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FORENSIC EXPLOSIVES AND FIREARMS TRACES: TRAPPING OF HPLC PEAKS FOR GAS CHROMATOGRAPHY

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ABSTRACT

Trace amounts of explosives compounds, separated from cleaned-up extracts of handswabs and clothing debris by high-performance liquid chromatography, may be trapped from the chromatography effluent onto a porous polymer (acrylonitrile or methacrylate copolymer) microcolumn for confirmatory examination by gas chromatography (GC). The microcolumn eluate is injected directly into a GC retention gap of unmodified silica, whereby explosives down to HMX in volatility may be chromatographed. Retention gaps with variously modified

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surfaces have usually given distorted chromatograms. The overall technique enables the elimination of evaporative concentration procedures in the sample work-up, and minimizes any question of whether the confirmatory technique is responding to the relevant component.

INTRODUCTION

A recent paper demonstrated that traces of RDX and PETN may persist in readily detected amounts on skin surfaces for periods of up to a week following a single contact with the explosive Semtex[1]. The analyses were based on high-performance liquid chromatography (HPLC) with electrochemical reductive detection. For confirmation of their identities the HPLC peaks were trapped out and examined by gas chromatography (GC) with a Thermal Energy Analyser (TEA) detector. The present paper gives further details of the techniques and of their more general application.

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EXPERIMENTAL

HPLC and peak-trapping

The HPLC is conducted according to previously described procedures[2]. Columns (15 cm * 4.6 mm) of Hypersil-ODS, 3 µm, are eluted at 1 ml/min with

deoxygenated methanol:aqueous phosphate (pH 3), 100:86 v/v, at 40°C. The pendent mercury drop electrode (PMDE) detector is a Princeton Applied Research model 310, the inlet line and eluent jet of which have been replaced with a length of silica capillary tubing, 0.32 mm i.d., to improve the electrical insulation between the detector and the chromatograph. The distance between the end of the capillary (from which the HPLC effluent projects onto the PMDE) and the base of the mercury drop is adjusted to 0.35 mm, with a drop diameter of 0.9 mm. The potential of the drop is held at -1.0 V vs. Ag/AgCl. For analytical work the injection volume of the deoxygenated samples is 10 µl. This is varied up to 50 µl for the peak-trapping when only small amounts of explosives are present.

A 4-port sampling valve is inserted between the HPLC column and the detector. This enables selected peaks to be diverted from the detector line to a microcolumn installed in one of the two remaining ports. The microcolumn (length, 75 mm; i.d., 1 mm) is packed with either Chromosorb-104 (Johns-Manville; an acrylonitrile copolymer), 125-150 µm, or Porapak-T (Waters Assoc.; a methacrylate copolymer), 75-100 µm. The Chromosorb is slightly the more retentive adsorbent, and has been used for most of the work. However, to accommodate its much greater degree of swelling and

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contraction as the composition of an eluent is varied, a ptfe column tube is used whereas stainless steel may be used for the Porapak. In either case the column lifetime is prolonged. To the 4th port of the valve is connected a microsyringe (500 µl, ptfe-tipped plunger) fitted with a micrometer screw gauge. This enables microlitre amounts of an eluent to be delivered to the microcolumn whilst the HPLC effluent is directed to the detector after the collection of an HPLC peak. The microcolumn is eluted with ethyl acetate:acetonitrile, 3:2 v/v, of which 20 µl following the break-through volume (ca. 50 µl) is collected in a silanized glass microcone. The break-through volume may be determined beforehand as the point at which the effluent wets silanized filter paper; the HPLC effluent displaced from the microcolumn does not do so. After a peak-trapping the microcolumn is washed with 100 µl of the ethyl acetate mixture and then flushed with a similar volume of the HPLC eluent.

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GC procedures

The chromatograph is fitted with an on-column injector, followed by a 2 m retention gap[3] of 0.32 mm i.d. silica capillary with an unmodified surface (Thames Chromatography, U.K.) and a 5-m length of 0.32 mm i.d. silica capillary column supporting a bonded phase of SE52, 0.5 µm (same supplier). The retention gap (which

is regularly replaced) and the column are joined with a glass press-fit connector[4]; metal connections can cause severe peak distortion. This arrangement accommodates sample injections of up to 4 µl. The chromatograph is temperature-programmed from 60-230°C with an inlet carrier gas (He) pressure of 1 Kg/cm² (12 ml/min at 60°C).

