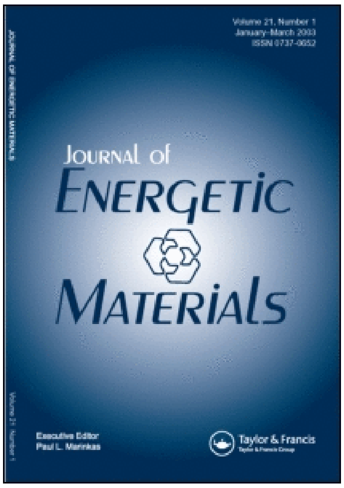

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Liquid chromatography of firearms propellants traces

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LIQUID CHROMATOGRAPHY OF FIREARMS PROPELLANTS TRACES

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ABSTRACT

Most of the major components of firearms propellants likely to occur on the skin or clothing after the discharge of a firearm may be detected sensitively and with substantial specificity by liquid chromatography methods. The components include nitrocellulose, nitroglycerin and diphenylamine. Impurities and metabolites of nitroglycerin may occur on the skin. On clothing the traces are strongly persistent. The techniques employed include size-exclusion and high-performance liquid chromatography, with amperometric detection at a mercury drop electrode, and coulometric detection at porous carbon electrodes. Progress in the use of the Thermal Energy Analyser as a complementary technique is reported.

INTRODUCTION

I wish first to present some results from the application of liquid chromatography techniques with electrochemical detection to the examination of intact firearm propellants; and, second, to review the present position in my work on the application of

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these techniques to the detection of firearms discharge residues. The overall object is to improve the efficiency with which such residues are at present detected in firearms cases.

Several Authors have already described the application in this area of other explosives detection techniques, principally based on gas chromatography[1], although some liquid chromatography results have appeared[2,3].

PROPELLANTS COMPONENTS

Nitrocellulose

The major propellants component, nitrocellulose, is readily detected by its reduction at a mercury electrode (PMDE) held at potentials in the region of 0 V *vs*. Ag/AgCl. Coupled to size-exclusion chromatography (SEC) this has been shown to give a technique with nanogram-sensitivity in a run-time of about 2½ min. Full details are given in the literature[4], they are summarized in Table 1.

TABLE 1
Size-exclusion Chromatography Conditions

Column	150 mm by 4.5 mm, silica Si 300, 5 µm.
Eluent	Acetonitrile + water, 100 + 5 v/v, 0.01 M in tetramethylammonium perchlorate; deoxygenated.
Flow-rate	1.5 ml min^{-1}.
Temperature	Ambient.
Detector	PMDE, -0.1 V vs. Ag/AgCl; drop size 1.5 mg; output signal range settings 2-200 nA.
Sample	In deoxygenated acetonitrile, 1-10 µg ml^{-1}, 10 µl injected.

The intention here is to obtain rapidly a fingerprint rather than detailed molecular mass data. However, the higher molecular mass nitrocelluloses often used in propellants are distinguishable, and can be differentiated from one another to some extent. Examples of three propellants are shown in Fig. 1. A common result is represented in chromatogram A, which is dominated by an intense high molecular mass spike of totally excluded material. Chromatogram C represents the low molecular mass extreme, which includes much material characteristic of nonpropellant nitrocelluloses. Chromatogram B is an intermediate example centered approximately in the 10^5 mass region. The majority of propellants fall in the range A-B.

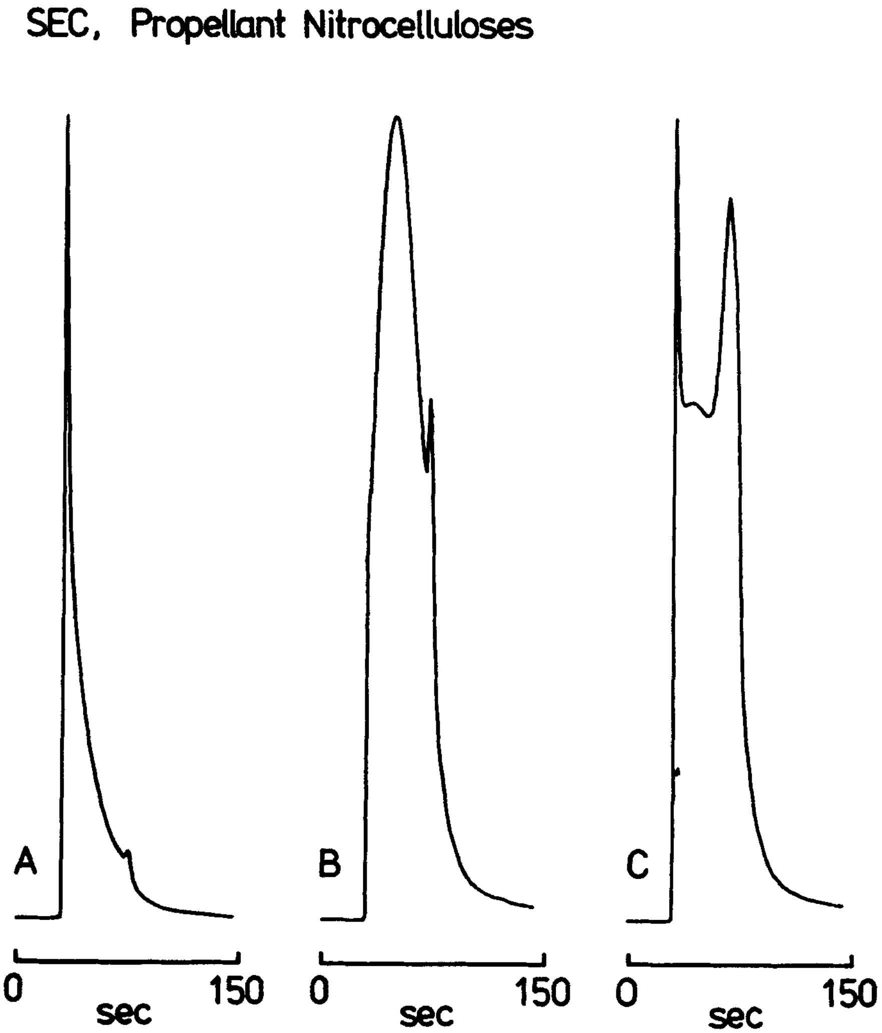

FIGURE 1

SEC (conditions, Table 1) of examples of propellant nitrocelluloses.

Nitro and Nitrate Compounds

The other active components of propellants may be detected analogously, in conjunction with high-performance liquid chromatography (HPLC). The technique was described at the last Symposium[5], the details together with others relevant in the following are summarized in Table 2. Some chromatograms given by double base propellants are shown in Fig. 2. The most common contain nitroglycerin (NG) with or without 2,4-dinitrotoluene (2,4-DNT) as in the first two traces (A,B). A less usual example

TABLE 2
HPLC Conditions

Column	150 mm by 4.5 mm, ODS-Hypersil, 3 µm.
Eluent	Methanol + aqueous phosphate (pH 3, 0.035 M), either 100 + 85 (A) or 100 + 65 (B) v/v; deoxygenated.
Flow-rate	1 ml min^{-1}.
Temperature	40°C.
Detector 1	Coulometer (Environmental Sciences Associates Inc), screening electrode +0.5 V, monitored electrode +0.8 V; output signal range settings 50-5000 nA.
Detector 2	PMDE, -0.9 V *vs*. Ag/AgCl; drop-size 6 mg; output signal range settings 5-500 nA.
Samples	Dissolved in eluent to give not more than 2 µg ml^{-1} of detected compounds; 10 µl, deoxygenated; injected.

