

Note

Dynamic headspace method for the improved clean-up of gunshot residues prior to the detection of nitroglycerine by capillary column gas chromatography with thermal energy analysis detection

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The detection of traces of nitroglycerine (NG) and other explosive materials is of forensic importance^{1–4}, and a gas chromatographic (GC) method with thermal energy analysis detection (TEA)⁵ has been in use here for the last 18 months. The system has primarily been employed for the detection of NG in gunshot residues, but other explosives have also been studied. With pure standards it is possible to detect down to about 5 pg of NG but such sensitivity cannot be achieved with extracts from handswabs or vacuumed samples from clothing, for such extracts are substantially contaminated with lipid and other materials. Clean-up is essential to minimise column deterioration and detector noise, and without it detection limits of 5–20 ng of NG/swab are the best attainable. The clean-up procedure previously developed here⁶ exploits selective solid phase extraction on to Amberlite XAD-7 polymeric beads and subsequent elution with solvent mixtures of the appropriate polarity and volatility. The clean-up is adequate for many samples, but during experiments on clothing it was frequently found that contamination was too great, and this led to the development of the procedure described in this paper.

The procedure exploits the volatility of NG to provide a primary clean-up. This approach has frequently been used before^{7–10}, but by trapping out the NG vapour on to the XAD-7 beads, followed by solvent elution a novel and convenient method for a GC-TEA end analysis has been developed. Although mainly applied to the detection of NG in gunshot residue samples, it is apparent that many volatile explosives can be isolated from coextractives by the described method, and hence it could be more generally applicable to the detection of explosive residues. It has been found in the case of NG that after the two-stage clean-up as much as 20% of the final extract can be analysed; this equates with detection limits on filters of about 50–100 pg.

EXPERIMENTAL

Reagents

Nitroglycerine (NG), ethyleneglycol dinitrate (EGDN), butane-1,2,4-triol-trinitrate (BTN), triethyleneglycol dinitrate (TEGDN), 2,4,6-trinitrotoluene (TNT) and RDX (hexogen) were obtained from the Propellants Explosives and Rocket Motors Establishment (PERME) (Waltham Abbey, U.K.). Nitrobenzene (NB), and 4-nitro-

toluene (4-NT) were obtained from Aldrich (Gillingham, U.K.). 2,4-dinitrotoluene (2,4-DNT) was obtained from Fluka (Glossops, U.K.) and Musk Tibetine was supplied by Givaudin (Whyteleafe, U.K.).

All solvents used were pesticide grade (Fisons, Loughborough, U.K.) except for methyl *tert.*-butyl ether (MTBE) which was HPLC grade (Rathburn Chemicals, Walkerburn, U.K.) and diethyl ether which was Analar grade (BDH, Poole, U.K.).

Sample preparation

Firing was conducted under the conditions described previously⁶. Handswabs and vacuumed clothing samples (sampled at an air flow-rate of 2.6 l/min) were generated using procedures described in the same publication. The filters from vacuuming experiments were spiked by applying known quantities of explosives dissolved in redistilled diethyl ether. The ether was allowed to evaporate by standing at room temperature for about 10 min.

Sample pretreatment

Handswabs were placed in a luer-lock glass syringe fitted with filters identical to that used for vacuuming. The MTBE solvent on the swab was removed under a gentle stream of nitrogen and the swab was then moistened with 400 μ l of acetone and allowed to stand for 5 min. The acetone was then removed under a gentle stream of nitrogen before the syringe was inserted in the dynamic head-space apparatus. For other explosives where nitrocellulose was not present the acetone treatment just described was not necessary.

Syringes containing filters on which residues had been trapped by vacuuming were moistened with 200 μ l of acetone. Care was necessary to wash the walls of the syringe to ensure complete transfer of particulate matter on to the filter. The filter was allowed to stand for 5 min and the solvent was then removed under a stream of nitrogen. The syringe was then inserted in the dynamic headspace apparatus. The addition of acetone was not necessary if explosives were present in the absence of nitrocellulose.

