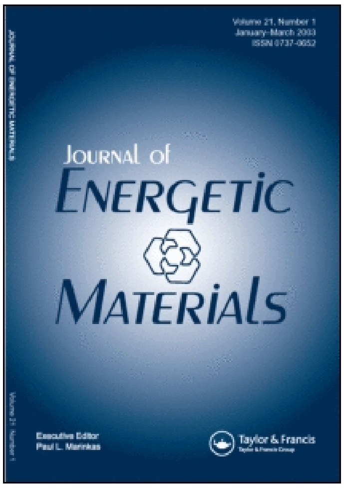

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Trace analysis of explosives and firearm discharge residues in the metropolitan police forensic science laboratory

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TRACE ANALYSIS OF EXPLOSIVES AND FIREARM DISCHARGE RESIDUES IN THE METROPOLITAN POLICE FORENSIC SCIENCE LABORATORY

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Improved methods were developed for the isolation and purification of explosives traces on handswabs. Silica capillary column gas chromatography with electron capture detection was used to analyse the cleaned-up extracts. The methods were applied to the analysis of nitroglycerine in firearm discharge residues deposited on hands and clothing by various weapons and different types of ammunition. We also describe improvements in the thin layer chromatography of nitroaromatic explosives on handswabs using an iminobispropylamine spray to form charge transfer complexes.

INTRODUCTION

Research on the trace analysis of explosives, including organic firearm discharge residues (OFDRs), has been carried out in the Metropolitan Police Forensic Science Laboratory for the last five years [1-5]. Three aspects of our recent work are described in this paper, namely improvements to the method used to isolate and purify traces of explosives on handswabs, the application of the improved method to the analysis of nitroglycerine on hands and clothing at various intervals after firing and, thirdly, the use of 3,3'-iminobispropylamine to detect nitroaromatic explosives on thin layer plates by the formation of charge-transfer complexes.

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MATERIALS AND METHODS

Most of the explosives studied were donated by PERME, Waltham Abbey, U.K. 2,4-Dinitrotoluene (2,4-DNT) was obtained from Fluka, Glossop, U.K. 2,4,6-Trinitrobenzene containing 2,4,6-trinitrotoluene (TNT) as an impurity was obtained from BDH, Poole, U.K. Other abbreviations used in the text are: EGDN = ethylene glycol dinitrate, NG = glycerol trinitrate, PETN = pentaerythritol tetranitrate, RDX = 1,3,5-trinitro-1,3,5-triazacyclohexane, TNX = 2,4,6-trinitro-1,3-xylene, TNA = 2,4,6-trinitroanisole.

Nitromusks were a gift from Givaudin, Whyteleafe, U.K.

Methyl tert.-butyl ether (MTBE) was HPLC grade (Rathburn, Waterburn, U.K.). Other solvents were Distol grade (Fisons, Loughborough, U.K.).

Amberlite XAD-7 resin was 100-200µm Servachrom analytical grade (Uniscience, London, U.K.).

Ethafoam expanded polyethylene foam was purchased from Foam Engineers, High Wycombe, U.K.

All glassware was silanised. Before use it was rinsed with MTBE and dried.

Handswabs

Cotton wool for handswabs was cleaned by three MTBE extractions in an ultrasonic bath and then air dried at room temperature. Handswabs consisted of 10mg portions of cotton wool freshly moistened with MTBE.

Blank handswabs were taken from laboratory staff who had not handled explosives nor fired weapons, and from garage mechanics whose hands were grossly contaminated with dirt and grease. The palm and fingers of one hand per subject were rubbed repeatedly by an assistant wearing two pairs of disposable polythene gloves. Both pairs of gloves were changed after swabbing each subject. Handswabs from subjects who had fired weapons were taken similarly by swabbing the back of the firing hand and the radial surfaces of the thumb and forefinger.

Spiked handswabs were prepared by adding solutions of explosives to swabs of blank hands.

Used swabs were extracted with several aliquots of MTBE (total 5ml/swab) by agitating in a beaker with a glass rod. The combined extracts were then centrifuged to remove solid debris.