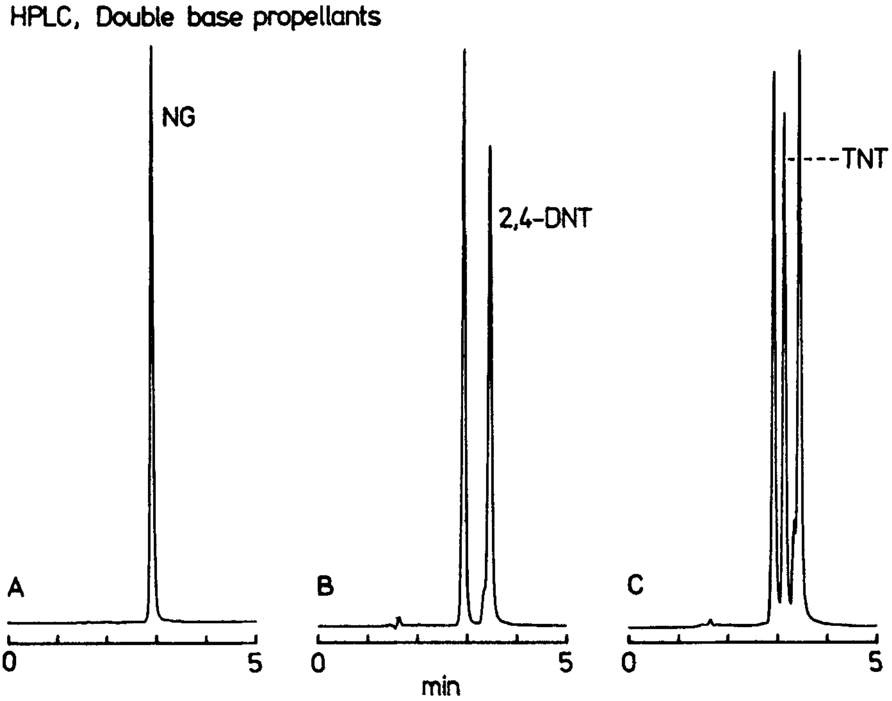

FIGURE 2

HPLC, PMDE detection (Table 2, eluent B), of double base propellants.

with a peak characteristic of TNT is also shown (C). Single base compositions usually show none of these features, but the dinitrotoluene is sometimes present.

If double base propellants are run at high sensitivities, two more peaks are seen (Fig. 3). These are the 1,2- and 1,3-glyceryl dinitrates (12GDN, 13GDN). They occur in virtually all nitroglycerins, and sometimes at elevated levels as described below.

Diphenylamines

Of the common propellant stabilizers, only diphenylamine (DPA) is electrochemically detected, oxidatively, at relatively low potentials[6] and hence detected amperometrically with good sensitivity by HPLC as several Authors have described[1,2,7]. In the present work coulometric detection has been used, in which the monitored current yield from the oxidation of a compound as it passes through a porous carbon working electrode is practically complete. The coulometer (Environmental Sciences Associates) is fitted with two such electrodes, which enables compounds more readily oxidized than diphenylamine to be removed at the first electrode before the second, monitored, electrode is reached. The conditions are indicated in Table 2. The sensitivity is similar to the amperometric detectors, and amongst a number of advantages, particularly valuable is the low dead

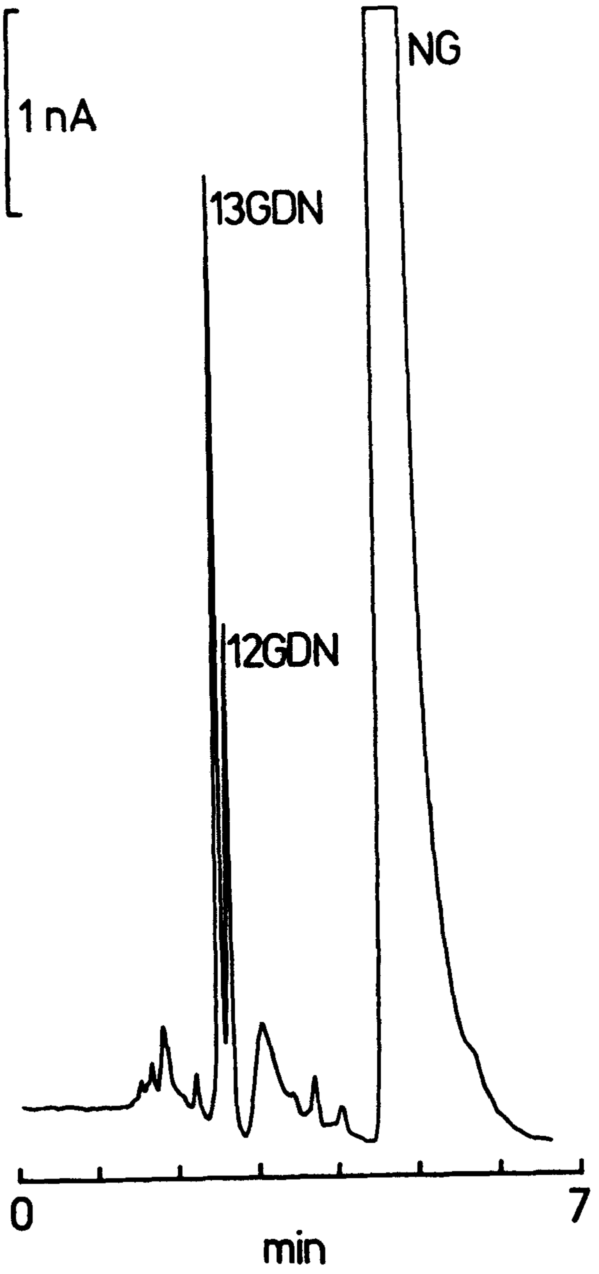

FIGURE 3

HPLC, PMDE detection (Table 2, eluent A), of a double base propellant. The chromatogram has been expanded to show the glyceryl dinitrates.

volume of the detector. Hence it may be inserted upstream of the PMDE, which enables nitrated compounds as well as diphenylamine, and its degradation products, to be detected on one chromatogram. Also, oxidation products from the coulometer can be detected reductively at the PMDE, so that the characterization of diphenylamine, for instance, is based very specifically on its behaviour at three different electrodes. A typical example from a diphenylamine-stabilized double base propellant is shown in Fig. 4. The oxidative coulometric response, shown uppermost, exhibits a strong diphenylamine peak. This is matched by a reductive response in the second trace. Two degradation products are present. One of these is responded to by both detectors, and is due to 4-nitrodiphenylamine (DPA-NO2). The other is detected only reductively, and is due to N-nitrosodiphenylamine (DPA-NO). The identifications are based on comparisons with the actual compounds.

Propellant Compositions

The described techniques have been applied to a set of 52 propellants collected from British forensic science work. The results may be qualitatively classified into seven groups, as shown in Table 3. Further discrimination is given by the nitrocellulose chromatograms and by the quantitative compositions.

