Solid-phase microextraction versus single-drop microextraction for the analysis of nitroaromatic explosives in water samples

ARTICLE *in* JOURNAL OF CHROMATOGRAPHY A · JANUARY 2002

Impact Factor: 4.17 · DOI: 10.1016/S0021-9673(01)01417-0 · Source: PubMed

2 AUTHORS:

Elefteria Psillakis
Technical University of Crete
84 PUBLICATIONS **3,251** CITATIONS
SEE PROFILE

Nicolas Kalogerakis
Technical University of Crete
219 PUBLICATIONS **4,705** CITATIONS
SEE PROFILE

ELSEVIER

Journal of Chromatography A, 938 (2001) 113–120

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Solid-phase microextraction versus single-drop microextraction for the analysis of nitroaromatic explosives in water samples

Elefteria Psillakis, Nicolas Kalogerakis*

Department of Environmental Engineering, Technical University of Crete, Polytechneioupolis, GR-73100, Chania, Crete, Greece

Abstract

This paper compares solid-phase microextraction (SPME) with a recently developed extraction method called single-drop microextraction (SDME) for the analysis of nitroaromatic explosives in water samples. The two techniques are examined in terms of procedure, chromatographic analysis and method performance. All practical considerations for both techniques are also reviewed. SPME requires dedicated apparatus and is relatively expensive, as the fiber's lifetime is limited. However, it has the advantages over SDME that it can be easily used for headspace analysis and has lower detection limits for all the target analytes. SDME requires more elaborate manual operations, thus affecting linearity and precision.

Keywords: Water analysis; Environmental analysis; Solid-phase microextraction; Single-drop microextraction; Extraction methods; Explosives; Nitro explosives

1. Introduction

Determination of explosives in water samples involves an initial sample pretreatment step for the isolation of target analytes, using liquid–liquid extraction (LLE) or solid-phase extraction (SPE) techniques prior to gas (GC) or high-performance liquid (HPLC) chromatographic analyses [1,2]. Both sample pretreatment methods, but mainly LLE, are considered expensive, time-consuming and labor-intensive methods, which result in the production of toxic laboratory waste, as they demand the use of high-purity organic solvents [3].

The quest for novel sample preparation procedures has led to the development of a fast, simple and solventless method called solid-phase microextraction (SPME) [4]. It is based on extraction using a thin polymeric-coated fused-silica fiber, fitted in a special syringe-type holder for protection and sampling [5]. When the fiber is exposed to an aqueous solution or to the headspace above it, organic compounds are extracted from their matrix. Once sampling is completed, the fiber is transferred to the heated injection port of a GC system where analytes are thermally desorbed. The whole extraction and transfer process usually takes only a few minutes, and can be easily automated [6]. SPME has gained the attention of many research groups around the world and over the last decade it has been applied to the determination of a large variety of volatile and semi-volatile analytes (including nitroaromatic explosives) in several types of environmental matrices [6–14].

The recent trend in sample preparation methods involves miniaturization of the traditional liquid–liquid extraction method by greatly reducing the

*Corresponding author. Tel.: +30-82-137-473; fax: +30-82-137-474.

E-mail address: kalogera@mred.tuc.gr (N. Kalogerakis).

0021-9673/01/$ – see front matter
PII: S0021-9673(01)01417-0

solvent-to-aqueous ratio. Single-drop microextraction (SDME) evolved from this new approach [15]. According to this technique, a microdrop of a water-immiscible solvent is left suspended on the tip of a conventional microsyringe, immersed in a water-contaminated sample [16,17]. Organic contaminants are transferred from the aqueous to the organic phase and after sampling for a set period of time the microdrop is retracted into the syringe and transferred into a GC system for further analysis.

Recently, our group applied SDME to the trace analysis of 11 nitroaromatic explosives in water samples [18]. The purpose of the present work is to provide, for the first time, an experimental comparison between SPME and SDME based on the results obtained for the analysis of explosives in water samples. The paper is divided into two sections. In the first, the two techniques are compared in terms of procedure, with the main advantages/drawbacks of each method being reviewed. In the second, the two methods are compared in terms of method performance by examining linearity, precision and limits of detection for each nitroaromatic compound.