Pooled blank handswab extracts consisted of the combined MTBE extracts of swabs of blank hands. Pooled extracts were stored at 4°C and volumes corresponding to single handswabs were used in experiments. These were spiked when required by adding small volumes of explosives in solution.

Amberlite XAD-7 Extraction Procedure

Amberlite XAD-7 extraction columns were prepared as described previously [5] but were plugged with Ethafoam rather than silanised glass wool. Before use, columns were washed sequentially with ethyl acetate (2ml) and the appropriate MTBE/n-pentane mixture (3ml). Silanised Pasteur pipettes were used as funnels to facilitate the addition of extracts or solvents to the columns.

Analytes were isolated from handswab extracts with Amberlite XAD-7 columns. The centrifuged MTBE handswab extracts were decanted into conical glass tubes and their compositions were adjusted according to the guidelines in Table 1. When necessary, prior evaporation of some of the MTBE under nitrogen at room temperature ensured that the final volume, which is not a critical parameter, was between 1 and 10ml. The extracts were passed through the XAD-7 columns which were then washed with MTBE/n-pentane (1ml) of the same composition as the extract. Explosives were eluted from the columns with ethyl acetate (400μl) which was collected in conical glass tubes, evaporated to 100μl under nitrogen at room temperature and analysed by capillary gas chromatography with electron capture detection (capillary GC-ECD). Ice formation on the ends of the columns during collection of the eluents was avoided by protruding the ends of the columns about 0.5cm into the conical tubes.

Capillary GC-ECD

Conditions for capillary GC-ECD were as follows. Chromatograph: Carlo Erba Model 4130 with a Model 40 ^{63}Ni ECD (operated at 250°C) and a Model 400 control module (Erba Science, Swindon, U.K.). Injector: splitless mode, 175°C, as described previously[6]. Column: BP-1 fused silica capillary, 12m x 0.25mm (SGE, Milton Keynes, U.K.), stationary phase film thickness, 0.25µm. Temperature programme: 60°C for 1 min then 39.9°C/min to 250°C, held 1 min. Carrier gas: helium, 17.6ml/min (25°C). Pulse frequency at 60°C oven temperature: 0.359kHz. Injection port liner: cleaned after each working day[6]. Other conditions as previously described[6].

OFDR Experiments

The following .38 handguns were all used with Winchester .38 Special ammunition: Astra; Blackhawk; Colt Python; Detective Special; Llama; Rossi; Security 6; Smith and Wesson Models 19 (two different guns), 27 and 36. A .22 Star handgun was used with CCI .22 Rimfire ammunition.

Long-sleeved, thick woollen pullovers were worn by subjects in OFDR experiments. The pullovers were laundered between experiments then vacuum sampled to check that there was no OFDR carryover.

Pullovers were vacuum sampled as previously described[4] using a glass-fibre disc (AP40 Prefilter, catalogue number AP4001000, Millipore, Harrow, U.K.) in a 2ml glass Luer-Lock syringe barrel (Chance Brothers, Malvern Link, U.K.) connected to a vacuum line by the syringe Luer fitting. The chest and the fronts of the arms of each pullover were vacuumed twice using a single syringe/disc. NG was extracted from the particulate matter retained on the disc by putting ethyl acetate (2ml) in the syringe barrel and allowing it to run slowly through the disc and debris. The ethyl acetate extracts were then analysed by GC-ECD without further treatment, after evaporation to small volume under nitrogen at room temperature or after the XAD-7 isolation procedure using 50% MTBE in n-pentane, depending on the amount of NG extracted and the cleanliness of the extracts.

In experiments concerning OFDRs on clothing only, the subjects washed their hands immediately after firing. When investigating OFDRs on hands only, no precautions were taken in one series of experiments to prevent transfer of OFDRs from clothing to hands. In other experiments, the subjects wore disposable plastic overalls with elasticated cuffs and hoods while firing. Immediately after firing, the overalls were carefully removed by cutting.