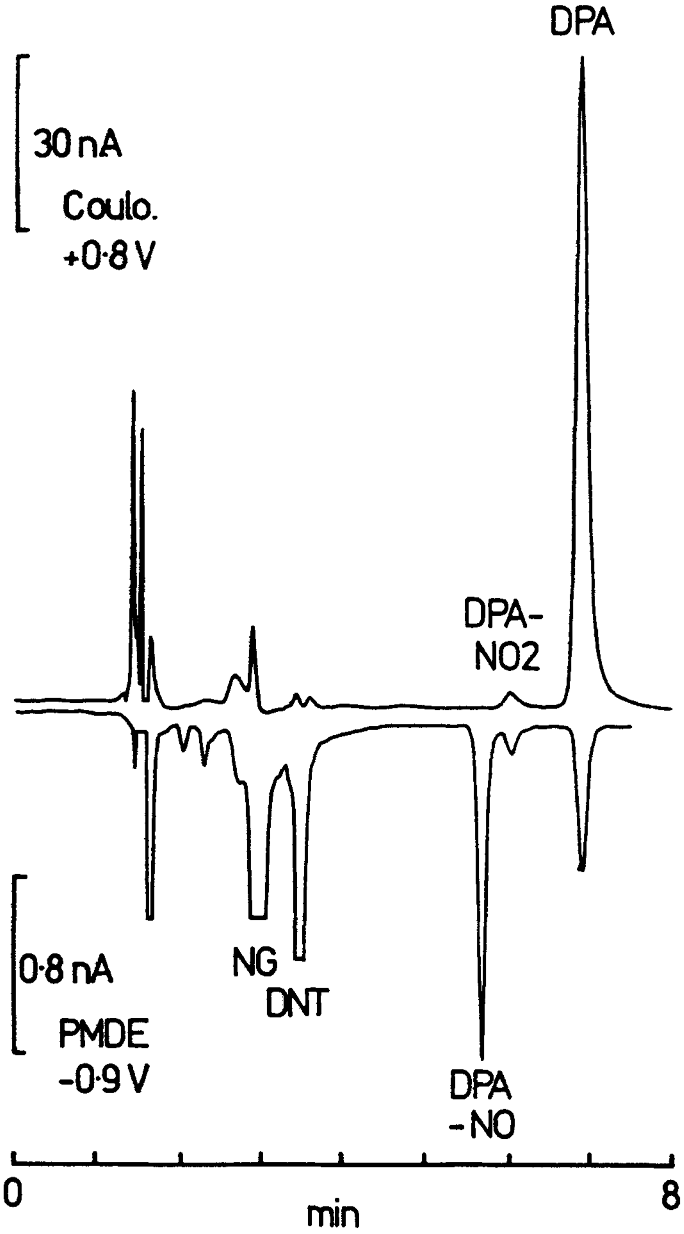

FIGURE 4

HPLC coulometric and PMDE detection (Table 2, eluent B), of a double base propellant.

TABLE 3
Qualitative Classification of 52 Samples of Firearms Propellants into Groups Containing the Indicated Numbers of Samples

	DPA present	DPA absent
Plain single base	15	-
Single base plus 2,4-DNT	2	-
Double base; 2,4-DNT absent	5	15
Double base; 2,4-DNT present	10	-
Double base; 2,4-DNT, TNT present	2	-
Black powders		3

For example, the nitroglycerin contents ranged between 5 and 50%. The results taken together with the shapes of the propellant grains enable a high level of discrimination. However, only a broad classification is relevant to the characterization of discharge residues.

CHARACTERIZATION OF DISCHARGE RESIDUES

Sampling Considerations

For the comprehensive sampling of discharge residue on skin the common swabbing techniques pose problems. Cellulosic materials tend to adsorb traces of nitrocellulose; and diphenylamine is an often-detectable impurity in organic solvents, even in high-grade solvents. Impurity levels above 10 p.p.b. interfere in the present application. The most satisfactory technique is the use of pre-extracted polypropylene filter cloth (Aldrich) swabs moistened with an HPLC grade isopropanol (Rathburn). The used swabs are pushed into disposable polypropylene syringe barrels and the remaining isopropanol is removed in a dried air flow, with protection against loss of particulates by a Gelman Acrodisc 1 µm filter (25 mm diameter) attached to the syringe outlet. Clothing debris is vacuumed onto the filters, with the membrane support section of a Swinnex membrane filter used as a coarse filter at the intake. Both types of sample are steeped and then extracted with 200-300 µl of acetonitrile at the centrifuge. This leaves any inorganic discharge residue retained on the filter or in the swab for subsequent scanning electron microscopy (SEM) examination.

The same swabs may be used for explosives traces. In this case the isopropanol containing the dissolved explosives is spun off immediately, and without the need for the filter if particulate material is unimportant.

In many instances the extracts can be chromatographed directly. However, for the highest sensitivity and specificity, and to maintain a good standard of instrumental performance, the extracts are routinely cleaned-up on disposable microcolumns containing in the region of 5 mg adsorbent and fed from the sample loop of a Rheodyne valve. Most of the details are in print[8,9]. They are summarized in Fig. 5. The separation of nitrocellulose depends on its selective adsorption and size-exclusion on Porapak T. Dinitrotoluenes, nitroglycerin and related compounds are separated according to their adsorption characteristics on Porapak T and charcoal. For diphenylamine, use is made of its strong adsorption from aprotic, nonbasic solvents onto the hydrogen-form of Amberlite 15. Because diphenylamine is so weakly basic, it is readily and very selectively displaced from the resin by slightly aqueous (2%) acetonitrile. Hence, on a column containing both Porapak T and the Amberlite, each of the detected components of single base propellants can be cleaned up and separated in one operation. Although the overall scheme appears involved, for most purposes only one microcolumn separation is required, and the actual

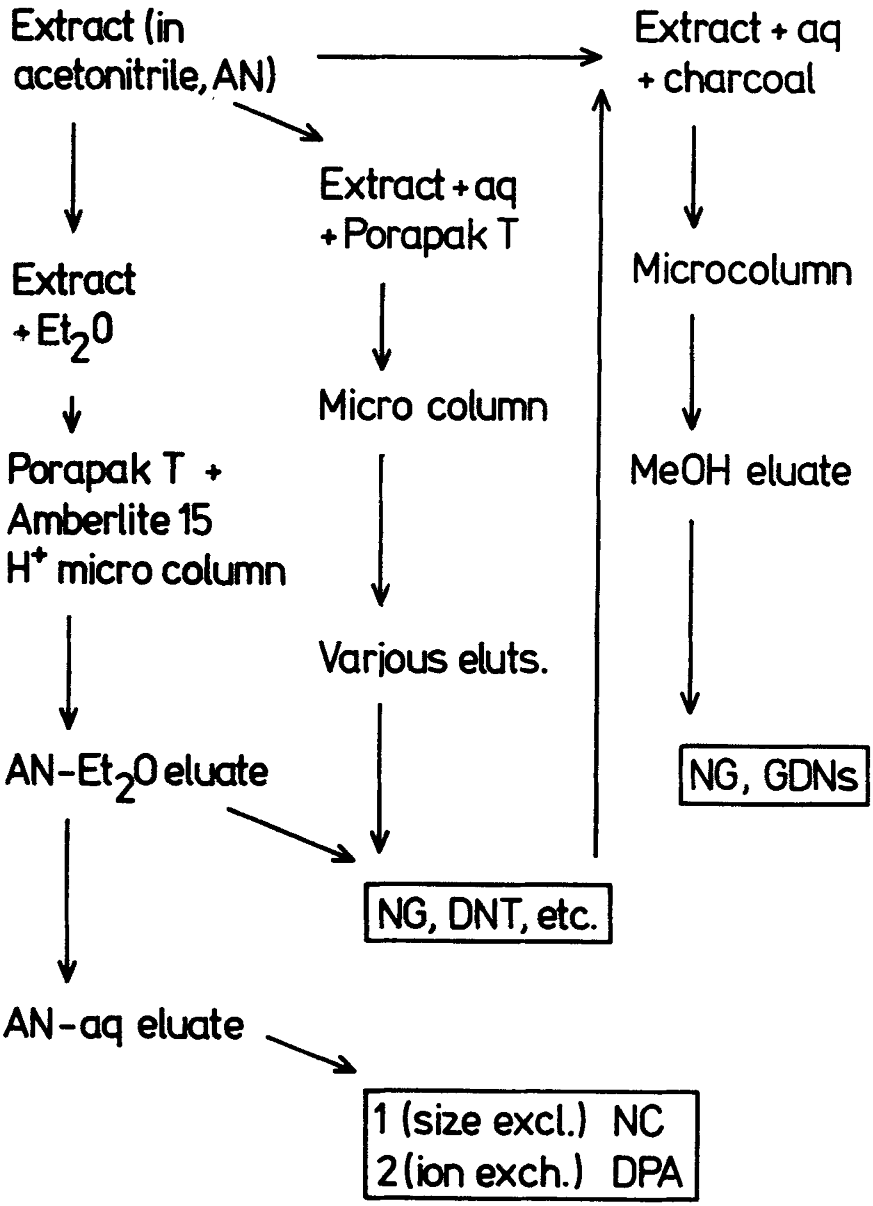

FIGURE 5

Clean-up scheme for propellants (and explosives) traces in extracts of swabs and debris.

limiting time on the analyses is the HPLC turn-round time of about 8 min.