2. Experimental

2.1. Chemicals

All solvents (pesticide-grade) were obtained from Merck (Darmstadt, Germany). The deionized water used for sample preparation was prepared on a water-purification system (EASYpure RF) supplied by Barnstead/Thermolyne (Dubuque, IA, USA). The US Environmental Protection Agency (EPA) 8330 explosive standards were obtained from Supelco (Bellefonte, PA, USA) in the form of two separate 1-mL acetonitrile solutions: mix A and mix B. Mix A contained 2-amino-4,6-dinitrotoluene (2-ADNT), 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrotoluene (2,4-DNT), 1,3,5-trinitro-1,3,5-triazine (RDX), nitrobenzene (NB), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), 1,3,5-trinitrobenzene (1,3,5-TNB), and 2,4,6-trinitrotoluene (TNT), each at 100 μg/mL. Mix B contained 4-amino-2,6-dinitrotoluene (4-ADNT), 2,6-dinitrotoluene (2,6-DNT), 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), 4-nitrotoluene (4-NT) and tetryl, each at 100 μg/mL. 2,3-Dinitrotoluene (2,3-DNT) (Riedel-de Haën, Seelze, Germany) was used as an internal standard.

For extraction using both microextraction techniques, 5 mL of the corresponding spiked solution were placed in 7-mL clear glass vials, equipped with 0.5-in. (1 in.=2.54 cm) stir bars and fitted with black Viton septa and screw caps with a hole, all purchased from Supelco. Magnetic stirring at 400 rpm was applied at all times. Details regarding sample preparation and extraction using SDME can be found elsewhere [18]. Each morning, standard solutions of the target analytes were extracted by using both SDME and SPME methods in order to ensure consistency.

For SPME, working standards at the concentration levels of interest were prepared daily, by spiking salted water (20%, w/v, NaCl) solutions. SPME was performed using a manual 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB) SPME fiber and a SPME fiber holder assembly all purchased from Supelco, Sigma–Aldrich. Direct immersion sampling of the salted aqueous sample solutions was chosen rather than headspace sampling since it has been shown to enhance extraction of all target analytes [13,14]. For all quantification experiments, the salted aqueous solutions were spiked prior to extraction with the exact amount of a 2,3-DNT acetonitrile solution. The SPME fiber holder assembly was then clamped at a fixed location above the glass vial containing the stirred spiked sample solution. The SPME fiber was exposed to the salted aqueous phase and after sampling for 15 min the fiber was retracted and transferred to the heated injection port of the GC–MS system for 5 min.

2.2. GC–MS analysis

A Shimadzu GC-17A, Version 3, QP-5050A GC–MS system (Shimadzu, Kyoto, Japan) equipped with a 10 m×0.25 mm, 0.25 μm HP-5MS capillary column (Hewlett-Packard, Palo Alto, CA, USA) was used for all analyses. A low-volume inlet liner, special for SPME, was used (Supelco). The system operated using helium (>99.999% pure) as a carrier gas at a flow-rate of 2.0 mL/min. The head-pressure was set at 29 kPa. The MS ionization mode was electron impact (70 eV) and data were acquired in the full-scan detection mode from 45 to 300 u at a

rate of 0.5 scan/s. For SDME, the injector, interface and oven temperatures were programmed as described in Ref. [18]. For SPME, the split/splitless injector operated at 260°C, with the purge flow closed for 5 min. The GC oven was programmed as follows: 60°C for 1 min, then to 150°C at 15°C/min, and to 250°C at 20°C/min. A solvent delay time of 1 min was used with the analysis starting at 1.50 min.

3. Results and discussion

3.1. Comparison of procedures and chromatographic analyses

The SPME process mainly comprises of two steps. First, all target analytes are extracted from a sample matrix by exposing a thin polymer-coated fused-silica fiber. The SPME fiber is then transferred to the heated injection port of a GC where the retained analytes are desorbed and subsequently separated and quantified. There are two main types of SPME sampling: immersion sampling, where the fiber is immersed in the aqueous sample, and headspace sampling, where the fiber is exposed to the headspace above the liquid or solid sample [5]. Comparison of the two sampling modes for the extraction of explosives revealed that immersion sampling enhances extraction, whereas headspace SPME sampling works relatively well for analytes of lower molecular mass (NB and the NT isomers) [13,14]. An increase in sample temperature would enhance headspace extraction [12], but for non-volatile and thermally unstable compounds such as HMX it is not recommended [13]. Additionally, by keeping the sample temperature at 20°C and using the immersion SPME sampling mode, direct comparison between the two microextraction methods was possible.

