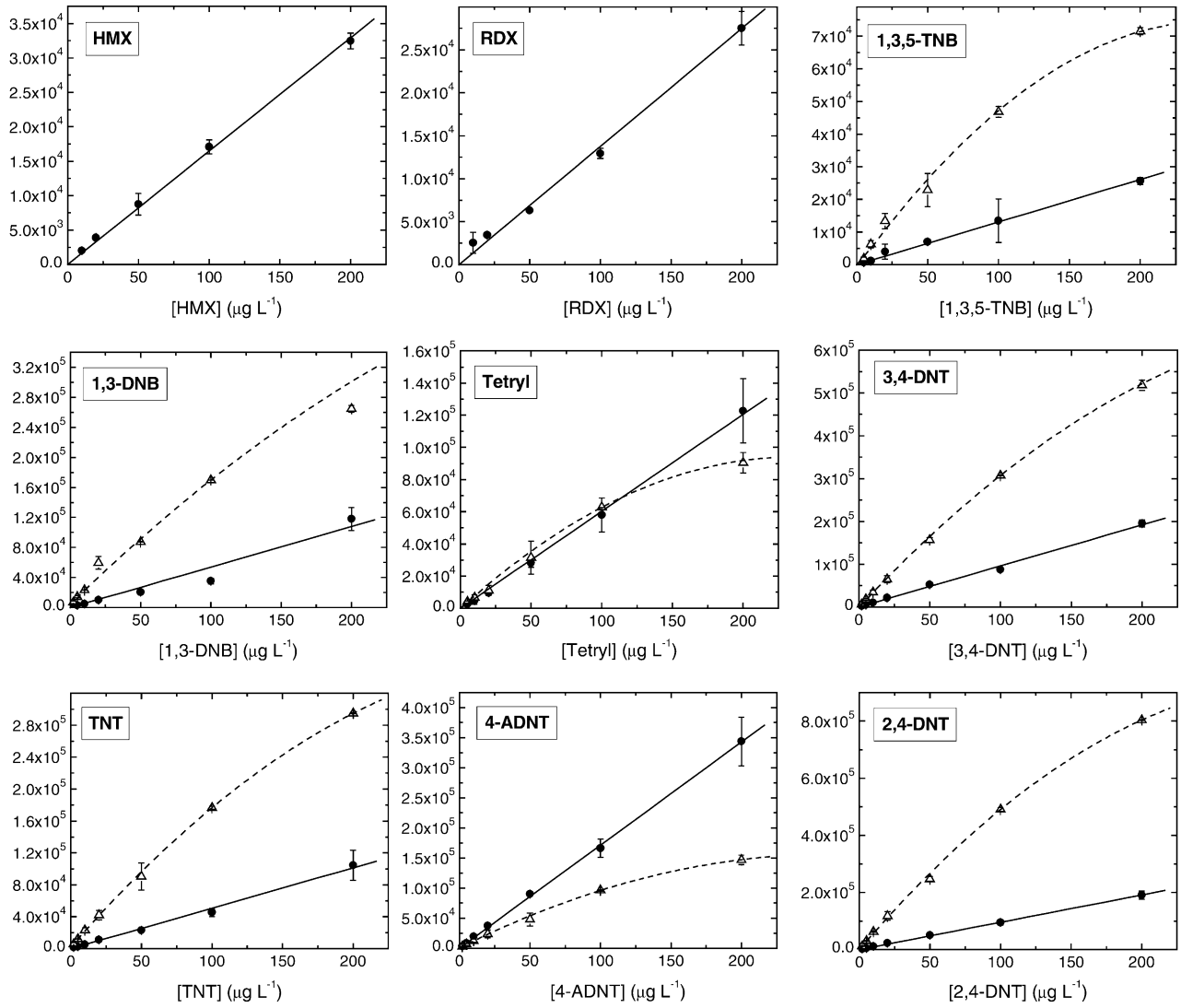

Fig. 5. Calibration curves established for nine analytes according to the following conditions: extraction vials contained various amounts of analytes, 350 μL of acetonitrile, 30% of NaCl and 35 mL water. Samples were stirred at 990 rpm and extractions were carried out for 30 and 60 min with the CW/TPR (—●—) and PDMS/DVB (—△—) fibers, respectively. Error bars represent standard deviation of duplicate measurements.