Diphenylamine Traces

Several papers have considered the possibility that the detection of diphenylamine may be taken as evidence of the presence of, or of contact with discharge residues[1,2,7,10-12]. An example from such a contact is given in Fig. 6, where 8 ng of the compound was recovered from the firing hand shortly after the discharge of four .22 rounds of diphenylamine-stabilized propellant. However, 2 ng was recovered from the same hand at an earlier time when no firearms source could have been involved. Indeed, diphenylamine is normally detectable on hands uncontaminated by firearms residue, occasionally in very large amounts. Thus, in nine swabs collected from ten manually employed subjects, with no known firearms contact, the levels of diphenylamine were in the region covered by Fig. 6. From the tenth swab 280 ng was recovered. Clothing debris also usually contains diphenylamine.

Although diphenylamine is little used directly in manufactured products, it is a widely used industrial intermediate, and may permeate the environment, therefore. Considerable amounts are recoverable from the surface of car tyres, where it is present presumably as a result of its incomplete reaction in the preparation of a rubber antidegradant.

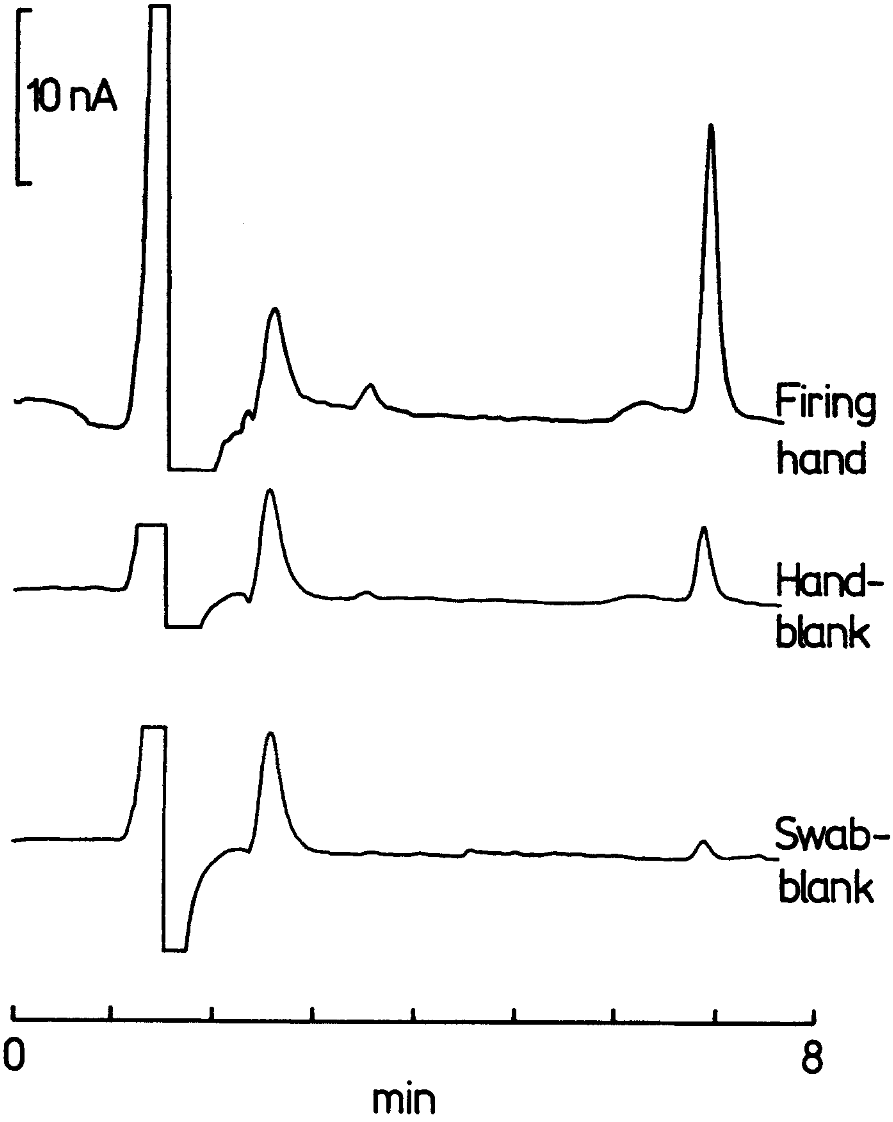

FIGURE 6

HPLC, coulometric detection (Table 2, eluent B), of cleaned-up diphenylamine fractions from a firing experiment (four rounds from a .22 semi-automatic pistol).

It is also used in the foodstuffs industry as a post-harvest treatment of apples against scald, and can be recovered in relatively large amounts simply by washing down the skin of a supermarket apple with an organic solvent. In my view, therefore, diphenylamine detected in the absence of other propellants components is not attributable to firearms contact, and cannot be used as evidence of such contact.

Nitrocellulose Traces

The evidential value of nitrocellulose traces is similarly conditioned by environmental levels. Also, the nitrocellulose remaining after the discharge of a weapon tends to be degraded in molecular mass, and may not be distinguishable, therefore, in the presence of the large amounts of environmental nitrocellulose sometimes present in clothing debris. Less interference is obtained from handswabs. An example is given in Fig. 7, which compares chromatograms from swabs collected before and shortly after a single .38 round had been fired. The unfired propellant is also shown. The quantity of degraded nitrocellulose transferred here is approximately 600 ng. Four other firings gave amounts varying extensively down to 34 ng. Other sources of nitrocellulose could give similar chromatograms. Even so, swabs taken from 20 subjects, mostly with heavily soiled hands but uncontaminated with firearms residues, showed only material at or barely resolved from the total permeation limit of the chromatograms.