Before firing, a control handswab was taken from the hand that was not used to pull the trigger (removal of lipids etc. by swabbing can affect subsequent adherence of OFDRs). Each subject fired three shots in still air, holding the weapon with both hands at waist to mid-chest level. After firing, the fans in the shooting range were used to clear discharge residues from the air. A handswab was taken from the hand used to pull the trigger and the pullover was vacuum sampled. Between firing and sampling, subjects carried out their normal laboratory duties but did not wash their hands before handswabs were taken. NG on handswabs was extracted by the XAD-7 procedure using 50% MTBE in *n*-pentane and analysed by capillary GC-ECD.

Thin Layer Chromatography

Thin layer chromatography (TLC) plates were Merck DC-Aufolien Kieselgel 60F 254, 7.5cm x 5cm x 0.2mm (BDH, Poole, U.K.). The eluting solvent was toluene:cyclohexane (7:3v/v)[2]. Separated compounds on the developed plates were located by observation under ultraviolet light (254nm) and then by spraying with 30% 3,3'-iminobispropylamine (Aldrich, Gillingham, U.K.) in reagent grade pyridine (May and Baker, Dagenham, U.K.)[7]. The plates were sprayed at room temperature; the characteristic colours appeared immediately and were stable for at least 24 hours. The sprayed plates were observed in daylight and then under laser illumination at 488 or 514.5nm from a 2W argon ion laser (Model 165-06, Spectra-Physics, St. Albans, U.K.) Laser safety goggles absorbing wavelengths below 530nm were worn to protect the eyes and to allow fluorescence in the remainder of the visible spectrum to be observed.

RESULTS AND DISCUSSION

Amberlite XAD-7 Extraction Procedure

A previous publication[5] described the use of Amberlite XAD-7 columns to isolate explosives from n-pentane solutions of handswab extracts. Explosives were selectively adsorbed by the XAD-7 resin while the bulk of the coextractives remained in the n-pentane and passed through the columns which were then washed with additional n-pentane. The adsorbed explosives were eluted with ethyl acetate and analysed by capillary GC with ECD or thermal energy analyser (TEA) detection. The method was effective in most cases but, with very dirty handswab extracts, significant levels of coextractives were observed in the chromatograms when ECD was used.

This paper describes how varying the polarity of the handswab extract can enhance the selectivity of the XAD-7 procedure, resulting in much cleaner extracts and improving the long-term stability of the GC capillary column.

Mixtures of MTBE and n-pentane were found to give the best results. Cyclohexane was tried as an alternative to n-pentane but resulted in higher levels of coextractives. Mixtures of ethyl acetate or methanol with n-pentane were too polar, preventing adsorption of explosives by the XAD-7 unless there was a high proportion of n-pentane in the mixture and therefore offering little scope for varying the selectivity.

Increasing the proportion of MTBE in the MTBE:n-pentane mixture improved the selectivity of the XAD-7 procedure by reducing the adsorption of coextractives by the resin, but the adsorption of explosives was also reduced. Optimum conditions were therefore determined for the selective recovery of the various classes of explosives from clean, dirty and very dirty handswabs and are given in Table 1. Percentage recoveries and minimum detectable levels (MDLs) of representative explosives are summarised in Table 2.

TABLE 1

MTBE (%v/v) in MTBE:n-Pentane Mixture for Selective Recovery of Explosives by the Amberlite XAD-7 Procedure.

Explosive Class	Clean Extract	Dirty Extract	Very Dirty Extract
Nitramine Trinintroaromatic	15	50	100
Tri- & tetranitrate esters	15	50	100
Dinitrate ester	15	15	15
Dinitroaromatic	15	15	15

TABLE 2

Percentage Recoveries and MDLs of explosives on spiked Handswabs* using the Amberlite XAD-7 Procedure.

	% Recovery of explosive (MDL ng/swab)		
MTBE (%v/v) in MTBE:n-pentane mixture	**15%**	**50%**	**100%**
RDX	72 (10)	76 (1)	41 (1)
TNT	44**(10)	78 (1)	47 (0.5)
NG	94 (10)	46 (1)	13 (0.5)
PETN	71 (20)	31 (5)	10 (20)
EGDN	92 (10)	9 (10)	4 (10)
2,4-DNT	87 (10)	8 (20)	0

* Blank handswabs taken from laboratory staff and spiked with 20ng/swab of each explosive before extraction.

