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Journal of Chromatography A, 963 (2002) 73–82

JOURNAL OF CHROMATOGRAPHY A

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On-line coupling of supercritical fluid extraction with high-performance liquid chromatography for the determination of explosives in vapour phases

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Abstract

An analytical method for determining nitroaromatic explosives in vapour phases is presented. Samples were collected by pumping air through glass fibre filters and polyurethane foam adsorbents, and an on-line extraction system combining supercritical fluid extraction (SFE) and high-performance liquid chromatography (HPLC) was developed. This allows analytes to be transferred from the adsorbent to the HPLC system via a porous graphitic carbon trap. When using gradient elution with a suitable mobile phase, most of the nitroaromatic isomers tested were separated. The proposed method is fully automated, allows a complete analysis to be processed in less than 30 min, and it is compatible with most of the organic solvents commonly used as SFE modifiers or additives. The method has been applied to the analysis of real samples obtained from headspace sampling of military-grade 2,4,6-trinitrotoluene and has been shown to constitute a promising alternative for assessing whether areas are mined in landmine-clearing operations.

Keywords: Supercritical fluid extraction; Explosives; Porous graphitic carbon; Mine detection; Nitroaromatic compounds; Nitrotoluenes

1. Introduction

The detection and elimination of buried landmines poses severe, long-term problems spread across many parts of the world. The United Nations estimates that up to $120 \cdot 10^6$ mines remain buried, at a clearance cost of US$ $30 \cdot 10^8$. Estimates for total clearance using existing technology range from decades to centuries, the most often quoted period being approximately 150 years, if no new mines are buried.

An approach currently being investigated is the chemical detection of vapour that evolves from explosives and is transported to the surrounding air or soil in the immediate vicinity of mines. Active research is being pursued into the detection of buried landmines using trained dogs [1], sensors [2,3], vapour sorption onto solid adsorbents [4–6] and solid-phase microextraction (SPME) [7–9].

Extraction of explosives from a solid adsorbent is usually done by using organic solvents [10,11] or thermal desorption [4,12]. After the desorption, components of the explosive mixtures can be separated and determined using high-performance liquid chromatography [13], gas chromatography [7–9,14], ion mobility spectrometry [15], capillary electrochromatography [16], supercritical fluid chromatog-

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0021-9673/02/$ – see front matter
PII: S0021-9673(02)00136-X

raphy (SFC) [17,18] or electrokinetic capillary electrophoresis [19].

Supercritical fluid extraction (SFE) is an environmentally friendly and efficient extraction technique that has received a great deal of attention in the last decades [20–22]. Briefly, SFE reduces or even eliminates the use of organic solvents, extracts samples quickly and simplifies concentration and cleaning of the extracted analyte. To date, SFE applications involving energetic materials have mainly focused on characterising solubility and phase equilibrium parameters, or the fractionation, of explosive material constituents [23–25], extraction of nitroaromatic compounds from native or spiked soils [26–31] and water analysis [32].

The most difficult step in the SFE analysis of nitroaromatic substances is reported to be trapping the analyte after extraction [33,34]. An on-line system could clearly be very useful in attempts to overcome this problem. An efficient on-line system should be able to focus the analytes during desorption from the adsorbent and give acceptable chromatographic performance. One of the major advantages of SFE is that it is suitable for on-line coupling. Thus, in other types of analyses it has already been coupled with HPLC [35–38], GC [39,40], LC–GC [41], SFC [42,43] and capillary electrochromatography [44].

The first aim of the study presented here was to develop a suitable on-line SFE–HPLC coupling system that could overcome the practical drawbacks reported for this kind of hyphenation. A further goal was to investigate the performance of the on-line method, by extracting and analysing organic explosives collected (from air samples) on glass fibre filters and polyurethane foam (PUF) plugs.

2. Experimental

2.1. Chemicals

The nitroaromatic reference substances were obtained from several sources: 1,2- (1,2-DNB, CAS identification number 528-89-0), 1,3- (1,3-DNB, CAS 99-65-0) and 1,4-dinitrobenzene (1,4-DNB, CAS 100-25-4) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). 2,4-, 2,6-Dinitrotoluene (2,4- and 2,6-DNT; CAS 121-14-2 and 06-20-2, respectively) and 2,4,6-trinitrotoluene (TNT, CAS 118-96-7) were obtained from the Swedish Defence Research Agency (Tumba, Sweden). Trinitrobenzene (TNB, CAS 99-35-4), 2,3- (2,3-DNT, CAS 602-01-7), 2,5- (2,5-DNT, CAS 619-15-8) and 3,5-dinitrotoluene (3,5-DNT, CAS 618-85-9) were purchased as 100 μg/mL acetone solutions from Promochem (Wesel, Germany). Reference standard solutions were prepared weekly in acetonitrile and were added, at known concentrations, to the blank filters and PUF adsorbents. The spiked filters and PUFs were wrapped in aluminium foil and allowed to equilibrate for at least 7 days at −4 °C before use.