The PDMS–DVB fiber was chosen for the present studies as it was found to yield the highest recoveries when compared to other commercially available SPME fibers [13]. Although today there are several types of commercially available SPME fibers, in some cases it is difficult to select a fiber coating of polarity close to the polarity of the target analytes [7]. In general, an analytical laboratory conducting SPME experiments needs a collection of fibers as the method selectivity towards classes of compounds depends on the polarity and film thickness of the coating phase. SPME fibers offer the advantage over other sorbent packings (such as SPE) that they can be used for up to 100 extractions [7]. However, these fibers are expensive, fragile and have a limited lifetime. From lot to lot, they may differ in length and coating character [19]. According to a recent report investigating new fibers by optical microscopy, damaged areas on the fiber coating and at the connection of the fused-silica fiber with the fiber attachment may be present, thus affecting method performance [20].

Before using a fiber for the first time, a thermal conditioning step is required. Even when this step is carefully performed, partial loss of the coating may occur, resulting in extra peaks during the chromatographic analysis [3]. This was the case here, where two extra peaks appeared and became intense after about 50 SPME extractions. One of these SPME contaminants co-eluted with tetryl and obscured the analysis. From our experience, SPME contaminants may differ from fiber to fiber even if they are of the same type.

Another effect that contributes to artifact formation and low repeatability of the SPME method is the potential for sample carry over between runs [21]. This is due to incomplete desorption observed for analytes of higher molecular mass and can invalidate the results. An extra cleaning step is recommended in such cases, usually carried out either by immersing the fiber in a water or solvent stirred solution or by thermal cleaning [19]. When SPME is coupled to GC, problems of peak tailing for the first-eluting analytes are quite common. Special low-volume SPME inlet liners are commercially available in order to overcome this problem. Their efficiency was demonstrated in the present studies.

For the nitroaromatic explosives as well as for other analytes, addition of salt to the aqueous sample prior to SPME enhances extraction due to the salting-out effect. However, high salt concentrations degrade the fiber, thus limiting its lifetime and introducing imprecision in the measurements [22]. In the case where the use of high salt concentrations is unavoidable, quick cleaning of the fiber between extraction and injection is recommended. This is done by directing, for few seconds, a stream of purified water from a wash bottle down the length of

the fiber [19]. It should be noted that this type of washing is effective for analytes with lower volatilities, but will impair precision for highly volatile compounds.

In order to eliminate the SPME fiber as a source of imprecision it is recommended to monitor the fiber's response on a regular basis, and to inspect visually the SPME coating using a stereomicroscope. Depending on whether any significant changes or irregularities are identified, the fiber should be kept, cleaned or discarded [19].

SDME represents a miniaturization of the traditional LLE sample preparation technique. According to this method, microextraction is performed simply by suspending a 1-μL drop directly from the tip of a microsyringe needle immersed in a stirred aqueous solution containing the target analytes (Fig. 1). After extracting for a prescribed period of time, the microdrop is retracted back into the microsyringe needle and transferred to the GC system for further analysis. As extraction involves only a few microliters of organic solvent, SDME can be viewed as a virtually solvent-free sample preparation technique. In addition, it utilizes inexpensive apparatus commonly found in laboratories having GC and/or HPLC facilities, thus minimizing the costs of analysis per sample. There is a restriction, however, when using this preconcentration method, as headspace sampling of organic analytes has not yet been reported. Previous attempts to adapt solvent microextraction for headspace analysis concerned the sampling of atmospheric gas streams and aerosols [23].