The TEA instrumentation (Thermo Electron) used for the GC detection includes a model 543 analyser, modified to improve its response characteristics[5,6], and a model 610 furnace maintaining the pyrolysis tube at 850°C.

Sampling and Sample processing

Explosives and firearms residues are collected from skin surfaces on swabs of unwoven cotton cloth moistened with aqueous isopropanol, and from clothing by a vacuuming onto membrane filters. In both cases the extraction of the samples is by a solid phase extraction under aqueous conditions to produce 60 µl of an aqueous acetonitrile concentrate for the HPLC separation. The details are fully described elsewhere[2,7].

RESULTS AND DISCUSSION

An example of the HPLC separation of a standard mixture of 18 explosives is given in Figure 1. The

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identities of the peaks are listed in order of the retention times in Table 1.

TABLE 1

HPLC Peak Identities and Retention Times (RT), Figure 1

Explosives Compound	RT (s)
Nitroguanidine	88.7
Cyclotetramethylenetetranitramine, octogen (HMX)	108.5
Styphnic acid	116.5
Picric acid	128.3
Cyclotrimethylenetrinitramine, hexogen (RDX)	150.5
Ethylene glycol dinitrate (EGDN)	172.5
Isosorbide dinitrate (ISDN)	206.8
1,3-Dinitrobenzene (DNB)	235.2
Trinitro-2,4,6-phenylmethylnitramine, (TETryl)	245.0
Nitrobenzene (NB)	274.8
Glycerol trinitrate, nitroglycerin (NG)	283.1
2,4,6-Trinitrotoluene (TNT)	298.5
2,6-Dinitrotoluene (26DNT)	337.5
2,4-Dinitrotoluene (24DNT)	346.5
2-Nitrotoluene (2NT)	417.4
4-Nitrotoluene (4NT)	446.0
3-Nitrotoluene (3NT)	477.4
Pentaerythritol tetranitrate (PETN)	491.4

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The trapping procedure was developed to ensure that in the characterisation of an HPLC-detected component other techniques, such as GC/TEA, referred specifically to that component, within the limits of the resolution of the HPLC applied to the mixture in question.

Despite the high flow rate of the HPLC eluent diverted through the microcolumn (ca. 2 cm/s), the trapping efficiency is adequate for qualitative work. The efficiencies found in experiments in which 4-10 ng amounts of explosives were trapped out are given in Table 2. The determinations were made by the reinjection into the HPLC of the trapped peak and an internal standard (6-nitroquinoline). The microcolumn elution here was with neat acetonitrile (ethyl acetate, the other usual component, perturbs the response of the detector). As the mixed eluent gives practically complete elution, there is unlikely to be a significant effect on the results due to this stronger eluent.

Given that the compromise between convenience and specificity is acceptable, several peaks may be trapped on a column and eluted together, although there may be some loss of the earlier trapped material due to breakthrough during a later trapping. The 2nd set of RDX results in Table 2 is an example. These were obtained after the longer retained PETN had been trapped out from the same chromatograms. The variability

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exhibited by each set of results is probably due to varying levels of drainage of the samples out of the syringe used for their deoxygenation prior to the HPLC injection.

TABLE 2

Microcolumn Trapping Recoveries

Explosive	Amount (ng)	Recovery (%)
HMX	10	73.1, 65.0
RDX	10	74.6, 84.9, 77.8, 73.7
RDX	6 (PETN 2nd)	50.3, 50.7, 49.8, 69.5, 55.9
NG	10	79.8, 74.7
PETN	4	53.9, 60.9, 57.1, 66.3, 71.8

The presence of the ethyl acetate in the microcolumn eluent is necessary to ensure that the surface of the GC retention gap is wetted and that the volatility of the mixture is compatible with the GC conditions. If these requirements are not met, distorted chromatograms result[3]. The described conditions enable explosives varying in volatility from EGDN to HMX to be chromatographed with a run-time of 7 min. An example from a 4-µl injection of a standard mixture is given in Figure 2.