Trifluoroacetic acid (TFA, purity >98%) and triethylamine (TEA, purity >99.5%) were purchased from Fluka (Stockholm, Sweden); methanol, dichloromethane and acetone (Suprasolv quality for liquid chromatography) were from Merck (Darmstadt, Germany). Acetonitrile and 2-propanol (Chromasolv quality for liquid chromatography) were from Riedel-de Häen (Seelze, Germany).

2.2. Air sampling

Air sampling was performed with a personal sampler, as previously described [45]. Briefly, it consists of an anodised aluminium holder which contains a 25-mm binder-free A/E borosilicate glass fibre filter (Gelman, Ann Arbor, MI, USA) and two 15×15 cm cylindrical polyurethane foam plugs (Specialplast, Gillinge, Sweden) used to trap the analytes. Air was pumped through the sampler using a battery-operated personal sampler pump (224-PCXR7, SKC, Eighty Four, PA, USA).

Prior to sampling, the glass fibre filter was ultrasonically treated (Bransonic 220, Scantec Lab, Sweden; output power, 50 W; frequency, 48 kHz) for 20 min in methanol, acetone, and dichloromethane, respectively. The PUF adsorbent plugs were boiled in water for 4 h and then Soxhlet-extracted with dichloromethane for 24 h.

2.3. Supercritical fluid extraction

An AutoPrep 44 (Suprex, Pittsburgh, PA, USA) stand-alone SFE system was used. Extractions were

performed using a 1-mL stainless steel extraction vessel (Suprex). The system also included a MPA-1 Solvent Modifier Pump (Varian, Walnut Creek, CA, USA), which was used for dynamic modifier delivery, and a variable restrictor able to provide supercritical fluid flow-rates in the range 0.5–7.0 mL/min.

High-purity carbon dioxide (C-50 quality) under helium headspace (pressure, 13.8 MPa) was purchased from AGA (Sundbyberg, Sweden).

2.4. High-performance liquid chromatography

The HPLC system consisted of a Varian 9012 HPLC gradient pump, a 9050 Varian programmable multi-wavelength UV detector and an Hypercarb analytical column with 5 μm beads (100 mm×4.6 mm) from ThermoQuest (Cheshire, UK).

The analytical column was maintained at a constant 60 °C and analytes were chromatographically separated and eluted by a linear, 15 min gradient from A–B (20:80, v/v) to 100% B, where A was Milli-Q water, and B was a mixture of acetonitrile–2-propanol (90:10, v/v), both containing 3 m*M* TFA and 3 m*M* TEA. After the gradient, the column was washed with 100% B for 5 min. The solvent was then returned to the initial composition over 1 min, and the column was finally equilibrated for 10 min with this mixture before the next analysis. Eluting compounds were detected by UV absorbance at 254 nm and the flow-rate was 0.8 mL/min throughout.

2.5. On-line SFE–HPLC coupling

The SFE and HPLC systems were hyphenated using two air-actuated (Valco, Houston, TX, USA) six-port switching valves. A schematic diagram of the SFE–HPLC system and valve diagrams for each step are shown in Fig. 1. The first step (A) is supercritical fluid extraction, in which supercritical CO_2, with or without a modifier, is passed through the extraction vessel and the heated (60 °C) restrictor, where it is depressurised, and onto the 1-cm porous graphitic carbon (PGC; Hypercarb; room temperature) pre-column which retains extracted analytes. Since the supercritical fluid passes through a variable restrictor, a range of flow-rates could be used, and no limitations in supercritical fluid flow due to the hyphenation system are to be expected.

When supercritical extraction is completed, the filling valve is turned to the inject position (Fig. 1B), and the PGC trap and connecting tubes are filled with distilled water using an HPLC pump (LKB 2150, LKB, Bromma, Sweden). Any gas remaining in the system is then displaced before the chromatography begins, in order to avoid disturbing the chromatography and pressure instability.

Finally, by switching the filling valve back to the load position and the injection valve to the inject position (Fig. 1C), HPLC is started. The mobile phase passes through the Hypercarb trapping system and the analytes are desorbed. The effluent stream is then passed through the analytical column, and analytes are detected by UV absorption at 254 nm.