TNT, 0.29 μg/L RDX, 0.09 μg/L HMX, 0.14 μg/L 2,4-DNT, 0.27 μg/L 4-ADNT) while SPME detection limits were about 10 times higher (1.3 μg/L TNT, 5.6 μg/L RDX, 7.0 μg/L HMX, 1.3 μg/L 2,4-DNT, 1.3 μg/L 4-ADNT). Moreover, precision of SPE method (3% < RSD < 13%) was significantly superior to that of SPME (10% < RSD < 31%). However, the SPME method has the advantage of being rapid and organic solvent-free. For example, total SPME analysis including adsorption and analysis did not exceed 80 min as opposed to approximately 6 h (including time needed for cartridge conditioning, adsorption, elution and analysis) for the SPE method.

3.2.4. Application to real samples

SPE and SPME were then compared for their efficiencies to analyze ocean water and groundwater samples using HPLC-UV detection. Only the groundwater samples showed the presence of HMX, RDX and 4-ADNT (Table 3, Fig. 6B). Excellent agreement between SPME and SPE methods was obtained. Because no explosive was detected in any of the ocean water samples, a sample that had been collected in the reference site (UXO-7) and that had not been acidified was then fortified with known amounts of each of the nine analytes and with 27% (w/v) of sodium chloride to give a total salt concentration approximating 30% (w/v). Due to the higher sensitivity of the SPE method, spikes were performed at a concentration of 1 and 10 μg/L for SPE and SPME, respectively. The results for the quantification of the spiked natural sample are given in Table 3. Except for HMX, the accuracy of SPME method, as determined by the percent recovery ((measured concentration/actual concentration) × 100), was fairly good, with data ranging from 83 to 124%. Since a concentration of 10 μg/L was below the method quantification limit (MQL) for HMX, it is not surprising

Table 2
Comparison of detection limits, precision (% RSD) and accuracy (% recovery) for SPME/HPLC-UV and SPE/HPLC-UV

Analyte	SPME/HPLC with CW/TPR			SPME/HPLC with PDMS/DVB			SPE/HPLC		
	MDL[a] (μg/L)	% RSD[b] (at MQL)	% Recovery[c] (±S.D.)	MDL[a] (μg/L)	% RSD[b] (at MQL)	% Recovery[c] (±S.D.)	MDL[a] (μg/L)	% RSD[b] (at MQL)	% Recovery[c] (±S.D.)
HMX	7.0	11.7	108.0 ± 12.6	N.A.[d]	N.A.	N.A.	0.09	3.1	97.5 ± 3.0
RDX	5.6	27.2	121.9 ± 33.2	N.A.	N.A.	N.A.	0.29	10.0	97.0 ± 9.7
1,3,5-TNB	10.1	16.9	90.1 ± 15.2	3.3	17.4	110.1 ± 18.6	0.10	13.12	99.7 ± 3.0
1,3-DNB	6.4	10.2	67.2 ± 6.9	7.2	12.0	148.2 ± 20.0	0.03	4.4	100.3 ± 2.3
Tetryl	3.0	16.6	68.6 ± 8.4	13.10	31.1	75.6 ± 23.7	0.15	6.7	75.9 ± 5.1
3,4-DNT	1.3	22.3	103.6 ± 19.5	0.80	13.3	89.5 ± 10.8	0.18	6.4	98.8 ± 6.0
TNT	1.3	22.5	95.7 ± 16.3	1.4	9.8	94.5 ± 15.6	0.12	4.8	84.1 ± 4.0
4-ADNT	1.3	21.8	103.6 ± 17.7	1.5	17.9	85.1 ± 21.5	0.27	9.8	91.4 ± 8.9
2,4-DNT	1.0	21.7	105.4 ± 14.7	0.44	7.4	93.3 ± 8.5	0.14	4.6	97.6 ± 4.5

[a] Method detection limits were calculated using the equation, MDL = 3σ, where σ is the standard deviation of 7 (10 for SPE) measurements of low-concentration spikes.
[b] Percent relative standard deviation was based on 7 (10 for SPE) replicate analyses at a concentration not higher than 10 times the MDL.
[c] Percent recoveries were based on 7 (10 for SPE) replicate analyses at a concentration of 20 μg/L for SPME and 1 μg/L for SPE.
[d] Not applicable.