**Anomalous loss perhaps due to reaction with coextractives in injection port.

The recoveries of nitramines, trinitroaromatics and tri- and tetranitrate esters from 100% MTBE by the XAD-7 procedure is moderate to poor, but the virtual elimination of coextractives and the high sensitivity of capillary GC-ECD enable, for instance, 20ng NG in a very dirty handswab extract to be detected with ease (Fig. 3D). With less polar explosives such as EGDN and 2,4-DNT, there is a low or zero recovery from 100% MTBE. Their MDLs from handswabs are therefore higher than those of the nitramines etc. but, even with 15% MTBE in n-pentane, the reduction in coextractives enables very dirty swabs to be analysed with a reasonable chance of success.

In practice, the XAD-7 procedure is cheap, simple and fast, and enables useful results to be obtained using a relatively inexpensive ECD. Evaporation of the extracts to dryness and the consequent loss of volatile explosives is avoided. The procedure is also flexible since handswab extracts can be passed through several XAD-7 columns, starting with 100% MTBE and adjusting the MTBE:n-pentane ratio between passes.

Figs. 1-7 illustrate the effectiveness of the XAD-7 procedure. Fig. 1 shows the analysis of a range of explosives and musk tibetine (a nitromusk present in cosmetics) by capillary GC-ECD. Fig. 2 shows the analysis of NG, TNT and RDX (20ng/swab) in a 'clean' pooled handswab extract from laboratory staff and demonstrates the reduction in coextractives as the proportion of MTBE in the MTBE:n-pentane mixture is increased from 0 to 100%. Fig. 3 shows comparable chromatograms from a very dirty pooled handswab extract from garage mechanics and illustrates the selectivity of the procedure with grossly contaminated extracts. Figs 4-7 show the analysis of handswabs spiked with various explosives, some at very low levels.

OFDR on Hands and Clothing

The persistence of NG on hands and clothing was investigated in the hope of estimating a post-firing interval within which positive handswabs or vacuum samples might be obtained. The results, uncorrected for incomplete recovery, are shown in Tables 3 and 4.

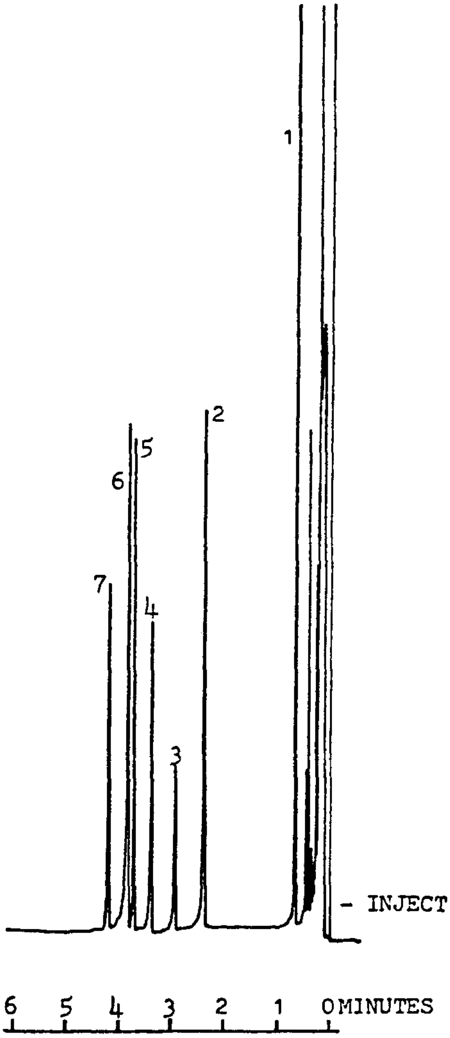

FIGURE 1

Capillary GC-ECD of 125pg each of EGDN(1), NG(2), 2,4-DNT(3), TNT(4), PETN(5), RDX(6) and Musk Tibetine(7). Attenuation x64.