From several water-immiscible solvents differing in polarity and water solubility, toluene was used as an extractant solvent since it combined good selectivity and showed no significant solvent loss during extraction [18]. In general, for SDME the choice of organic solvent should be based on a comparison of selectivity, extraction efficiency, incident of drop loss, rate drop dissolution, as well as level of toxicity. The main drawbacks of SDME when compared to SPME are that prolonged extraction times and faster stirring rates are not recommended, since they usually result in drop dissolution and/or dislodgment. In addition, when using this drop-based technique, addition of salt to the aqueous sample prior to extraction does not enhance the extraction [18,24]. For the nitroaromatic explosives studied here it was assumed that, apart from the salting-out

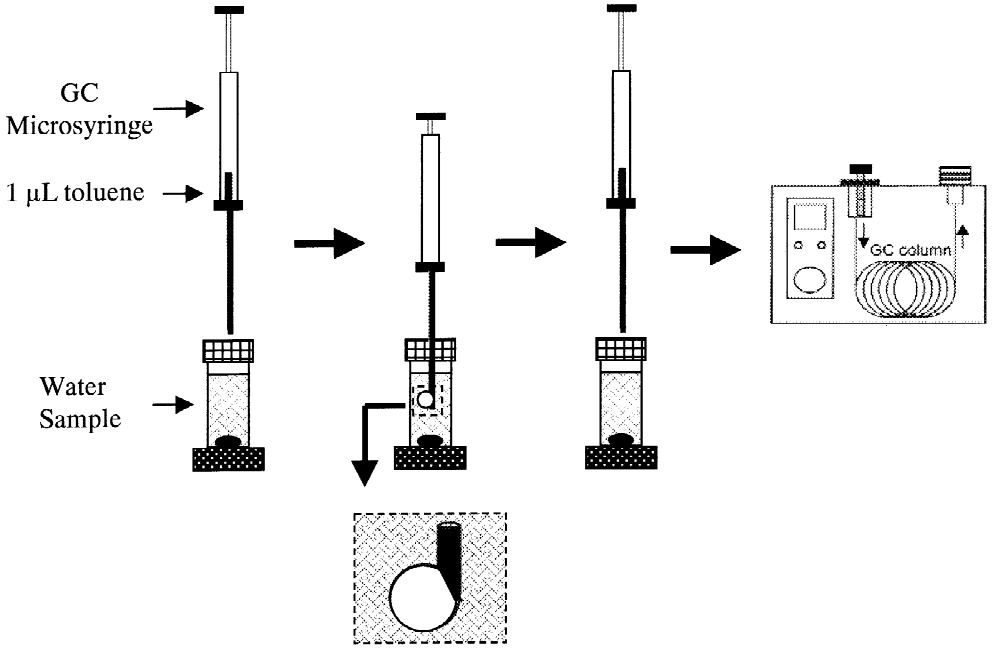

Fig. 1. Schematic representation of the SDME procedure used. The technique was first introduced by Jeannot and Cantwell in 1997 [16].

effect, the presence of salt caused a second effect, adverse for the extraction film as the diffusion rates of target analytes into the drop were reduced or remained the same [18].

SDME eliminates the problems of peak tailing and sample carry-over. However, the microdrop-based method described here requires more careful and elaborate manual operations, as incidents of drop loss and drop dislodgment have been reported [16]. There is also a limit in detecting analytes when using a GC system due to the solvent peak, which may obscure early-eluting analytes. In the present studies, investigation of nitrobenzene was not possible, as it co-eluted with the organic solvent during the GC–MS analysis [18].

Table 1 compares the peak areas obtained after sampling with immersion SPME for 15 min a 5-mL aqueous solution (20% NaCl) containing 100 μg/L of each target contaminant and after exposing for 15 min a 1 μL toluene drop to a 5-mL aqueous solution spiked at 100 μg/L for each analyte. To avoid incidents of drop loss or dissolution, a 15-min sampling time was adopted for SDME [18]. In order to allow direct comparison between the two methods, a 15-min sampling time was chosen for SPME. At 15 min of sampling both SPME [10,13] and SDME [18] are still in the rising portion of their equilibration time profile. For quantitative analysis, however, it is not necessary for the analytes to have reached equilibrium, only to allow sufficient mass transfer onto the SPME fiber [10] or into the drop [18] in the case of SDME. Table 1 shows clearly that, for all target contaminants, SPME results in a greater analytical response of the instrument. Under the present experimental conditions, detection of HMX was not possible with either of the extraction techniques due to the thermal instability of the analyte [13], as well as the carrier gas linear velocity necessary for the chromatographic separation of the other analytes. In addition, SDME resulted in a limited detection of RDX [18]. For comparative reasons, RDX, HMX and NB were not included in the studies regarding the performance of the two methods.