Some degree of peak distortion is often apparent. Thus in the case of Figure 2 HMX is tailed. This and

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other effects, to which the less volatile explosives and NG are particularly susceptible, have varied between GC capillary columns of the same type - more especially between columns from different manufacturers. Also, different classes of explosives, e.g. nitramines and nitrate esters, are differentially affected. The uncoated silica tubing used as a retention gap has also caused a similar variation.

Many surface-modified retention gaps were evaluated for use in explosives work. These included: two lots of tubing sold as deactivated by different suppliers; tubing silanized following published procedures[8] and others; and tubing treated under a variety of conditions with acids and alkalis, with chelating agents. with detergents, and with carbowax. In general the products were inferior to the specified (Experimental) unmodified silica tubing. In every case the performance deteriorated after a few days' use, presumably because of material retained in the gap. The performance was not fully restored when afterwards the gaps were washed or the deactivation repeated.

A few examples of variation caused by different retention gaps to the NG-HMX region are given in Figure 3: (A) one batch of uncoated tubing caused tailing particularly of the nitrate esters and the nitramines; (B) HMX was lost entirely, and PETN and NG were lost

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substantially, on a marketed deactivated product; (C) an acid-washed gap caused severe tailing of HMX and losses of NG and PETN; (D) after this last gap had been silanized PETN was lost almost completely. The chosen procedure has been the use of retention gaps of selected unmodified silica, which are replaced when any deterioration in performance becomes apparent, usually after several days' use. Under the conditions the lifetime of the analytical capillary column is unrestricted; and the common necessity for the periodic removal of the deteriorated front segment from columns subject to on-column injection is avoided.

Examples of the results from some trapping experiments are shown in Figures 4 and 5. Figure 4 A is the HPLC result from a heavily contaminated handswab to which 2 ng of NG had been added. The indicated area was trapped to give the GC/TEA response shown uppermost at B. The retention time of the peak assigned to NG was within 0.3 s of an adjacent standard. No response was obtained in a comparable experiment on an unspiked swab (B, lower trace). Figure 5 A shows a pair of GC/TEA results obtained from articles of clothing, one of which was known to have been in contact with firearms discharge residue. The HPLC result indicated the presence of 1.8 ng of NG on the clothing, the shown chromatogram confirmed the identification. The weak

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early peak in these chromatograms is due to an impurity in one of the solvents. Figure 5 B shows the result from a multiple trapping. Here, each peak was trapped from a single chromatogram of an extract of a handswab. The swab had been spiked with 5 ng-amounts of TNT, PETN and RDX.

CONCLUDING COMMENTS

When only traces of explosives are present either GC/TEA or HPLC/PMDE applied alone to a typical extract will produce an unconfirmed result based on a chromatogram in which a number of irrelevant components are likely to be present in significant relative amounts. Both techniques are affected, usually the HPLC technique to the greater extent, but as the examples show the ambiguity may be resolved by the described procedure. The procedure is not designed for TEA detection specifically, although most casework applications to date have made use of this GC detection mode. Recent work indicates that the much greater information content of mass spectrometric detection may be analogously exploited.

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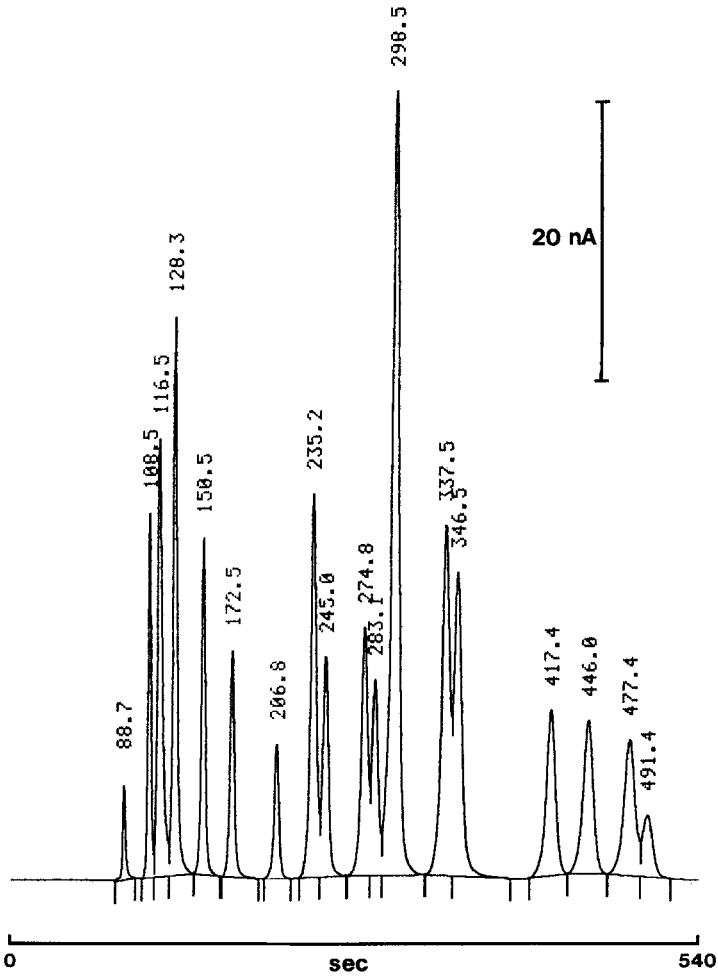