3. Results and discussion

3.1. General remarks

The suitability of the mechanical and chemical properties of PGC materials for use in supercritical chromatography was initially reported by Engel and Olesik [46]. Furthermore, a recent study has observed that PGC can strongly retain nitroaromatic explosives when using HPLC [47]. The retention mechanisms of PGC have not been entirely established, but it is accepted that solvophobic theory is not sufficient to explain the strong retention of polar molecules on the PGC surface. Different contributions of dispersion forces, Lewis acid–base and dipolar interactions between the analyte and the graphitic surface can be obtained by varying the mobile phase composition and modifiers [48,49].

These unique characteristics were exploited in the on-line system to focus the analytes in a PGC trap and to transfer them from the supercritical phase to a liquid phase. To separate the nitroaromatic isomers PGC was also used in the analytical column.

The analytes selected were then designed to include key components in the chemical signature of the volatiles from military-grade explosives and landmine material [9,14]. Several isomers of the analytes of interest were also introduced to obtain information about extraction and chromatographic performance.

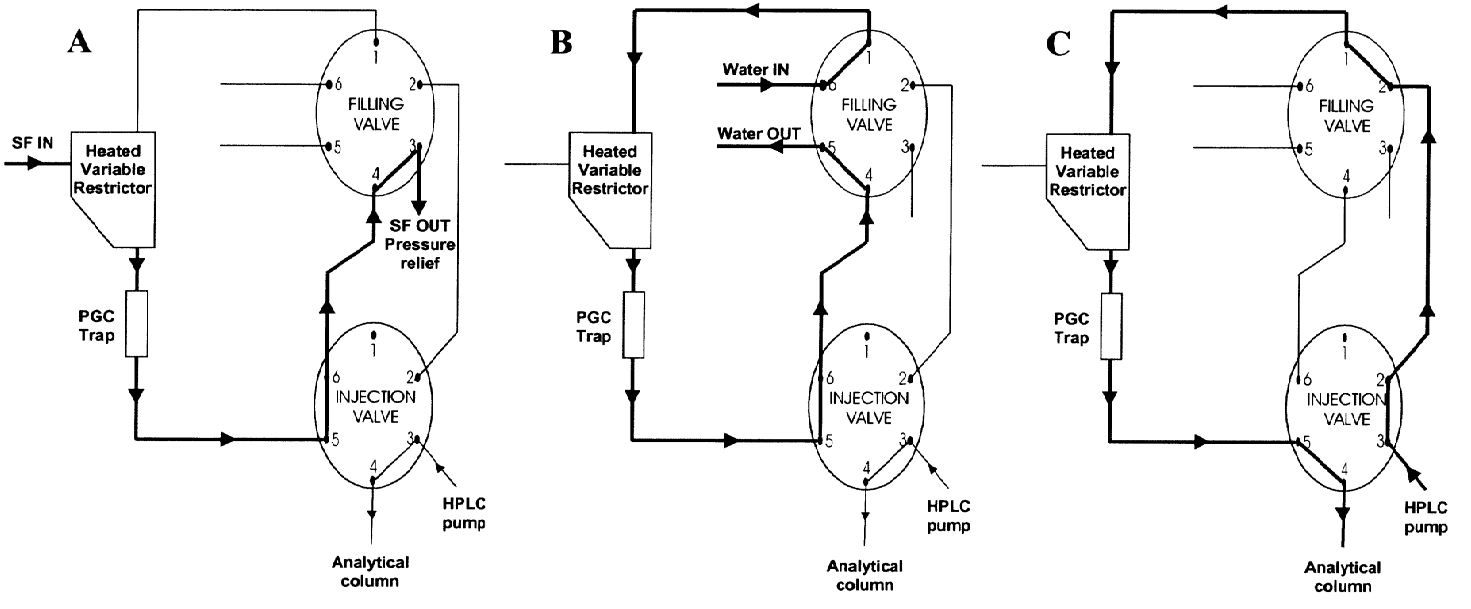

Fig. 1. SFE–HPLC system configuration. (A) SFE extraction; (B) trap water filling; (C) HPLC analysis.

3.2. SFE conditions

The effects of four parameters, namely extraction pressure, extraction temperature, and the duration of static and dynamic extraction (the latter expressed as total mass of supercritical fluid used at a flow-rate of 2.5 mL/min), on the extraction efficiency of spiked glass fibre filters and PUF adsorbents were investigated. Table 1 lists the upper, mid and lower values of each parameter tested. The values of these parameters giving the best SFE results (Experiment 7) are shown in bold and were used in further investigations. For illustrative purposes, the supercritical fluid density range is also listed in Table 1. Recovery experiments were performed by comparing on-line SFE–HPLC analysis of spiked PUF and glass fibre filters with analysis by direct liquid injection of the standard solution used to spike the samples.