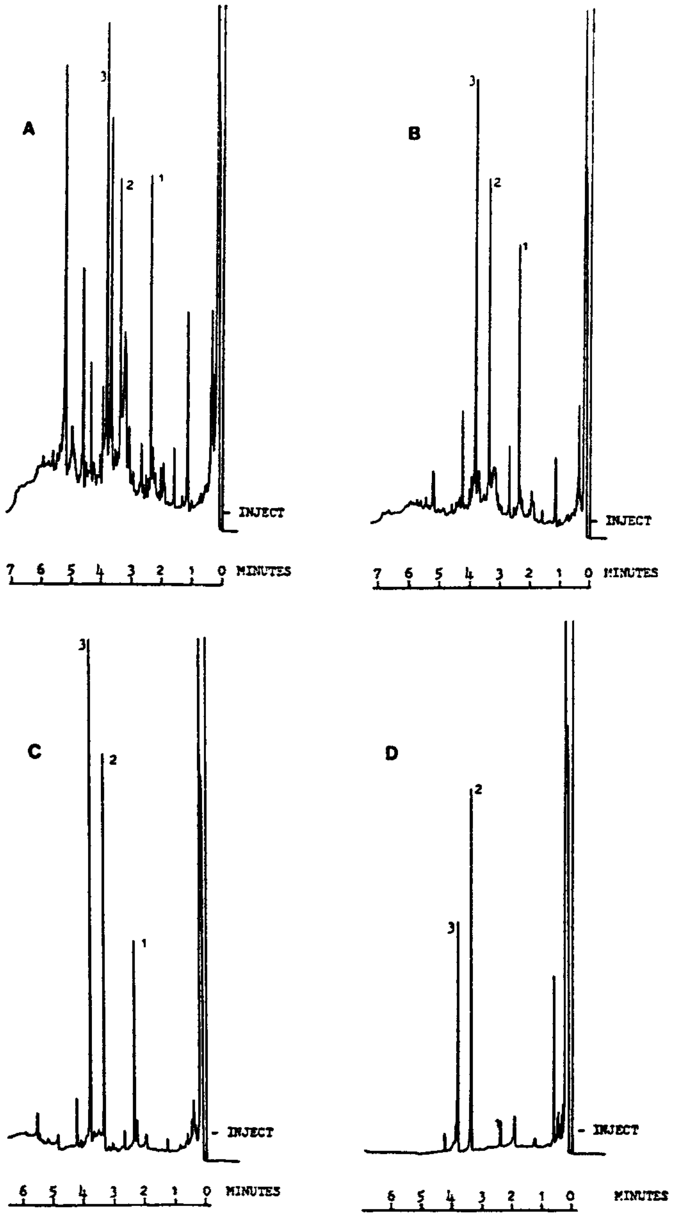

FIGURE 2

Capillary GC-ECD of a pooled handswab extract (from laboratory workers) spiked with 20ng each of NG(1), TNT(2) and RDX (3), extracted by the Amberlite XAD-7 procedure using 0%(A), 15%(B), 50%(C) and 100%(D) MTBE in *n*-pentane. 0.7% of each sample analysed; attenuation x64.