Table 1
Peak area ($\times 10^5$) of analytes after sampling with immersion SPME for 15 min a 5-mL aqueous solution (20% NaCl) containing 100 μg/L of each target contaminant and after sampling for 15 min a 5-mL aqueous solution containing 100 μg/L of each analyte with a 1 μL toluene drop (SDME)

Analyte	Peak area ($\times 10^5$)	
	SPME	SDME
2-NT	374.3	109.3
3-NT	397.8	112.7
4-NT	381.5	103.8
1,3-DNB	122.7	53.49
2,6-DNT	237.3	75.96
2,4-DNT	201.9	58.22
TNB	20.23	18.91
TNT	96.77	37.12
4-ADNT	80.48	17.27
2-ADNT	74.97	22.46
Tetryl	9.262	5.977

3.2. Comparison of method performance

Quantification of target analytes is possible with either method. For SPME, a known amount of internal standard is added to the contaminated water sample (20% NaCl) just before extraction, whereas for SDME the organic phase consists of a 1 μL internal standard toluene solution. All experimental data concerning the SDME technique were taken from Ref. [18].

The precision of each method was determined by performing five consecutive extractions under the same operating conditions. The spiked aqueous solutions used contained 100 μg/L of each target contaminant. The results are summarized in Table 2. Overall, the reproducibility expressed as relative standard deviation (RSD) was found to be satisfactory for SPME (ranging from 2.0 to 8.9%, with a mean value of 3.5%) and was similar to other values obtained previously [10,13]. Regarding SDME, the RSD values were somewhat worse and varied between 4.3 and 9.8%. An additional consideration for both extraction techniques is that higher RSDs are expected when, as in this case, extractions are carried out under non-equilibrium conditions. The linearity of the detector's response using both extraction techniques was verified in the concentration range 20 to 1000 μg/L. Triplicate analyses were run for each of the five concentration levels chosen within this range. For SPME, the correlation coefficient (r^2) ranged from 0.9917 to 0.9979 and for SDME from 0.9498 to 0.9857 (Table 2). It is evident that, with

Table 2
Main method parameters for SPME (immersion sampling for 15 min of a 5-mL spiked salted aqueous solution) and for SDME (1 μL toluene drops for 15 min in 5-mL spiked aqueous solutions)

Analyte	SPME			SDME[a]		
	Correlation coefficient (r^2)	LOD[b] (μg/L)	RSD[c] (%, $n=5$)	Correlation coefficient (r^2)[a]	LOD[b] (μg/L)	RSD[c] (%, $n=5$)
2-NT	0.9938	0.03	3.4	0.9857	0.11	9.3
3-NT	0.9925	0.03	3.6	0.9849	0.08	8.2
4-NT	0.9926	0.03	3.5	0.9850	0.09	8.1
1,3-DNB	0.9979	0.30	2.3	0.9608	0.47	4.5
2,6-DNT	0.9966	0.11	3.3	0.9777	0.41	4.3
2,4-DNT	0.9972	0.10	2.1	0.9652	0.53	8.2
TNB	0.9975	0.70	3.7	0.9584	0.71	8.4
TNT	0.9957	0.27	2.4	0.9711	0.40	6.8
4-ADNT	0.9963	0.21	3.1	0.9656	1.3	8.9
2-ADNT	0.9930	0.29	2.0	0.9784	0.80	8.7
Tetryl	0.9917	1.1	8.9	0.9498	1.2	9.8

[a] Data taken from Ref. [18].
[b] Lowest detectable concentration for a S/N ratio of approximately 3.
[c] Spiking level 100 μg/L; mean values for five determinations.

SPME, better precision and linearity are obtained for all target analytes. This conclusion reflects the fact that SDME requires more elaborate manual operations giving rise to less reproducible results. In addition, during extraction with the microdrop-based technique, the internal standard present in the organic drop may partition between the two immiscible liquid phases, thus affecting the precision [25].