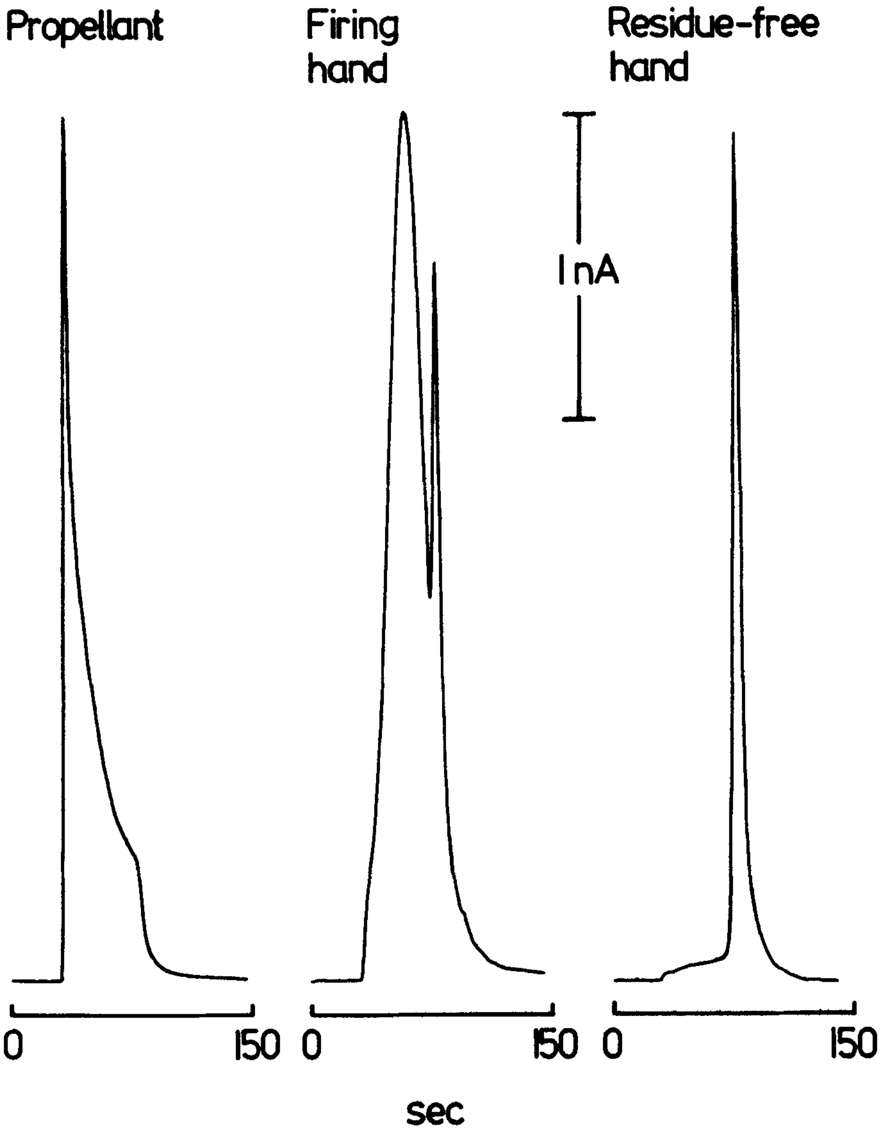

FIGURE 7

SEC (Table 1) of cleaned-up nitrocelluloses from a firing experiment.

Because of the considerable speed with which they are obtained, the nitrocellulose chromatograms can provide useful information in multisample survey work, e.g., in plotting the surface distribution of residues. In this respect they could be evidentially significant. Otherwise, for nitrocellulose detected alone, the position is similar to the diphenylamine case. Where these materials are detected together the result could be of some indicative use, as they are the only organic components detected at relevant sensitivity levels in residues from the majority of single base propellants. Clearly, further research into this important area is a priority.

Nitro and Nitrate Compound Traces

Unlike the components of most single base propellants, the additional characteristic components of double base propellants are not subject to environmental interference. As was shown by Jane et al. at the last Symposium[1], nitroglycerin can be characterized by gas chromatography on clothing several hours after a weapon has been discharged. The liquid chromatography technique now enables such residues to be characterized after many days. Some results with a .38 Smith and Wesson revolver are shown in Table 4. The garments used were pullovers carrying considerable amounts of non-firearms debris. The firing was done in an indoor range with the extraction system working continuously. The firer wore a fresh disposable overall underneath each garment. After each firing the garment was immediately packaged for subsequent wear with unrestricted activity and mainly as an outer garment.

From the results, it seems that, as with other contact traces, substantial loss of presumably superficial material occurs initially, followed by a very slow depletion of more strongly embedded material. Qualitatively similar results to these were obtained in earlier preliminary work, without clean-up, with a .22 semi-automatic pistol. In one of these instances a negative result was obtained. Clearly, the results are subject to many factors *e.g.*, the nature of the fabric, the weapon and ammunition, the environmental conditions, the detailed activity of the firer; and their evidential significance will depend on the attitude taken by the prosecution and defence in any particular case.

TABLE 4
Persistence on Clothing of Nitroglycerin Residues from a .38 Smith & Wesson Revolver.
Ammunition: Winchester Western 38 Special 125 grain

Rounds Fired	Period of Wear	Nitroglycerin found (ng)
4	0 hr (stored on bench top for 1 month)	170
4	2 hr	780
4	5 hr	42
4	29 hr (2 separate days)	57
1	15 hr (1 day)	114
1	30 hr (2 days)	38
1	75 hr (5 days)	80

The data shown in the Table are summations over all of the front surface of each garment (Traces also occurred in samples taken from the back surfaces). For the five-day case, the results for the individual areas are shown in Fig. 8, and two of the actual chromatograms are shown in Fig. 9. From these results it would not be apparent that the right hand in fact was the firing hand. It might reasonably be argued that the long wear-time was reponsible. However, I find that even with freshly contaminated clothing ambiguous results are obtained. Fig. 10 is the result with a disposable overall sampled after three firings from the right hand. Although the density of nitroglycerin is highest on the right sleeve, substantial amounts are distributed elsewhere including the left leg. In other experiments with fewer shots the non-firing sleeve was sometimes the more contaminated, but a downwards drift of residues was generally apparent, and the same observation has been made in casework.

Handswabs taken after each of six single-round firings under the conditions of Table 4 yielded characteristically varying levels of nitroglycerin, between 25 and 825 ng. The persistence times given by the analytical techniques remain to be determined, but preliminary work indicates that these will be at least several hours. An example after 2½ hr is shown in Fig. 11.

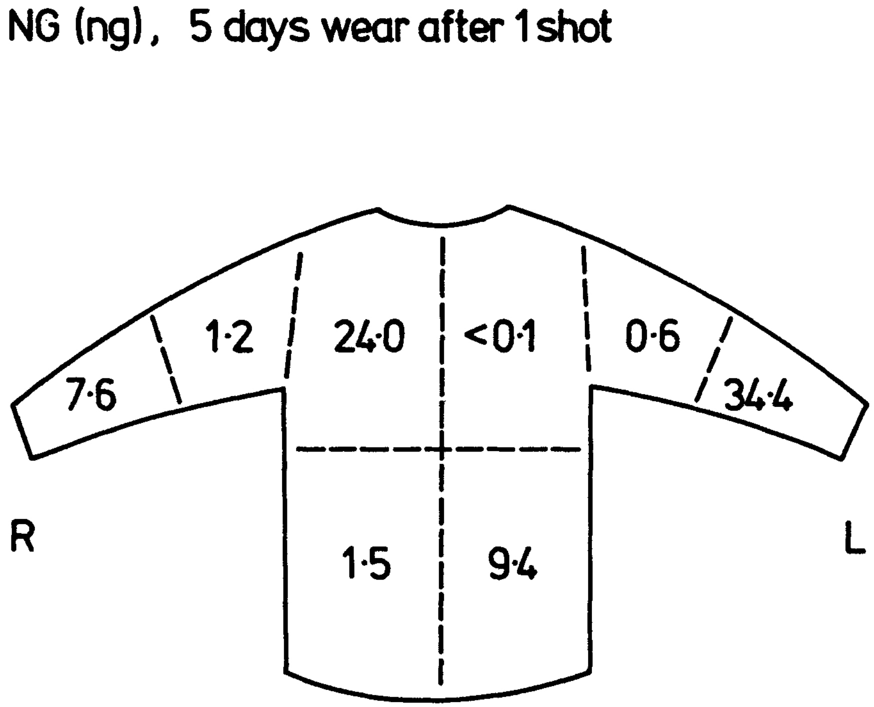

FIGURE 8

Distribution of nitroglycerin over the front of a pullover worn 5 days after the wearer had discharged a single .38 double base round.