The next step in the SFE method development was to study the role of potential modifiers. For this, four different modifiers at two concentration levels (2 and 10%, v/v, of the supercritical CO_2 stream in dynamic mode, or of the extraction vessel volume in static mode) were tested, as listed in Table 1.

SFE efficiency strongly depends on the way the modifier (if present) is applied. Two different systems of modifier addition can be used, static or dynamic. The first involves direct liquid addition of the modifier to the sample matrix (described as ''static modifier'' in the following text). In contrast, when using dynamic systems, the modifier is mixed with the supercritical fluid using an external pump, and the interaction of the modifier and the analytes take place in the supercritical state. A previous study concerning the extraction of nitroaromatic explosives from contaminated soil concluded that addition of the modifier directly to the sample matrix prior to the extraction increases the extraction efficiency compared to premixed fluids [31].

For the SFE of glass fibre filters and PUFs, acetonitrile and acetone gave the highest extraction recoveries, using either static or dynamic addition systems. The recoveries, shown in Tables 2 and 3, are presented as average percentages of the optimum recoveries obtained using pure carbon dioxide. The highest recovery was obtained using the dynamic method, in contrast to the previous study that found the static mode to be best for extracting nitroaromatic explosives from contaminated soil [31].

These results can be explained as follows. When the static modifier approach is used, the main effect is related to the matrix itself, which means, with the change of some physical properties of the matrix, for instance, by penetrating into the matrix and facilitating the accessibility of the supercritical fluid to the analytes. In the dynamic mode, the main modification is related to changes in supercritical fluid polarity and thus in the solubility of the extracted compounds. When the analyte/matrix interactions are strong, as when compounds are extracted from soil, the first alternative should be selected, but if the matrix has a weaker influence, as expected for the

Table 1
SFE parameters varied in the extraction efficiency evaluation

Variable	Level			Experiment																
	(+)[a]	(0)	(−)	1	2	3	4	5	6	7[b]	8	9	10	11	12	13	14	15	16	17
Extraction pressure (atm)[c]	450	325	200	−	−	+	−	−	−	**0**	+	−	+	+	+	−	+	+	−	+
Extraction temperature (°C)	150	100	50	+	+	+	−	−	+	**0**	+	+	−	−	+	−	−	+	−	−
Static extraction time (min)	10	5	0	+	−	+	+	+	+	**0**	−	−	+	−	+	−	+	−	−	−
Supercritical fluid mass in dynamic extraction (g)	35	20	5	−	−	−	−	+	+	**0**	+	+	−	−	+	−	+	−	+	+
Type of modifier	(+)	(−)		Modifier identity																
Static	2%	10%		Methanol				Dichloromethane				Acetone				Acetonitrile				
Dynamic	2%	10%		Methanol				Acetone				Acetonitrile				Acetonitrile (0.1% TFA)				

[a] Supercritical fluid densities: (+) 0.788 g/mL; (0) 0.695 g/mL; (−) 0.332 g/mL.
[b] Represents three replicates at the central point.
[c] 1 atm: 101 325 Pa.

Table 2
Static modifier study ($n=10$)[a]

Analyte	Methanol		Dichloromethane		Acetone		Acetonitrile	
	2%[b]	10%[c]	2%	10%	2%	10%	2%	10%
1,2-DNB	86	74	88	79	**107**	106	106	99
2,6-DNT	93	79	59	39	**111**	98	106	109
1,3-DNB	95	87	80	95	107	101	103	**114**
2,4,6-TNT	67	49	56	69	86	90	**108**	72
1,3,5-TNB	71	56	68	66	90	91	**102**	65
2,4-DNT	99	86	82	93	104	100	99	**110**
Average	85	72	72	74	101	98	**104**	95

[a] Results represent the average of those obtained for spiked filters ($n=5$) and PUFs ($n=5$).
[b] Represents 20 μl (2%) of the modifier added to a 1-mL extraction vessel.
[c] Represents 100 μl (10%) of the modifier added to a 1-mL extraction vessel.

samples described in the present work, the second system is preferred. The data listed in Tables 2 and 3 provide experimental confirmation of these hypotheses.