Dynamic headspace sampling

The equipment used for the headspace clean-up is shown in Fig. 1. The luer-lock glass syringe containing the filter or swab was connected to a glass column containing 18 mg of Amberlite XAD-7 resin; the dimensions of this column were identical to the clean-up columns described in a previous publication⁶. The column and syringe were butt-connected using a short length of PVC tubing (3 mm I.D.,

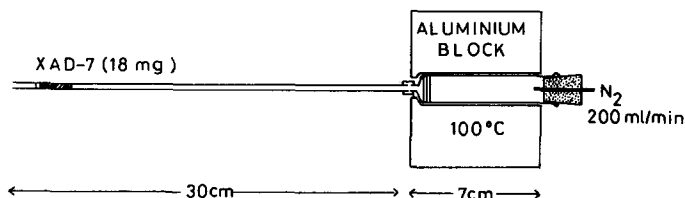


Fig. 1. Dynamic headspace system.

5 mm O.D. transparent tubing from Gallenkamp, Loughborough, U.K.) and the syringe barrel was plugged with a rubber bung (BS No. 13 solid, BDH). Nitrogen (high purity grade, Air Products, Southampton, U.K.) was passed at a rate of 200 ml/min through a stainless-steel hypodermic needle (size 21 gauge \times 1.5 in.) inserted through the rubber bung. The apparatus was then inserted into a machined aluminium block held at 100°C which was mounted in a heated unit (Reactitherm, Pierce, Chester, U.K.). After 7 min, the syringe and column were separated, removed from the aluminium block and allowed to cool.

Elution of explosives from the porous polymer

The column containing the XAD-7 beads was mounted vertically and was eluted in the following sequence: (1) 1 ml of pentane to elute NB and 4-NT; (2) 1 ml of pentane-MTBE (1:1, v/v) to elute unwanted coextractives; (3) 0.4 ml of ethyl acetate to elute NG and other explosives. Fraction 1 was reduced in volume to about 50–100 μ l by warming on the aluminium block. Fraction 3 was concentrated under a gentle stream of nitrogen to a final volume of 5–20 μ l.

Elution of less volatile explosives from the residue in the glass syringe

The syringe containing residual material was clamped vertically and 2 ml of MBTE was passed through it. The solution was then passed through a glass column containing a freshly prepared bed of XAD-7 beads, and a further 1 ml of MBTE was added to remove unwanted coextractives. Explosives were eluted with 400 μ l of ethyl acetate and this fraction was evaporated under a stream of nitrogen to a final volume of about 5–20 μ l.

Detection of NG and other explosives by GC-TEA

Chromatography was carried out using the chromatographic conditions previously described⁵, and 1 μ l aliquots of the appropriate fractions were injected. The TEA detector was used in the modified form described in the reference just cited. NG and most other explosives were monitored with a pyrolytic breakdown at 625°C, NB, 4-NT and 2,4-DNT required a pyrolysis temperature of 750°C.

RESULTS AND DISCUSSION

By examining both the XAD-7 beads and the residual material left on filters after dynamic headspacing it was found that effective transfer of NG to the beads from gunshot residues only took place if the filter was moistened with acetone before sampling. This was attributed to the NG being trapped inside nitrocellulose particles, and only becoming available for vaporisation by dissolution of the particles in acetone. The temperature of the aluminium block, the nitrogen flow-rate and the residence time in the block were optimised by experiment. The efficacy of a single XAD-7 trap was confirmed by mounting two traps in series and establishing that no NG was breaking through to the second trap. Recovery of NG from filters spiked at 5 ng was 77% (relative standard deviation, R.S.D., for $n = 5$ was 3.9%).