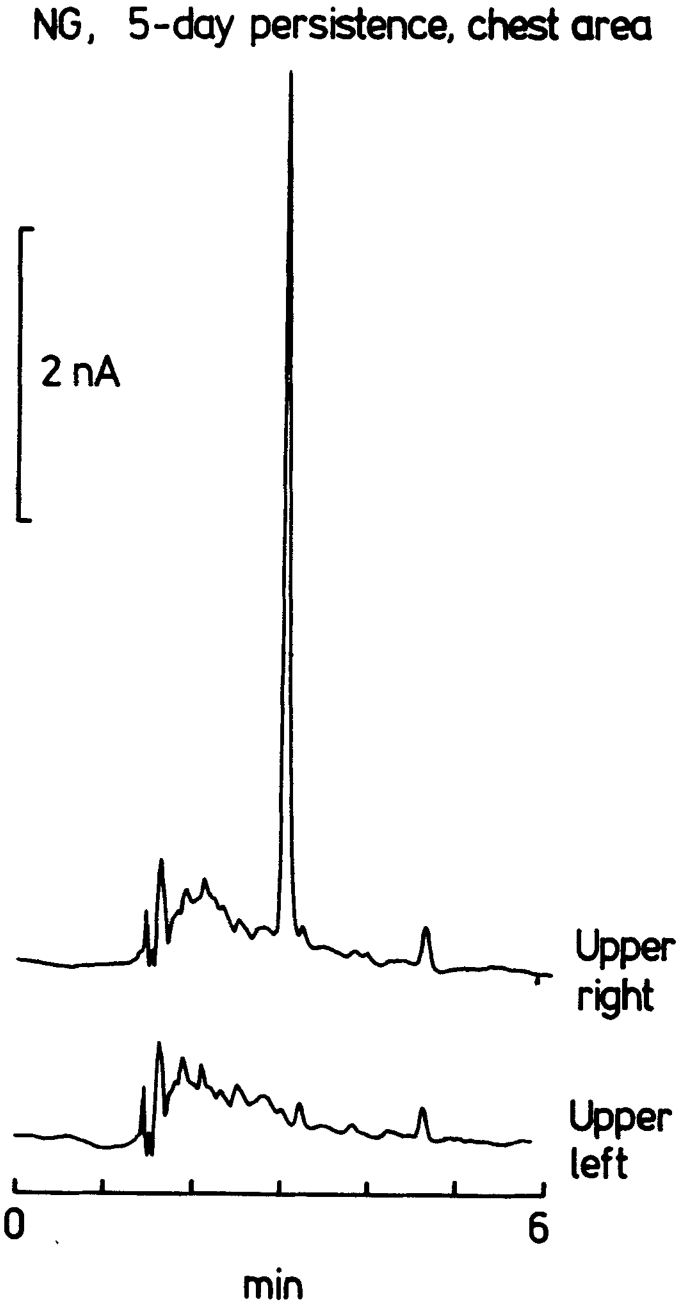

FIGURE 9

HPLC, PMDE detection (Table 2, eluent B), of cleaned-up (charcoal) samples from the indicated areas of the pullover shown in Fig. 8.

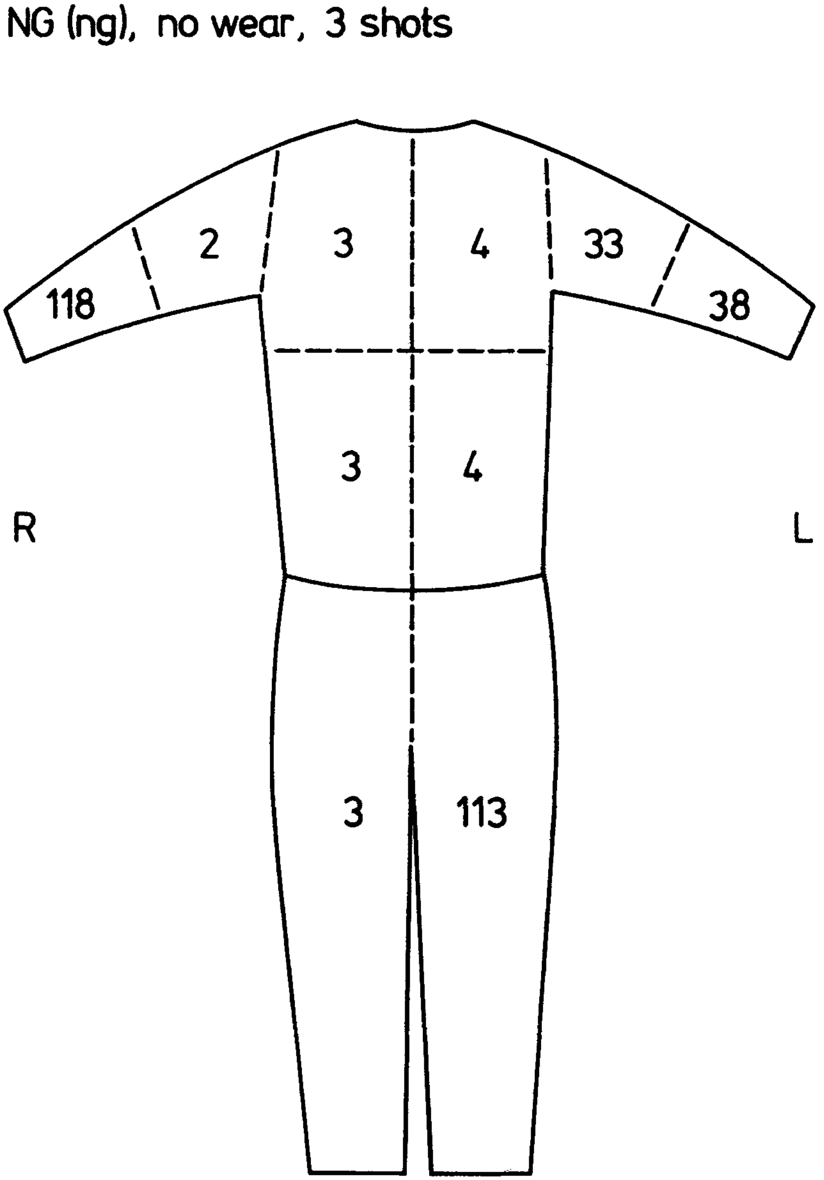

FIGURE 10

Distribution of nitroglycerin over the front of an overall, the wearer of which had fired three .38 rounds. The overall was not worn subsequently.

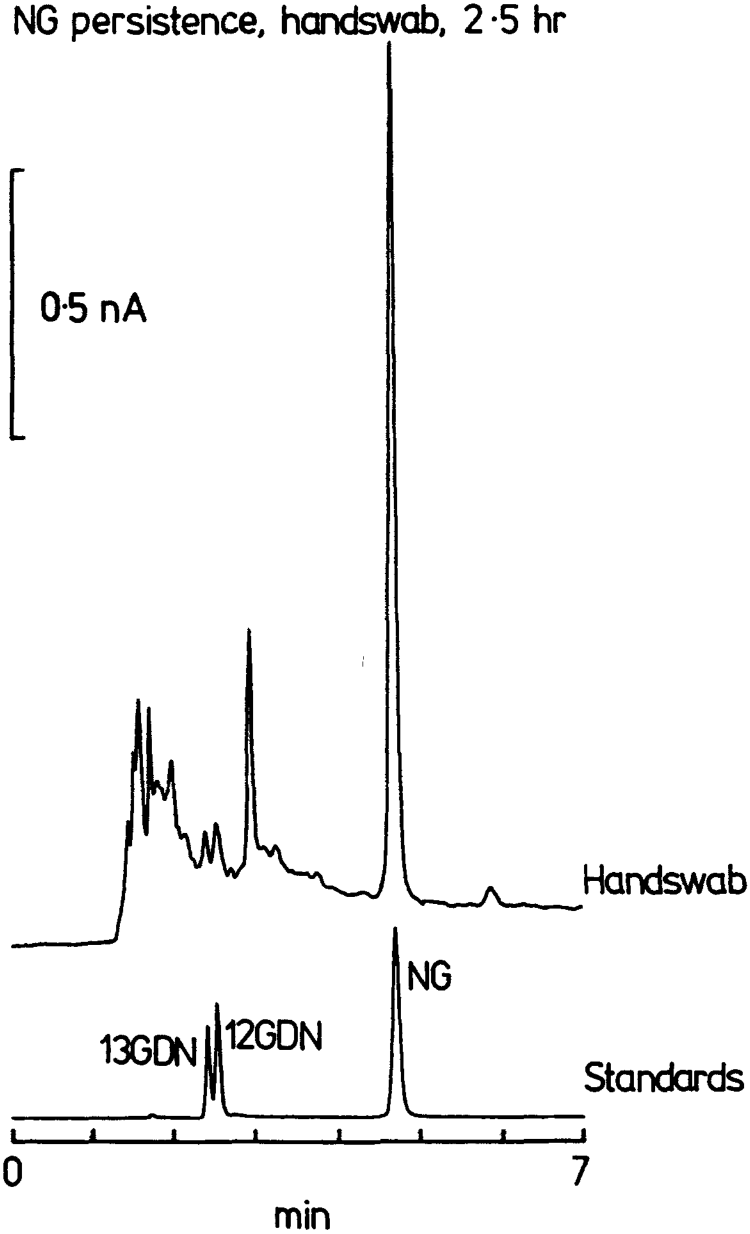

FIGURE 11

HPLC, PMDE detection (Table 2, eluent A), of the cleaned-up (charcoal) extract of a handswab collected 2½ hr after the discharge of a single .38 double base round.