It is important to highlight the fact that any increase in the modifier concentration when using a dynamic addition system will cause a dramatic reduction in the extraction recovery for all nitroaromatic compounds. Further, the chromatographic performance will also be significantly impaired. Similar results have been reported by other authors [31], and it has been recorded that when the concentration of a modifier in the supercritical fluid increases, the values of the critical pressure and temperature required to maintain the mixture in the supercritical state also increase [50]. It has to be taken into account that, after passing the heated restrictor and before reaching the solid trap, the supercritical fluid is exposed to decompression and cooling. This can cause separation of the supercritical mixture into two phases. Due to the high solubility of the analytes in the modifier, this can inhibit retention of the analytes in the solid trap and also cause chromatographic problems.

To increase the polarity of the modifier, the use of small amounts of highly polar substances, known as additives, has been described [51]. Both the cited study and our own experience [47] suggested that TFA, a highly polar organic acid, could be a suitable compound for this purpose, so its effects were evaluated, at a concentration of 0.1% (v/v). As Table 3 shows, only a minor improvement in the recovery of TNT was obtained, whereas the recovery of the other analytes decreased by between 7 and 11%.

Table 3
Dynamic modifier study ($n=10$)[a]

Analyte	Methanol		Acetonitrile		Acetone		0.1% TFA 2%
	2%[b]	10%	2%	10%	2%	10%	
1,2-DNB	100	27	**110**	29	102	27	103
2,6-DNT	114	37	**125**	41	112	37	117
1,3-DNB	87	36	**98**	60	88	58	87
2,4,6-TNT	110	103	168	86	164	29	**169**
1,3,5-TNB	105	104	**145**	61	121	35	118
2,4-DNT	88	54	**102**	71	91	64	90
Average	101	60	**125**	59	113	42	114

[a] Results represent the average of those obtained for spiked filters ($n=5$) and PUFs ($n=5$).
[b] Represents percentage (v/v) of dynamic modifier in supercritical fluid stream.

Thus, acetonitrile at 2% (v/v) was found to be the best of the modifiers tested, in both static and dynamic modes.

3.3. Analytical performance

Having developed the method outlined above, it was then validated. To calculate the extraction recovery, the results of direct liquid injection of 20 μL of the reference standard solution were compared with SFE–HPLC analysis of samples spiked with an equal concentration of the reference standard solution (with analyte concentrations in the range 75–100 ng). As Table 4 shows, with the sole exception of 3,5-DNT, recoveries were found to be in the range 87–103% ($n=6$), which indicates that no breakthrough occurred during the analyte trapping step under these conditions. Further, these studies also corroborate the finding that complete elution of the analytes from the sorbent was obtained, using the selected mobile phase gradient.

In order to determine the precision of the overall method, 15 filters and PUFs were spiked with the reference standard solution at concentrations ranging from 75 to 100 ng. Table 4 shows the recoveries and RSDs observed for both sorbent materials. No differences were found between filters and PUFs.

Method detection limits (MDLs) are also shown in Table 4. To determine these limits for each analyte with the on-line method, 15 filters and PUFs were spiked with 100 ng of the analyte per sample. MDLs were then calculated as the product of the standard deviation of the 15 replicates and the two tailed *t*-value for 14 degrees of freedom at the 95% confidence level ($t=2.14$) [52,53]. The limits of detection are at the ng level for both the filter and the PUF. This analytical method may be useful for area reduction in demining, since many air sampling techniques using high sampling volumes are available.

Table 4
Analytical performance

Analyte	Recovery (%)		RSD[a] (%)		MDL[a,b]
	Filter	PUF	Filter	PUF	
1,2-DNB	91	93	3.2	3.0	24.2
2,6-DNT	102	101	5.0	5.0	35.6
2,3-DNT	99	91	6.7	7.1	19.8
1,3-DNB	89	93	5.4	4.8	56.8
1,4-DNB	87	89	6.4	7.4	53.1
TNT	103	100	4.0	3.6	25.3
2,5-DNT	101	102	2.6	2.8	9.5
2,4-DNT	94	98	6.2	5.6	28.5
TNB	96	97	7.5	9.3	48.6
3,5-DNT	80	75	9.1	10.9	36.4

[a] $n=15$.
[b] Expressed as ng of analyte on filter or PUF to be extracted.