Although the headspace procedure was effective in separating NG from less volatile compounds it was still found necessary to selectively elute volatile impurities from the XAD-7 beads before injecting samples on to the GC-TEA system. The

two-fold clean-up process permitted the final extract to be reduced to a very low volume and as a result detection levels of about 100 pg of NG per swab or filter could be attained. For quantitation it was found that use of BTN as an internal standard permitted linear calibration plots to be constructed.

The GC-TEA system has been found to be a robust combination and for the detection of NG a pyrolysis temperature of 625°C provides both sensitivity and selectivity. Nitromusks, low-cost nitrated materials extensively used in perfumery, are also detectable under these pyrolysis conditions and being volatile materials are not separated from NG by the headspace procedure. These compounds have frequently been observed in clothing extracts, but selective elution from the XAD-7 beads and substantial GC retention time differences between them and NG suggests that they will not create an interference problem. Chromatograms of a handswab and clothing of a person having fired a hand-gun are shown in Fig. 2. The silica pyrolysis tube mounted between the GC and the TEA detector has proved to be very resistant to contamination and the one used in this work has been in use for over 6 months, whereas three GC columns had to be discarded during the same period because of contamination. With the clean-up procedure which has been developed it is anticipated that the GC columns will also have a greatly extended operational life and the pyrolysis tube may well be usable for a year or more.

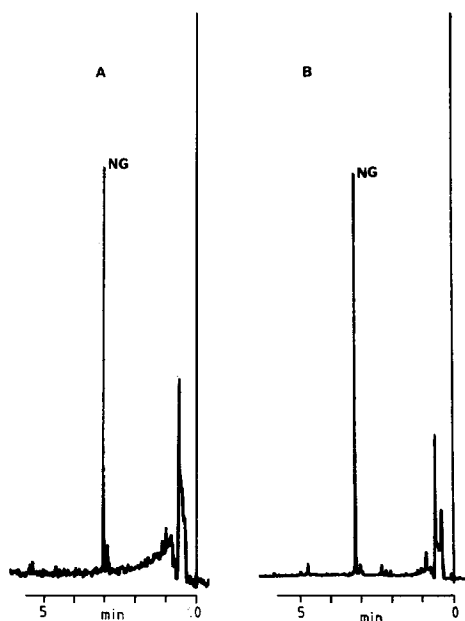


Fig. 2. Chromatograms of handswab and clothing extracts subjected to dynamic headspace clean-up. (A) Handswab extract taken from the firing hand of a subject 1 h after having discharged three rounds of Winchester Super X ammunition from a Smith & Wesson Model 19 handgun. Pyrolysis temperature, 625°C; attenuation, 20 mV; injection volume 1 μ l from 114 μ l. (B) Clothing extract sampled from shirt of a subject 21.3 h after discharging a handgun as at (A). Pyrolysis temperature, 625°C; attenuation, 50 mV; injection volume, 1 μ l from 25 μ l.

Although primarily directed at the detection of NG in handswabs many other volatile explosives and nitrated molecules can be separated and trapped by the dynamic headspace procedure described. The retention times for a selection of compounds amenable to this form of clean-up are shown in Table I, together with optimum pyrolysis temperatures. The nitramines, nitrate esters and trinitro-aromatics are all adequately detected at a pyrolysis temperature of 625°C, but the more stable

TABLE I

RELATIVE RETENTION TIMES OF EXPLOSIVES OF FORENSIC INTEREST

GC conditions: chromatograph, Carlo Erba Model 4160; injector, splitless mode at 175°C; column, BP-1 fused-silica capillary 12 m × 0.25 mm I.D. (SGE, Milton Keynes, U.K.), stationary phase film thickness, 0.25 µm; temperature programme, 60°C for 1 min then 39.9°C/min to 250°C, held for 1 min.