Other skin surfaces are much more useful sources of residues. This is illustrated by the results in Table 5, which are from single shots discharged by six subjects (laboratory staff), essentially under the conditions of Table 4. Each firer used a different revolver, and during the firing wore a disposable overall, which was immediately discarded. The face and throat areas, as well as the hands, were swabbed up to 7 hr later. As the Table shows, despite several handwashes residues were detected on the hands over the full time scale of the experiments, but much higher levels were present on the other surfaces. As with the clothing, there is an element of considerable randomness in the distributions.

TABLE 5
Persistence on Skin Surfaces of Nitroglycerin Residues Following a Single Shot (Conditions, Table 4).
Two-handed grip.

Subject	Time since firing (hr)	Handwashes	Nitroglycerin found (ng/swab)*			
			R.hand	L.hand	Face	Throat
A	3½	1	0.24	0.63	1.19	8.72
B	3½	0	0.16	0.16	3.32	0.57
C	6½	2	0.08	0.08	0.06	0.37
D	6½	3	0.28	<0.05	1.63	7.02
E	7	3	0.84	0.69	1.16	0.58
F	7	1	0.21	0.55	0.20	1.42

* The practicable detection limits are in the region of 0.1 ng.

It was mentioned earlier that the glyceryl dinitrates were detectable in propellants. They are just detectable also in recovered residues as in Fig. 11, but the result is useful mainly in a negative sense: to exclude the presence of nitroglycerin due to the more substantial and intimate contact that occurs with explosives. Recent work indicates that the dinitrates are produced from nitroglycerin by enzyme action on the skin surface to give levels comparable to any remaining nitroglycerin[13]. In Fig. 12, for example, is shown the result from a handswab collected 20 hr after contact with a gelignite. The nitroglycerin peak corresponds to 24 ng/swab. The glyceryl dinitrates total is 12.4 ng/swab.

Casework examples of the detection of residues in clothing extracts are shown in Figs. 13 and 14. In each case the suspect had said that he had not been in the vicinity of a discharging firearm. In the case of Fig. 13 a 12-bore shotgun had been discharged, and traces of a double base propellant were present in the spent cartridge. From a localized area of the outer garment (a sweat shirt) a strong response coincident with nitroglycerin was observed. None was found in adjacent areas - consistent with particulate contamination - as the Figure shows. Fig. 14 shows the result in which a double base propellant containing 2,4-dinitrotoluene was used in a sawn-off shotgun.

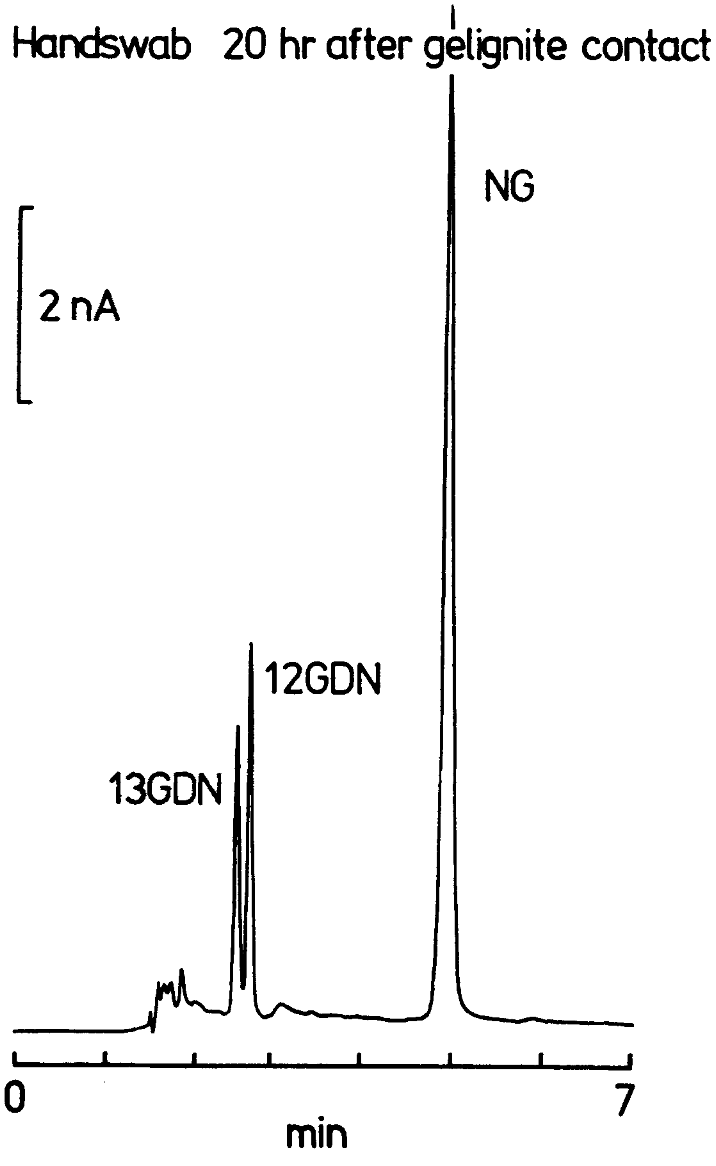

FIGURE 12

HPLC, PMDE detection (Table 2, eluent A), from the cleaned-up (charcoal) extract of a handswab collected 20 hr after contact with a gelignite.