Fig. 2 shows chromatograms obtained from the analysis of spiked, ''aged'' glass fibre filters and PUFs. The bottom trace in Fig. 2 shows the results of a blank analysis resulting from an on-line extraction performed just after the repeatability experiments with the spiked glass fibre filters. The blank chromatogram is included to emphasise that the on-line

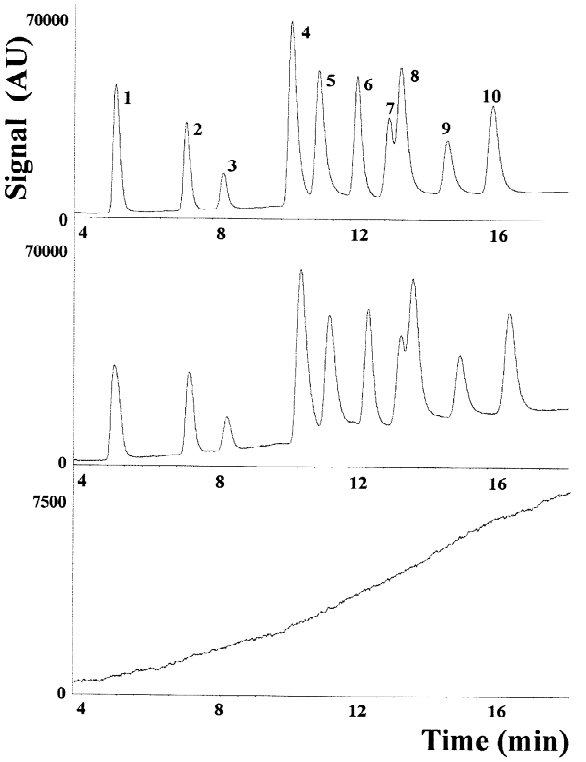

Fig. 2. Chromatograms obtained by performing SFE using CO_2 modified with 2% acetonitrile. Upper panel, spiked glass fibre filter (spiking level 100–150 ng). Middle panel, spiked PUF (spiking level 100–150 ng). Bottom panel, non-spiked glass fibre filter. Peak identification: (1) 1,2-DNB; (2) 2,6-DNT; (3) 2,3-DNT; (4) 1,3-DNB; (5) 1,4-DNB; (6) 2,4,6-TNT; (7) 2,5-DNT; (8) 2,4-DNT; (9) 1,3,5-TNB; (10) 3,5-DNT.

system does not exhibit any artefacts, ghost peaks, or memory (carry-over) effects from the PGC trapping or the analytical system.

3.4. Application to real samples

The overall method was applied to the analysis of real samples. Sampling was performed in a desiccator containing 10 g of military-grade (99% purity) TNT at 20 °C for 15 min at a sampling rate of 4 L/min. After sampling, the glass fibre filters and PUFs were collected and stored in a freezer (−18 °C) until the analysis was carried out. Fig. 3 shows examples of chromatograms obtained from the air sampling analysis, and the concentrations of the major nitroaromatics detected are presented in Table 5.

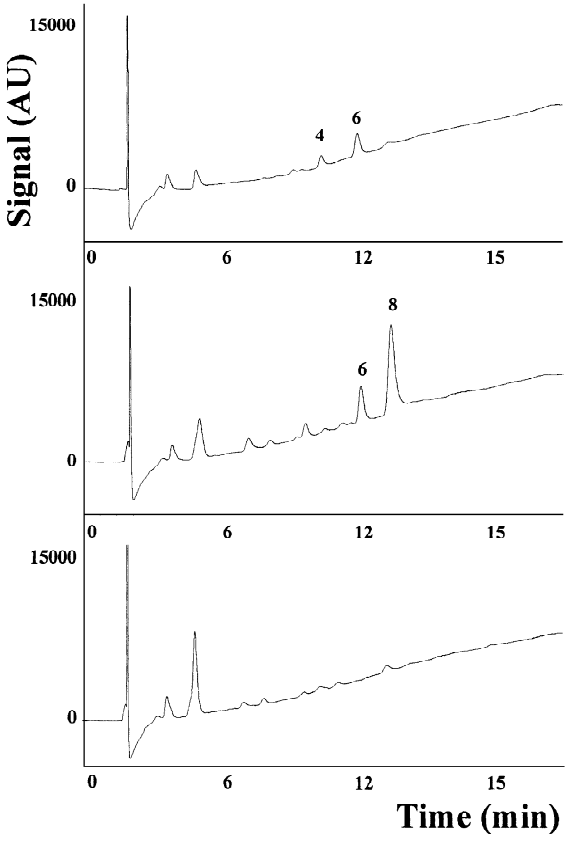

Fig. 3. Headspace sampling of military-grade TNT. Upper panel, glass fibre filter. Middle panel, PUF A. Lower panel, PUF B. See Fig. 2 for analyte identification.

Table 5
Headspace concentrations of major volatiles above military-grade TNT (n=3)

Analyte	Headspace concentration (ng L^{-1} g^{-1}) at 20 °C[a]		
	Filter	PUF A	PUF B
1,3-DNB	0.08 (10)	–	–
TNT	0.19 (8)	0.31 (8)	–
2,4-DNT	–	0.59 (5)	–

[a] Numbers in parentheses represent RSD (%).