Table 3
SPME and SPE results for explosives in real samples using HPLC-UV for detection

Sample[a]	HMX (μg/L or ppb)		RDX (μg/L or ppb)		4-ADNT (μg/L or ppb)	
	SPME/CW	SPE	SPME/CW	SPE	SPME/CW	SPE
UXO-1	<7.0	<0.09	<5.6	<0.29	<1.0	<0.27
UXO-3	<7.0	<0.09	<5.6	<0.29	<1.0	<0.27
UXO-5	<7.0	<0.09	<5.6	<0.29	<1.0	<0.27
UXO-7	<7.0	<0.09	<5.6	<0.29	<1.0	<0.27
E1	34.3	33.2	210.4	213.9	[1.3][b]	1.6
E2	[8.4][a]	11.4	24.6	21.3	<1.0	<0.27

	HMX	RDX	1,3,5-TNB	1,3-DNB	Tetryl	3,4-DNT	TNT	4-ADNT	2,4-DNT
% Recovery data for spiked UXO-7									
SPME/CW (10 μg/L)	143	109	114	Interference[c]	83	96	109	88	96
SPME/PDMS (10 μg/L)	N.A.[d]	N.A.[d]	122	117	124	109	110	112	104
SPE (1 μg/L)	106	108	113	114	88	123	93	65	112

[a] UXO-1–7 are ocean samples from Hawaii; E1–2 are groundwater samples from MA, USA.
[b] Numbers in brackets indicate measured concentrations that are semi-quantitative (>MDL but <MQL (method quantification limit)).
[c] An interference was present that did not allow quantifying 1,3-DNB.
[d] Not applicable.

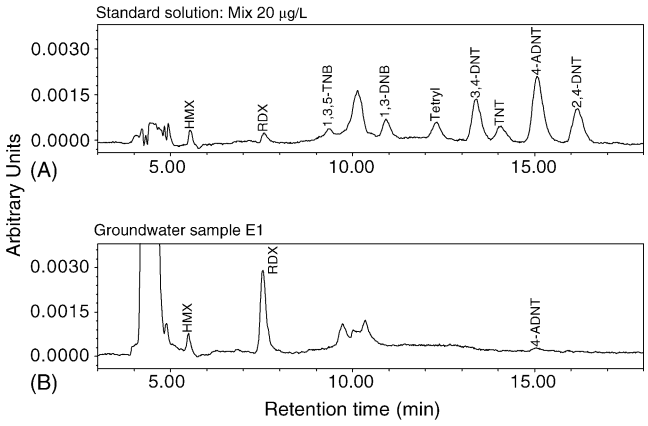

Fig. 6. Typical SPME/HPLC chromatograms of (A) a standard solution of a mixture of explosives, each at 20 μg/L; and (B) a groundwater sample from MA, USA. Samples (350 μL of acetonitrile, 30% of NaCl and 35 mL water) were stirred at 990 rpm and extracted for 30 min using a CW/TPR fiber.

that the measured value was significantly higher than the nominal concentration (143% recovery). Overall, the SPME method gave very satisfactory results when used to quantify explosives in ocean water and groundwater.

4. Conclusion

Solid-phase microextraction has been demonstrated to be a rapid, precise and reproducible method to analyze explosives above the ppb level in ocean water or groundwater. Several parameters have been optimized to ensure quantitative results. Addition of a high concentration of salt (30% (w/v)) guaranteed a good extraction efficiency and limited the variation that may be caused by the presence of a solvent like acetonitrile in the aqueous phase. Carbowax and polydimethylsiloxane/divinylbenzene coatings were both found superior to polyacrylate in terms of sensitivity. In addition

Carbowax coating had the advantage of being applicable to nitramines. Detection limits for SPME/HPLC-UV were found to be in the ppb range for the explosives used in this study, which are approximately 10 times higher than the detection limits obtained using SPE. However, although sensitivity of SPME is inferior to that of SPE, the precision and accuracy of SPME were proved to be excellent. With an analysis time around five times shorter than SPE/HPLC, SPME/HPLC becomes an appealing method to quantify explosives, including RDX and HMX, above the ppb level. Because of the need to detect trace (μg/L) concentrations of explosives to meet drinking water criteria, the present laboratory findings are important.

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