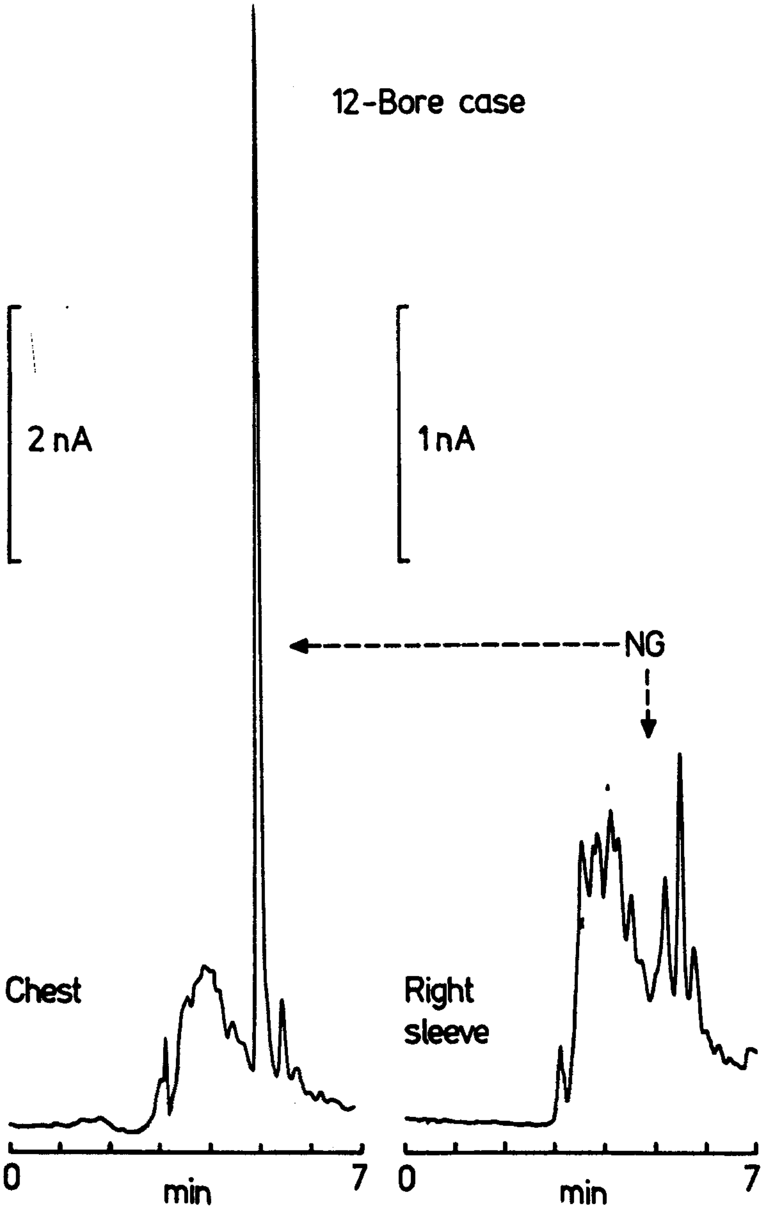

FIGURE 13

HPLC, PMDE detection (Table 2, eluent A), of cleaned-up (charcoal) clothing extracts from a case in which a 12-bore shotgun was discharged.

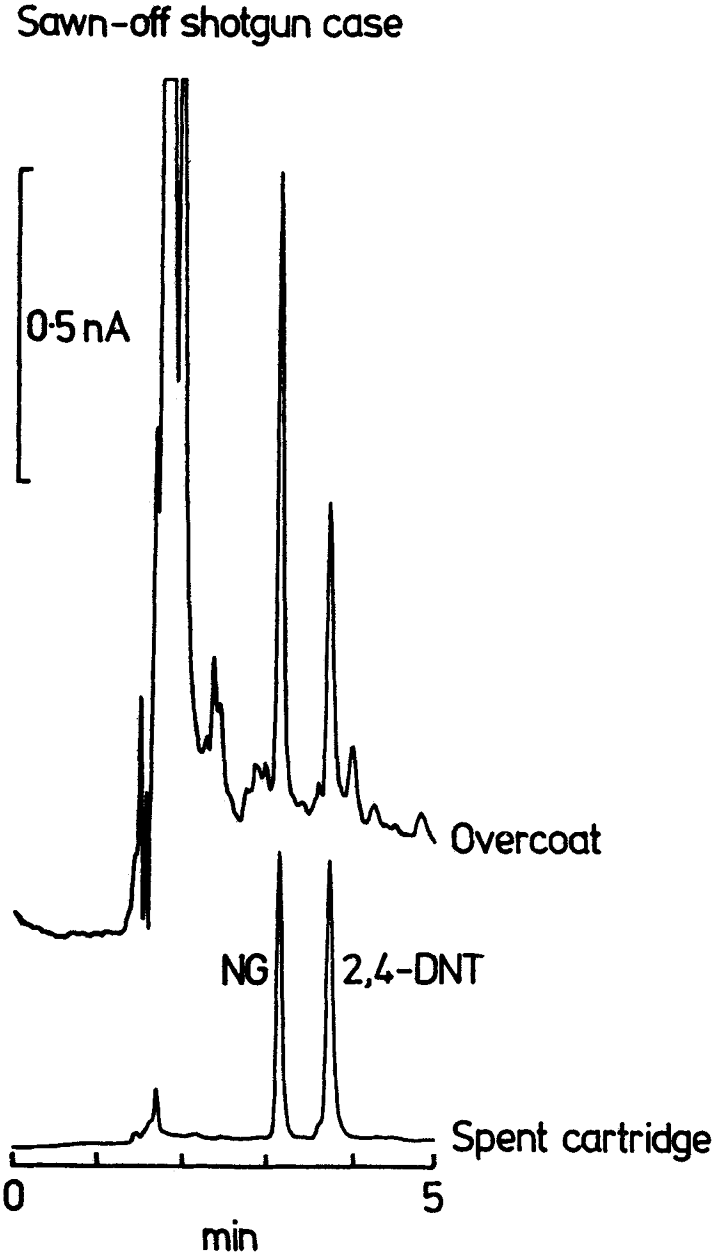

FIGURE 14

HPLC, PMDE detection (Table 2, eluent B), from the indicated samples in a case in which a sawn-off shotgun was used. (Porapak T clean-up).

The response from the spent cartridge and from the lower left sleeve of an overcoat are compared here. The clothing peaks correpond to the presence on the garment of 1.0 ng and 0.4 ng of nitroglycerin and 2,4-dinitrotoluene respectively.

As mentioned earlier, the techniques are designed to retain material for SEM examination. That they do so has been demonstrated in the few comparisons that operational constraints have permitted. In several instances of test firings, however, no residue was detected by the SEM technique, even though organic residues had been detected.

Confirmatory techniques

Few independent confirmatory techniques are at present available at the required levels of sensitivity and rapidity, given the highly complex samples involved. However, the Thermal Energy Analyzer (TEA) in the GC mode is one candidate, and is being applied to the same extracts used for the electrochemically-detected HPLC. The results available to date show that the TEA provides a good level of independence, although the practicable sensitivity is slightly lower than that of the electrochemical technique. This is shown for a clothing extract in Figure 15, where the responses to the nitroglycerin residue are presented at the same peak height. Both systems give a similar level of response to the non-propellant compounds in the extract. In my view, the use of entirely different detectors is preferable to

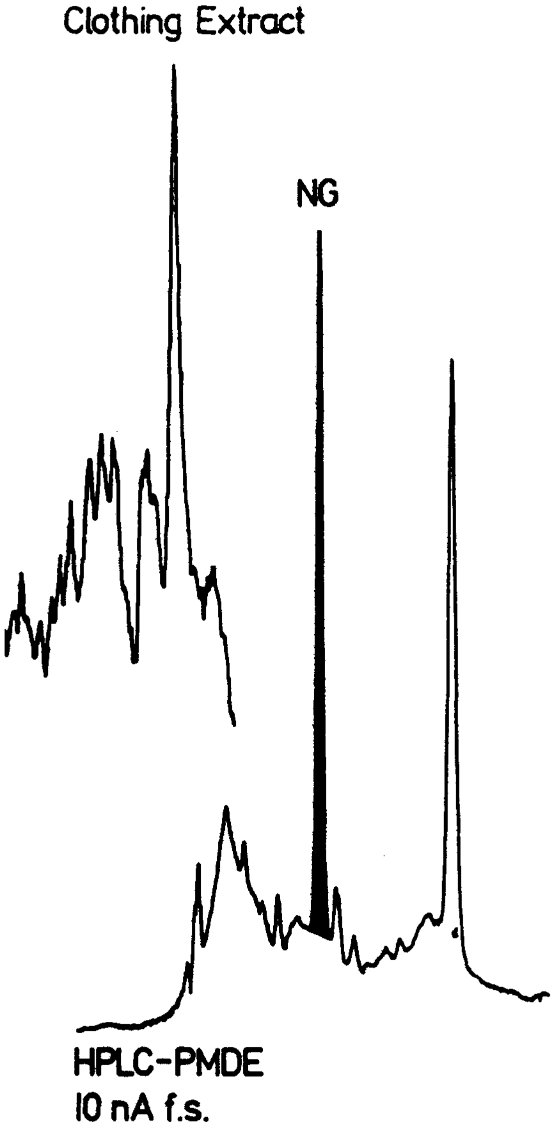

FIGURE 15

, eluent B) compared with GC-TEA results on a extract. The chromatograms have been scaled to the nitroglycerin present.

the use of the relevant TEA for each of the two separation techniques, for mutual confirmation. This might equally be done with one of the techniques employing two columns of different selectivity.

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