For the explosive tested, the volatile found in the highest concentration in the equilibrium headspace was 2,4-DNT, while both 1,3-DNB and TNT were consistently detected in all the analysed samples. These results largely agree with findings reported earlier by other groups [11], although the cited study detected lower levels of TNT. These compounds are related to the manufacture of military-grade TNT and can be used as chemical markers in landmine detection when using air-sampling techniques. The unidentified peak in PUF B corresponds to 1,2-DNB regarding retention time. Nevertheless, the presence of an impurity peak at almost the same retention time, as well as the fact that it only appears in PUF B, prevent a conclusive identification.

The distribution of nitroaromatics between the filter (particulate phase) and the PUFs (semi-volatile phase) is principally dependent on the vapour pressure of the compounds. The vapour pressure for TNT is $8.02 \cdot 10^{-6}$ mmHg/20 °C, in the same range of magnitude as that of pyrene, which shows a 50:50 distribution between filter and PUF [45]; 2,4-DNT has a vapour pressure ($1.47 \cdot 10^{-4}$ mmHg/20 °C) similar to phenanthrene [45], which shows a 2:98 distribution (1 mmHg=133.322 Pa).

4. Conclusions

Hyphenation of SFE with liquid chromatography was performed using a PGC trap to transfer nitroaromatic analytes quantitatively to the analytical column. Good reproducibility was obtained for the polar analytes investigated, and high tolerance towards different modifiers or additives was demonstrated. The results show that this method is an effective and rapid technique that can be used with

disposable sampling devices for the analysis of explosives in the vapour phase. Further, the combination of SFE with HPLC offers advantages over other potential analytical techniques in terms of reduced sample handling, higher precision and suitability for automation.

The system was applied to the extraction and analysis of air samples. The major target compounds used in the chemical detection of landmines containing military-grade TNT were detected. These compounds are related to the manufacturing process of landmines, and the concentration profile is expected to vary from one explosive material to another.

Further work will focus on the application of the overall methodology for the sampling and analysis of air samples from a real minefield, as well as on hyphenating the developed extraction system with LC–MS in order to increase both the selectivity and sensitivity of the technique.

Acknowledgements

This work was supported by the National Institute of Working Life (Solna, Sweden), the Swedish Defence Research Agency (Tumba, Sweden) and the Swedish Rescue Service Agency (Karlstad, Sweden). Patrick Goede is gratefully acknowledged for supplying a TNT standard. We are also very grateful to Luisa Pereira (Thermo Hypersil, Cheshire, UK) for providing Hypercarb columns and precolumns.