The limits of detection (LODs) for all target analytes at a signal-to-noise (S/N) ratio of approximately 3 using SPME were then determined. The LOD obtained previously with SPME varied depending on the polarity of the fiber and the type of detector attached to the GC instrument. A detailed discussion regarding the LOD values obtained with SPME for the extraction of explosives from water samples is reported elsewhere [13,18]. Overall, the two preconcentration methods examined here yielded LOD values well below the drinking water standards and health advisory numbers of the EPA for increased cancer risk of 10^{-4} (100 μg/L for TNT; 5 μg/L for DNB, 2,4-DNT and 2,6-DNT) [26]. The results show clearly that, under the present experimental conditions, SPME is a more sensitive technique than SDME, demonstrating the influence of salt addition prior to extraction. For SPME, lower LODs are expected by prolonging the extraction times combined with the single ion monitoring (SIM) method in the mass spectrometer instead of the full-scan mode used here. For SDME, however, prolonged sampling times may result in drop dissolution and dislodgment. Instead, when better sensitivities are required, the use of larger organic microdrops (resulting in an increase of the analytical signal of the detector) [24] combined with the SIM method for the mass spectrometer is more appropriate.

Groundwater collected from a well in Pelekapina-Chania and tap water from a chemistry laboratory were analyzed using the SPME method, in order to evaluate the effect of the matrix and compare the results with those obtained with SDME. It should be mentioned that the water samples used for the SPME ''recovery'' studies were collected on a different day than those used for the drop-based microextraction technique. Initial SPME extraction followed by GC–MS analysis of these water samples revealed that they were free of the test compounds. In addition, SDME extractions of these water samples, spiked at 100 μg/L, ensured consistency. Thus, five replicate samples from each water sample were prepared by spiking at 100 μg/L with the target analytes and by

Table 3
Average relative recoveries (%) and relative standard deviations (% RSD) for each target analyte after extracting with SPME (immersion sampling for 15 min; 20% NaCl) and SDME (1 μL toluene drop; 15-min exposure;) 5-mL tap water and groundwater samples spiked at 100 μg/L with each analyte. Mean values for five determinations ($n=5$)

Analyte	Relative recovery in % (RSD, %, $n=5$)			
	Tap water		Groundwater	
	SPME	SDME	SPME	SDME
2-NT	106 (1.9)	83 (11.0)	96 (5.9)	93 (9.3)
3-NT	108 (2.6)	84 (10.4)	95 (5.6)	94 (9.0)
4-NT	108 (3.4)	82 (11.3)	96 (6.0)	92 (9.7)
1,3-DNB	100 (2.2)	88 (7.5)	93 (2.6)	92 (10.5)
2,6-DNT	107 (0.9)	85 (9.6)	99 (5.2)	91 (10.9)
2,4-DNT	109 (1.0)	84 (8.8)	96 (3.0)	89 (10.9)
TNB	94 (4.6)	86 (6.0)	86 (8.1)	100 (12.2)
TNT	106 (2.1)	85 (8.5)	92 (1.5)	98 (11.3)
4-ADNT	103 (9.6)	97 (8.7)	105 (9.6)	92 (12.0)
2-ADNT	114 (1.9)	102 (7.1)	100 (3.5)	89 (13.0)
Tetryl	100 (6.3)[a]	92 (13.1)	95 (8.6)[a]	93 (10.4)

[a] As the analyte co-eluted with a SPME contaminant, calculations were based on the m/z 242 ion.

adding an appropriate amount of NaCl. The samples were subsequently analyzed under the selected SPME conditions. SPME, like SDME, is an equilibrium technique and not an exhaustive one. Hence, the term ''recoveries'' can be ambiguous. Here, instead of absolute recovery the term relative recovery, determined as the ratio of the concentration found in environmental and deionized water samples, spiked with the same amount of analytes, is used. The results obtained with SPME as well as those previously reported for SDME are given in Table 3. For SPME, the concentrations of the nitroaromatic explosives determined in the spiked environmental water samples agreed reasonably well with the known values. The average relative recoveries ranged from 94 to 114% for the tap water experiments and from 86 to 100% for the groundwater experiments, revealing that, in the present context, the matrix has little effect on the analysis of samples. A similar conclusion was deduced in the case of water samples analyzed with the SDME technique [18]. However, the RSD values obtained with the microdrop-based method were higher than those obtained with SPME, reflecting once again the fact that single-drop microextraction is a more elaborate method.