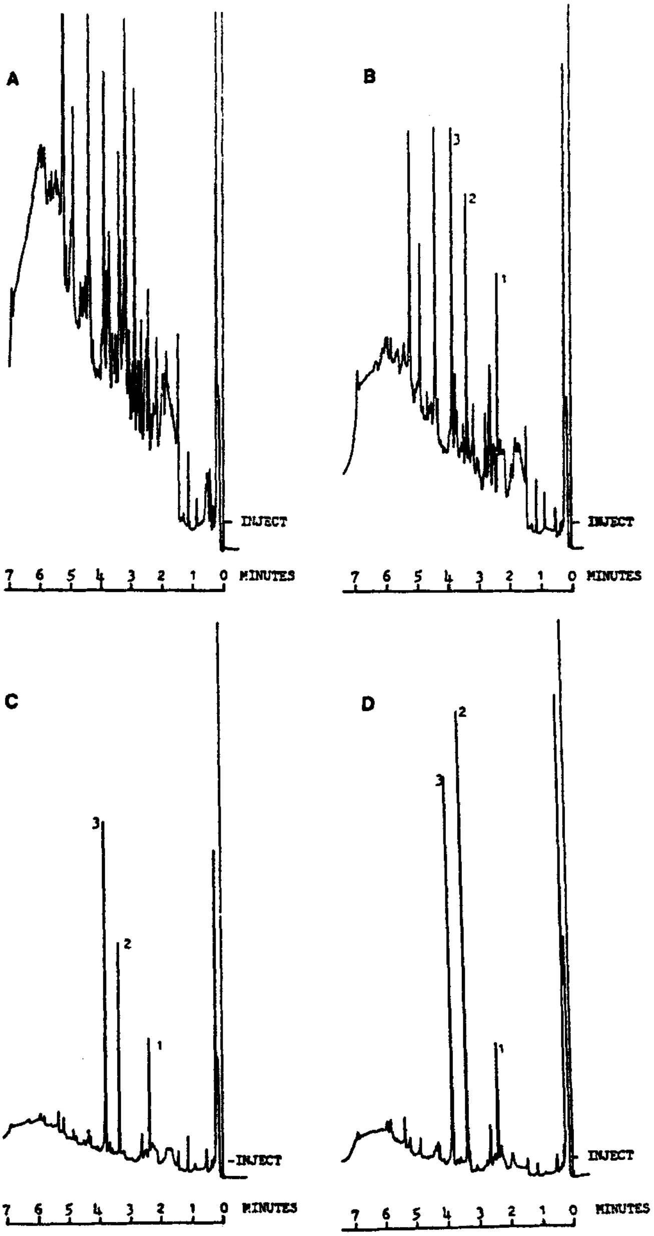

FIGURE 3

Capillary EC-ECD of a very dirty pooled handswab extract from garage mechanics. Details as for Fig. 2. 1% of each sample analysed; attenuation x64(A,B,C) or x32(D).

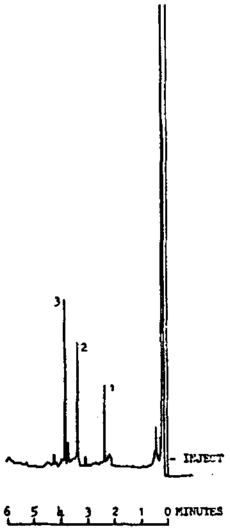

FIGURE 4

Capillary GC-ECD of a pooled handswab extract (from laboratory workers) spiked with 2ng each of NG(1), TNT(2) and RDX(3), extracted by the Amberlite XAD-7 procedure using 50% MTBE in n-pentane. 2% of the sample analysed; attenuation x64.

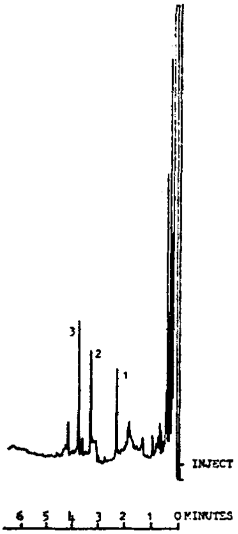

FIGURE 5

Capillary GC-ECD of a handswab (from a laboratory worker) spiked with 1.5ng of NG(1) and 0.5ng each of TNT(2) and RDX(3), extracted by the Amberlite XAD-7 procedure using 100% MTBE. 6.5% of the sample analysed; attenuation x32.

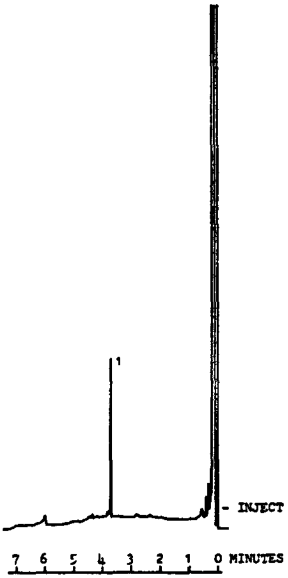

FIGURE 6

Capillary GC-ECD of a pooled handswab extract (from laboratory workers) spiked with 20ng of PETN(1), extracted by the Amberlite XAD-7 procedure using 50% MTBE. 1% of the sample analysed; attenuation x64.