FIGURE 1
HPLC/reductive detection of a standard mixture of explosives compounds, 5-20 ng amounts in a 10 µl injection. Retention times (s) are superscripted on the peaks. The peak identities are given in Table 1.

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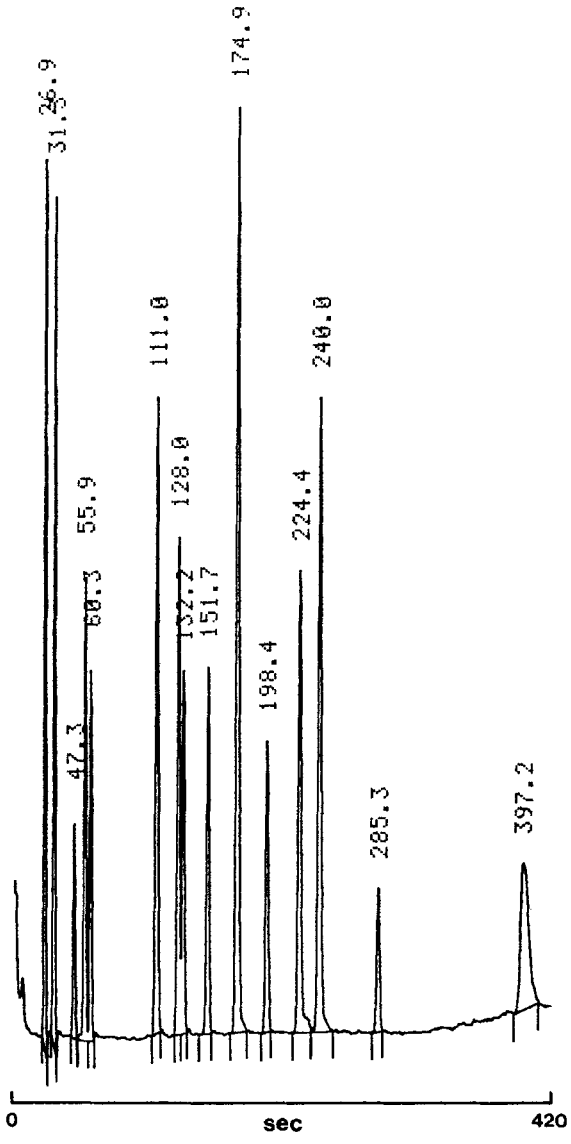

FIGURE 2
GC/TEA trace from a standard mixture; TEA attenuation, *64. Each compound, ca. 0.4 ng except ISDN (0.8 ng). Retention times (s) are superscripted on the peaks: EGDN 26.9; NB 31.3; 2NT 47.3; 3NT 55.9; 4NT 60.3; NG 111.0; DNB 128.0; 26DNT 132.2; 24DNT 151.7; ISDN 174.9; TNT 198.4; PETN 224.4; RDX 240.0; TET 285.3; HMX 397.2 s.