<i>Explosive</i>	<i>Optimum pyrolysis temperature (°C)</i>	<i>Fraction^a</i>	<i>Relative retention time</i>
EGDN	625	b	0.27
NB	750	a	0.34
4-NT	750	a	0.47
NG	625	b	0.57
2,4-DNT	750	b	0.72
TNT	625	b	0.83
RDX	625	c	0.91
Musk Tibetine	625	b	1.00 (4.84 min)

^a a = Eluted from XAD-7 beads with pentane; b = eluted from XAD-7 beads with ethyl acetate; c = retained on filter and eluted with MBTE.

mono- and dinitroaromatics (NB, 4-NT and 2,4-DNT) require a temperature of 750°C before they give an acceptable signal. Chromatograms of test mixtures analysed under the two alternative pyrolysis conditions are shown in Fig. 3. Fig. 4 shows chromatograms of mixtures of explosives volatilised from spiked filters and subsequently eluted from the XAD-7 trap with pentane (in the case of NB and 4-NT) or ethyl acetate for the more polar explosives. Of the explosives tested only NC and RDX remained behind on the filter after being subjected to the dynamic headspace clean-up procedure and Fig. 5 shows the chromatogram produced when a sample originally spiked with 6 ng of RDX and TNT was analysed by the procedure described under *Elution of less volatile explosives from the residue in the glass syringe* after volatilisation. The chromatogram shows that a trace of TNT also remained on the filter. Fig. 6 compares very dirty vacuum filter extracts spiked at the 5-ng level with NG. One sample (A) was cleaned-up by adsorption on to XAD-7 beads followed by elution with pentane-MTBE (1:1)⁶, the other (B) was subjected to the dynamic head spacing procedure described above. It is apparent from the chromatograms that higher signal to noise levels were attainable in sample B and that a higher proportion of the extract could be directly analysed.

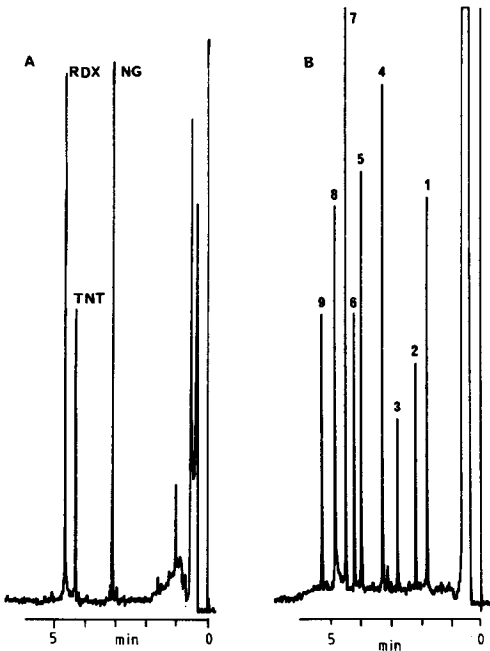


Fig. 3. Chromatograms of test mixtures of explosives. (A) 50 pg of each explosive. Pyrolysis temperature, 625°C; attenuation, 20 mV. (B) 1 = EGDN, 45 pg; all other compounds 90 pg, 2 = NB; 3 = 4-NT; 4 = NG; 5 = 2,4-DNT; 6 = TEGDN; 7 = TNT; 8 = RDX; 9 = Musk Tibetine. Pyrolysis temperature, 750°C; attenuation 20 mV.