4. Conclusions

SPME and SDME are two fast microextraction methods recommended for the determination of nitroaromatic explosives in water samples. The main drawbacks of SPME are (i) it requires dedicated and expensive apparatus, increasing the costs of analysis per sample and (ii) the fiber's lifetime is limited as it degrades with increased usage, resulting in peaks that may co-elute with the target analytes. However, SPME can be easily used for headspace analysis and yields lower detection limits for the tested analytes. SDME, on the other hand, requires more elaborate manual operations, which affect linearity and precision. Overall, both techniques represent powerful alternatives to the conventional extraction methods due to their speed, negligible volume of used solvents and the ability to detect analytes at very low concentrations.

References

[1] M.E. Walsh, T.A. Raney, Determination of nitroaromatic, nitramine, and nitrate ester explosives in water using SPE and GC/ECD; comparison with HPLC, Special Report 98-2,

US Army Cold Regions Research and Engineering Laboratory, Hanover, NH, 1998.
[2] SW-846, Method 8330, Nitroaromatics and nitramines by high performance liquid chromatography (HPLC), US Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, 1994.
[3] M. de Fatima Apendurada, J. Chromatogr. A 889 (2000) 3.
[4] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[5] H. Lord, J. Pawliszyn, J. Chromatogr. A 885 (2000) 153.
[6] A. Penalver, E. Pocurull, F. Borrull, R.M. Marce, Trends Anal. Chem. 18 (1999) 557.
[7] J. Namiesnik, B. Zygmunt, A. Jastrzebska, J. Chromatogr. A 885 (2000) 405.
[8] R. Eisert, J. Pawliszyn, Crit. Rev. Anal. Chem. 27 (1997) 103.
[9] J.Y. Horng, S.D. Huang, J. Chromatogr. A 678 (1994) 313.
[10] S.A. Barshick, W.H. Griest, Anal. Chem. 70 (1998) 3015.
[11] M.R. Darrach, A. Chutjian, G.A. Plett, Environ. Sci. Technol. 32 (1998) 1354.
[12] K.P. Kirkbride, G. Klass, P.E. Pigou, J. Forensic Sci. 43 (1998) 76.
[13] K.G. Furton, J.R. Almirall, M. Bi, J. Wang, L. Wu, J. Chromatogr. A 885 (2000) 419.
[14] E. Psillakis, G. Naxakis, N. Kalogerakis, Presented at the 6th International Conference of Environmental Science and Technology, Samos, Greece, 30 August–2 September 1999.
[15] H. Liu, P.K. Dasgupta, Anal. Chem. 68 (1996) 1817.
[16] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 69 (1997) 235.
[17] Y. He, H.K. Lee, Anal. Chem. 69 (1997) 4634.
[18] E. Psillakis, N. Kalogerakis, J. Chromatogr. A 907 (2001) 211.
[19] H. Lord, J. Pawliszyn, J. Chromatogr. A 902 (2000) 17.
[20] C. Habenhauer-Troyer, M. Crnoja, E. Rosenberg, M. Grasserbauer, Fresenius J. Anal. Chem. 366 (2000) 329.
[21] H. Prosen, L. Zupancic-Kralj, Trends Anal. Chem. 18 (1999) 272.
[22] F. Hernadez, J. Beltran, F.J. Lopez, J.V. Gaspar, Anal. Chem. 72 (2000) 2313.
[23] K.E. Miller, R.E. Synovec, Talanta 51 (2000) 921.
[24] Y. Wang, Y.C. Kwok, Y. He, H.K. Lee, Anal. Chem. 70 (1998) 4610.
[25] L.S. de Jager, A.R.J. Andrews, Chromatographia 50 (1999) 733.
[26] Drinking Water Standards and Health Advisories, EPA-822-B-00-001, US Environmental Protection Agency, Office of