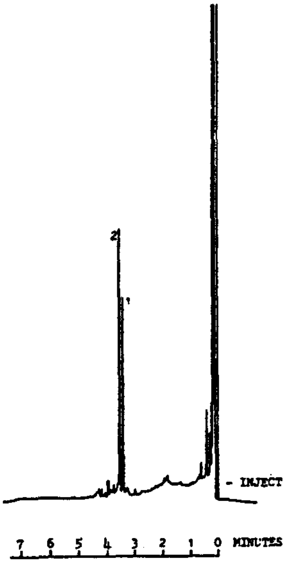

FIGURE 7

Capillary GC-ECD of a handswab (from a laboratory worker) spiked with 10ng each of TNX(1) and TNA(2), extracted by the Amberlite XAD-7 procedure using 100% MTBE. 2% of the sample analysed; attenuation x32.

TABLE 3

Recovery of NG from the Firing Hand

	Recovery (ng)				
Interval after Firing (hours)	**0**	**0.5**	**1**	**1.5**	**2**
Weapon					
Astra	22				
Blackhawk	26				
Colt Python	43				
Detective Special	0				
Llama	4				
Rossi	36				
Smith & Wesson, Model 19 (i)	31	0,0		0	
Smith & Wesson, Model 19 (ii)	38				
Smith & Wesson, Model 27	4				
Smith & Wesson, Model 36	114		0,0,0	0*,0*,0*	0*,0*,0*
Security 6	74				
Star	15				

* Disposable overalls worn while firing and removed immediately afterwards.

Even with the simple experimental protocol that was adopted, the scatter of results showed an extreme variability that was not due to the sampling procedure since repeated sampling showed that >90% of the recoverable NG was removed by a single handswabbing or vacuuming.

In our experiments, no NG was detected on hands 0.5 hours after firing. This was surprising since, in other studies[4,8], NG on the firing hand was detected 2 and 2.5 hours after firing. Further trials are planned, but the conclusion to be drawn at present is that OFDRs are rapidly lost from hands and so a zero result for NG on a handswab does not necessarily eliminate a suspect from further enquiry.

TABLE 4

Recovery of NG from Wollen Pullovers

Weapon	**Interval after Firing (hours)**	Recovery(ng)
Smith & Wesson Model 19	0	0,59,174
"	0.5	0*
"	1	0,76*
"	1.5	256,364*
"	2	0,0
"	2.5	230*
"	3	0,58
"	4	0*
Smith & Wesson Model 36	5	0,0,0,0*,148
"	6	0,0*,0*
"	6.5	0
"	7.5	0,0
"	23.5	0,0*

*Labcoat worn over pullover for at least some of the time between firing and sampling.

The deposition of NG on clothing (Table 4) was very variable (0-364ng) and in one instance residues were detected 5 hours after firing. Clothing as well as handswabs should therefore be examined in criminal cases involving firearms, particularly since residues have been shown to persist for at least 2 months on fabric (cotton sheet) stored undisturbed[4].

In general, the above findings correlate approximately with the rates at which inorganic primer residues are lost from hands and clothing[9-11]. It is a reasonable assumption that OFDRs, like inorganic primer residues, are largely particulate (though there is some evidence for partial deposition from a gaseous state[4]) and so similar factors may influence their deposition and loss. At present, any discussion of these factors is largely speculative though common-sense predictions are usually, but not invariably, borne out in practice[4]. We found, however, that a thin coating of grease on a subject's hands trapped a high level of OFDR.

TLC

The application of charge-transfer complexes to explosives analysis has been reviewed[12]. Detection limits of 1-2μg have been reported[13] for the TLC of explosives as charge transfer complexes with various aromatic amines. A preliminary study[2] of 3,3'-iminobispropylamine[7] as a charge-transfer TLC spray for nitroaromatic explosives has now been extended to encompass 29 explosives and 5 nitromusks. The results are shown in Table 5.