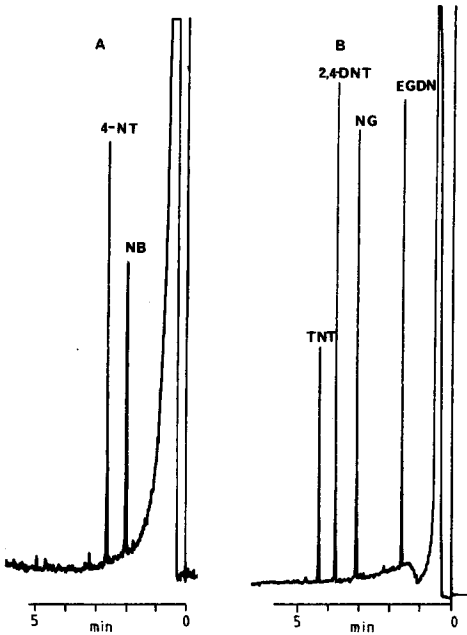


Fig. 4. Chromatograms of explosives volatilised from spiked filters. (A) Filter spiked with 200 ng of each compound. Pyrolysis temperature, 750°C; attenuation, 20 mV; injection volume, 1 μ l from 450 μ l pentane. (B) Filter spiked at the following levels 15 ng of NG and TNT, 30 ng of EGDN and 2,4-DNT. Pyrolysis temperature, 750°C; attenuation, 20 mV; injection volume, 0.75 μ l from 26 μ l EA.

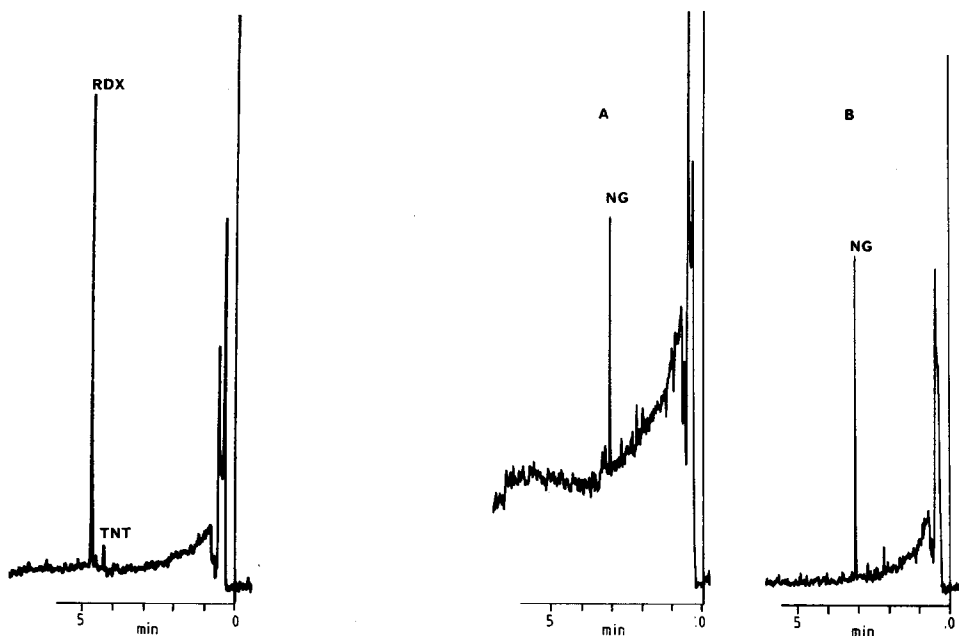


Fig. 5. Chromatogram of explosives retained on a filter after dynamic headspace. Filter spiked with 6 ng of RDX and TNT. Pyrolysis temperature, 625°C; attenuation, 20 mV; injection volume, 1 μ l from 20 μ l.

Fig. 6. A comparison of the chromatograms produced from very dirty vacuum filter extracts spiked at 5 ng with NG. (A) XAD-7 clean-up⁶. Injection volume, 0.75 μ l from 15 μ l (*i.e.*, 5% of extract). (B) Dynamic headspace clean-up. Injection volume, 1 μ l from 11 μ l (*i.e.*, 9% of extract). Pyrolysis temperature for both samples was 625°C.

CONCLUSIONS

The dynamic headspace procedure described permits volatile explosives such as NG to be effectively separated from involatile impurities that reduce the selectivity and column life of the GC-TEA procedure. By trapping the volatilised explosives on to XAD-7 beads and effecting additional clean-up by selective solvent extraction under the most favourable conditions, detection limits of sub-ng quantities per swab or filter can be achieved. Life of the GC columns is also extended by removal of involatile coextractives before injection.

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