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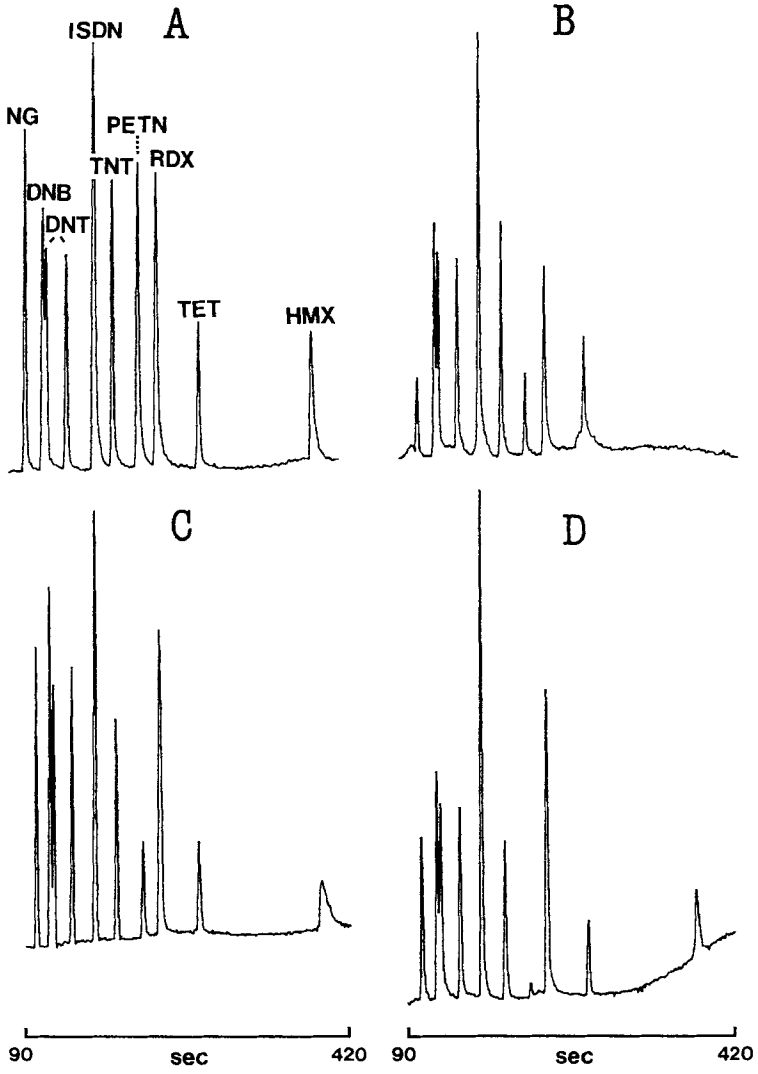

FIGURE 3
Examples of effects of variation in the silica retention gap, NG - HMX region, otherwise conditions as in Fig. 2: (A) bare silica (different batch), untreated; (B) commercial product sold as deactivated; (C) bare silica, phosphoric acid/acetone washed; (D) latter silanized (hexamethyldisilazane): arbitrary scales, actual responses to DNB and DNT peaks were similar throughout.

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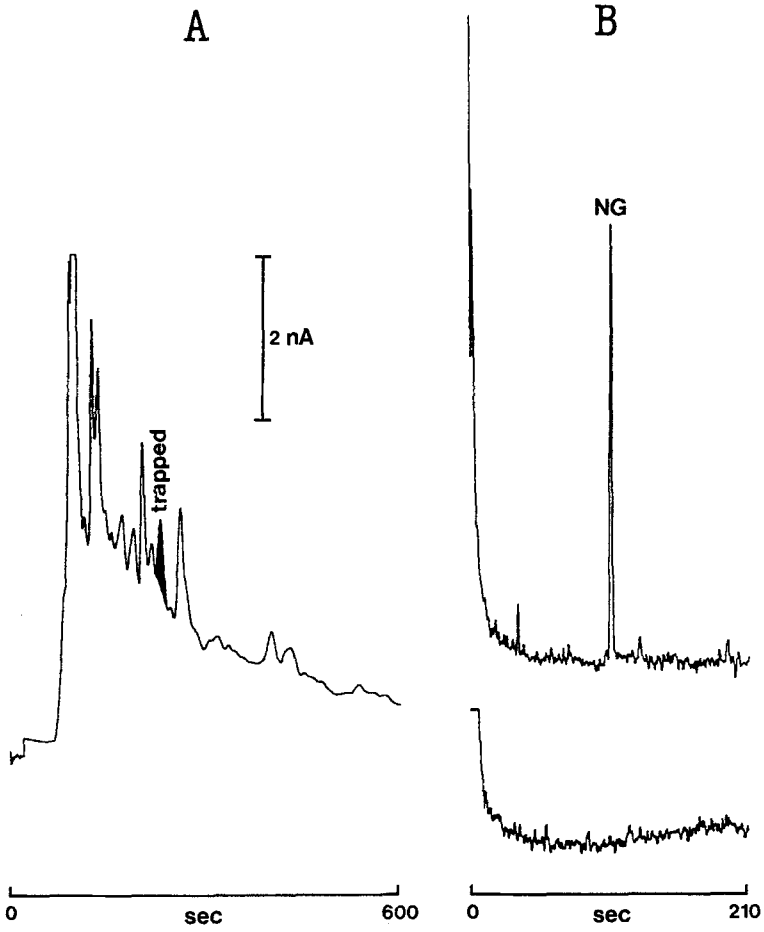