References

[1] K.G. Furton, L.J. Myers, Talanta 54 (2001) 487.
[2] X. Yang, X. Du, J. Shi, B. Swanson, Talanta 54 (2001) 439.
[3] E.J. Houser, T.E. Mlsna, V.K. Nguyen, R. Chung, R.L. Mowery, R.A. McGill, Talanta 54 (2001) 469.
[4] M.E. Sigman, C. Ma, R.H. Ilgner, Anal. Chem. 73 (2001) 792.
[5] J.B.F. Loyd, J. Chromatogr. 328 (1985) 145.
[6] M. Alstein, A. Bronshtein, B. Glattstein, A. Zeichner, T. Tamini, J. Almog, Anal. Chem. (ASAP article).
[7] K.P. Kirkbride, G. Klass, P.E. Pigou, Forensic Sci. Int. 43 (1998) 76.
[8] S.A. Barshick, W.H. Griest, Anal. Chem. 70 (1998) 3015.
[9] T.F. Jenkins, D.C. Leggett, P.H. Miyares, M.E. Walsh, T.A. Ranney, J.H. Cragin, V. George, Talanta 54 (2001) 501.
[10] I.H.L. Yip, Can. Forensic Sci. J. 15 (1982) 87.
[11] R.J. Prime, J. Krebs, Can. Forensic Sci. J. 13 (1980) 27.
[12] J.R. Hobbs, E. Conde, J. Energ. Mater. 4 (1986) 511.
[13] P.M. Gates, E.T. Furlong, T.F. Dorsey, M.R. Burkhardt, Trends Anal. Chem. 15 (1996) 319.
[14] M.E. Walsh, Talanta 54 (2001) 427.
[15] R.G. Ewing, D.A. Atkinson, G.A. Eiceman, G.J. Ewing, Talanta 54 (2001) 515.
[16] C.G. Bailey, C. Yan, Anal. Chem. 70 (1998) 3275.
[17] Y. McAvoy, K. Dost, D.C. Jones, M.D. Cole, M.W. George, G. Davidson, Forensic Sci. Int. 99 (1999) 123.
[18] S.R. Wallenborg, K.E. Markides, L. Nyholm, J. Chromatogr. A 785 (1997) 121.
[19] A. Hilmi, J.H.T. Luong, A.L. Nguyen, Anal. Chem. 71 (1999) 873.
[20] Q. Lang, C.M. Wai, Talanta 53 (2000) 771.
[21] W.H. Hauthal, Chemosphere 43 (2001) 123.
[22] S.B. Hawthorne, in: R.M. Smith (Ed.), Supercritical Fluids in Chromatography and Extraction, Elsevier, Amsterdam, 1997.
[23] J.B. Morris, J. Chem. Eng. Data 43 (1998) 269.
[24] V. Teipel, P. Gerber, H.H. Krause, Propellants, Explos., Pyrotech. 23 (1998) 82.
[25] M. Ashraf-Khorassani, L.T. Taylor, J. Chem. Eng. Data 44 (1999) 1254.
[26] L.T. Taylor, Am. Lab. 25 (1993) 22.
[27] E.S. Francis, M. Wu, P.B. Farnsworth, M.L. Lee, J. Microcol. Sep. 7 (1995) 21.
[28] G. Martinez, C. Ho, W.H. Griest, Anal. Lett. 28 (1995) 1499.
[29] S. Sennert, E. Berger-Preiss, K. Levsen, Vom Wasser 85 (1995) 215.
[30] C.E. Wujcik, J.N. Seiber, J. Environ. Sci. Health A 31 (1996) 1361.
[31] R. Deuster, N. Lubahn, C. Friedrich, W. Kleiböhmer, J. Chromatogr. A 785 (1997) 227.
[32] G.C. Slack, H.M. McNair, S.B. Hawthorne, D.J. Miller, J. High Resolut. Chromatogr. 16 (1993) 473.
[33] H. Engelhardt, J. Zapp, P. Kolla, Chromatographia 32 (1991) 527.
[34] H.R. Johansen, G. Becher, T. Greibrokk, Anal. Chem. 66 (1994) 4068.
[35] M. Ashraff-Khorassani, M. Barzegar, Y. Yamini, J. High Resolut. Chromatogr. 18 (1995) 472.
[36] B.E. Wenclawiak, T. Hees, C.E. Zöller, H.P. Kabus, Fresenius J. Anal. Chem. 358 (1997) 471.
[37] M.A. Stone, L.T. Taylor, J. Chromatogr. A 931 (2001) 53.
[38] S. Salleh, Y. Saito, Y. Kiso, K. Jinno, Anal. Chim. Acta 433 (2001) 207.
[39] M.D. Burford, K.D. Bartle, S.B. Hawthorne, Adv. Chromatogr. 37 (1997) 163.
[40] M.A. Stone, L.T. Taylor, Anal. Chem. 72 (2000) 3085.
[41] H.J. Cortes, S.L. Green, R.M. Campbell, Anal. Chem. 63 (1991) 2719.
[42] M. Ashraf-Khorassani, J.M. Levy, J. High Resolut. Chromatogr. 11 (1990) 742.
[43] M. Ashraf-Khorassani, M.L. Kumar, D.J. Koebler, G.P. Williams, J. Chromatogr. Sci. 28 (1990) 599.
[44] Y.S. Fung, Y.H. Long, J. Chromatogr. A 907 (2001) 301.

[45] C. Östman, H. Carlsson, A. Bermgård, A. Colmsjö, in: P. Garrigues, M. Lamotte (Eds.), Polycyclic Aromatic Compounds: Properties, Analytical Measurements, Occurrence and Biological Effects, Gordon and Breach, Yverdon, Switzerland, 1993.
[46] T.M. Engel, S.V. Olesik, Anal. Chem. 62 (1990) 1554.
[47] E. Holmgren, P. Goede, N. Latypov, C. Crescenzi, H. Carlsson, manuscript in preparation.
[48] T.M. Engel, S.V. Olesik, Anal. Chem. 63 (1991) 1830.
[49] Y. Cui, S.V. Olesik, Anal. Chem. 63 (1991) 1812.
[50] J. Hollaender, J. Sheine, W. Dott, M. Heinzel, H.W. Hageman, G.K.E. Götz, J. Chromatogr. A 776 (1997) 233.
[51] C. Friedrich, K. Cammann, W. Kleiböhmer, Fresenius J. Anal. Chem. 352 (1995) 730.
[52] L.A. Currie, Pure Appl. Chem. 67 (1995) 1699.
[53] J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry, Ellis Horwood, Chichester, UK, 1988.