Sixteen explosives, but none of the nitromusks, formed stable (>24 hours) coloured complexes with 3,3'-iminobispropylamine. In daylight, the MDLs were in the range 2.5-5ng except for 2,4,6-trinitrophenetol and 2,4,6-trinitro-1,3-xylene (MDLs 10ng). Under laser illumination at 514.5nm, 6 of the complexes fluoresced with MDLs from 0.5-2.5ng. Under the other available laser wavelength, 488nm, the fluorescence was less intense.

The method is highly selective and sensitive enough to provide an alternative to gas or liquid chromatography for the analysis of handswab extracts containing nitroaromatics that react with 3,3'-iminobispropylamine. Coextractives, particularly lipids, adversely affect the chromatography but may be removed by the Amerlite XAD-7 procedure.

TABLE 5
TLC of Nitroaromatic Compounds

Compound	Rf Value (Colour before Spraying)	Colour after Spraying (MDL)	Fluorescence under 514.5nm laser (MDL)
Ammonium picrate	0(FY)	NR	NF
Dinitrodiethylcentralite	0(NC)	NR	NF
4,4'-Dinitrodiethyldiphenylurea	0(NC)	NR	NF
2,2'-Dinitrodiphenylamine	0.39(Y)	NR	NF
2,4-Dinitrodiphenylamine	0.32(FY)	Y(5)	NF
2,3-Dinitrotoluene	0.41(NC)	NR	NF
2,4-Dinitrotoluene	0.54(NC)	NR	NF
2,6-Dinitrotoluene	0.43(NC)	NR	NF
3,4-Dinitrotoluene	0.55(NC)	NR	NF
Dipicrylsulphide	0.29(FY)	BY(5)	NF
N-Ethyl-2,4,6-trinitroaniline	0.29(NC)	BY(5)	P(1)
Hexanitrobibenzyl	0.13(NC)	B(2.5)	R(1)
Hexanitrodiphenylamine	0(O)	R(5)	NF
Hexanitrostilbene	0(NC)	NR	NF
N-methyl-2,4,6-trinitroaniline	0.22(NC)	BY(5)	PR(2.5)
4-Nitrodiphenylamine	0.23(FY)	NR	NF
Picric acid	0(FY)	NR	NF
Styphnic acid	0(Y)	NR	NF
2,2',4,4'-Tetranitrodiphenylamine	0.10(FY)	R(2.5)	NF
2,4,6-Trinitroaniline	0.22(FY)	Y(5)	NF
2,4,6,-Trinitroanisole	0.45(NC)	Y(5)	NF
1,3,5-Trinitrobenzene	0.47(NC)	R(2.5)	O (0.5)
Trinitro-<u>m</u>-cresol	0(Y)	NR	NF
2,2',4-Trinitrodiphenylamine	0.18(FY)	O (2.5)	P(2.5)
2,4,4'-Trinitrodiphenylamine	0.15(FY)	R(5)	NF
1,3,8-Trinitronaphthalene	0.15(NC)	Pi(2.5)	NF
2,4,6-Trinitrophenetol	0.55(NC)	Y(10)	NF
2,4,6-Trinitrotoluene	0.56(NC)	P(5)	P(2.5)
2,4,6-Trinitro-1,3-xylene	0.68(NC)	BlP(10)	NF
Musk Ambrette	0.71(NC)	NR	NF
Musk Ketone	0.48(NC)	NR	NF
Musk Moskene	0.80(NC)	NR	NF
Musk Tibetine	0.78(NC)	NR	NF
Musk Xylol	0.80(NC)	NR	NF

MDLs are given as ng pure compound applied to the TLC plate

NC = no colour
NF = no fluorescence
NR = no reaction

B = brown
Pi = pink
P = purple
R = red
Y = yellow
O = orange

BlP = blue/purple
BY = brown/yellow
FY = faint yellow
PY = purple/red

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