FIGURE 4
Used handswab spiked with 2 ng of nitroglycerin: (A) HPLC/PMDE of an extract representing ca. 17% of the swab; (B, uppermost) GC/TEA of the trapped HPLC peak, representing ca. 20% of the swab; (B, lower) the same area trapped from a blank used swab. TEA attenuation, *8.

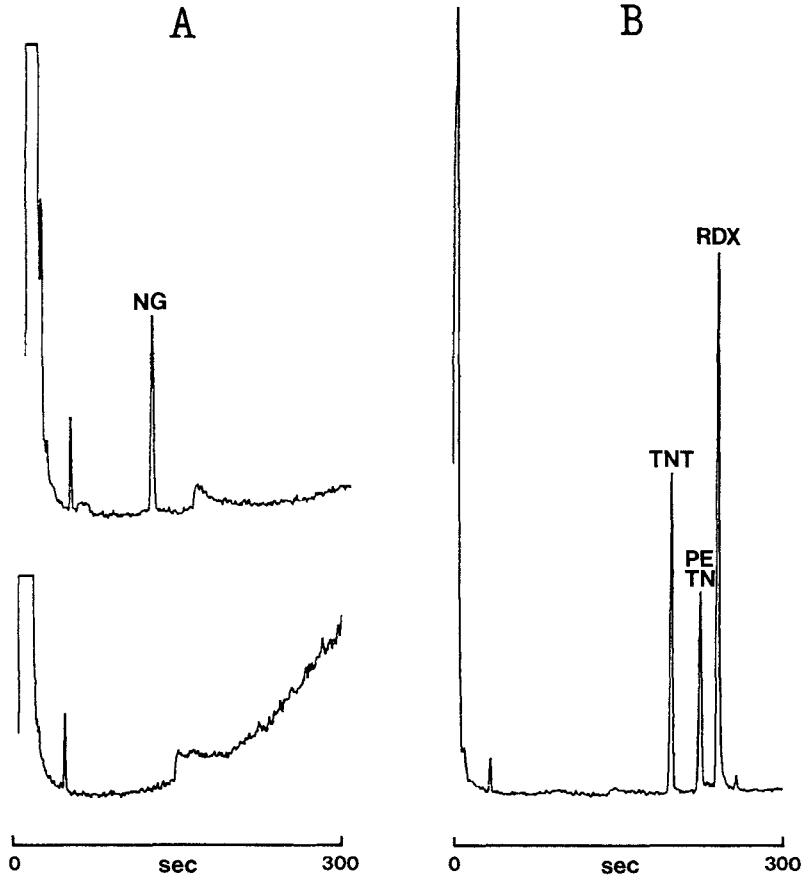

FIGURE 5
GC/TEA results from trapped HPLC peaks: (A, uppermost) NG peak from clothing with a known firearms association - the HPLC result indicated the presence of 1.8 ng of NG on the jacket concerned; (A, lower) the NG region from uncontaminated clothing; (B) TNT, PETN and RDX from a swab spiked with 5 ng of each. TEA attenuation, *16 in each case.

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