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Transfer of Nitroglycerine to Hands During Contact with Commercial Explosives

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ABSTRACT: The techniques of thin-layer chromatography, gas chromatography with electron capture detection, and gas chromatography/mass spectrometry were used to analyze hand swab extracts for the presence of nitroglycerine. Both the amount of nitroglycerine transferred to the hands after handling commercial explosives and its persistence were measured. Gas chromatography-electron capture detection was found to be the most accurate and sensitive technique for making such determinations, especially if the extract was partially purified by thin-layer chromatography prior to analysis. The lowest limit of detection was 10 ng of nitroglycerine, and residues could be detected over 20 h after handling the raw explosive.

KEYWORDS: criminalistics, explosives, nitroglycerine, gas chromatography, acetone, thin-layer chromatography, mass spectrometry

Although contamination of the hands with nitroglycerine (NG) is likely to occur on handling of commercial explosives, there appear to be no data in the literature concerning the quantities of explosive that can remain on the hands at various times afterwards. A short, qualitative report was published by Kempe and Tannert [*1*], who analyzed hand swab extracts using thin-layer chromatography (TLC) at various times after subjects had handled nitroglycerine-based explosives. Subjects who had handled properly wrapped cartridges gave no positive TLC spots an hour later, whereas a subject who had rubbed dynamite on his hands gave a positive result after the same time interval. When tested after 24 h the latter subject gave a negative test for the explosive. The value of these results is, however, limited by the lack of information on the detection limits of the technique.

The analytical techniques considered for analysis of NG in the hand swab extracts obtained during the current study were TLC [*2-4*], gas chromatography with electron capture

This study was carried out in 1977. Since then many of the techniques described have been replaced by more modern ones. Notes have been inserted in the text where such changes are relevant to the discussions. For example, capillary columns are now used for detecting explosives residues on hands as they give greater sensitivity and resolution. Received for publication 16 Dec. 1981; accepted for publication 20 Jan. 1982.

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detection (GC-ECD) [5], and gas chromatography/mass spectrometry (GC/MS). As it is clearly necessary to be able to detect NG for as long as possible after handling explosives, a special effort was made to develop procedures for partially purifying the extracts and, hence, to optimize the detection limits of the techniques. The method showing the best results was then chosen for the quantitative analysis in the major part of the study.

The aim of this investigation was to measure both the quantitities of NG transferred to hands from commercial cartridges and the quantities persisting at various times after handling. In practice the study of explosives transfer is incompatible with the study of their persistence, since swabbing inevitably terminates the persistence experiment. The project was therefore designed in two stages. Explosives were handled in various ways, and typical levels of NG contamination were established. Similar quantities of NG in solution were then applied to the hands of various individuals so that a well-controlled persistence study could be undertaken.

Experimental Procedure

Reagents

The acetone and toluene used in this work were reagent-grade solvents that had been redistilled in glass apparatus. A stock solution of NG in toluene (10 μg/μL) was prepared by extraction of a standard dynamite (68% NG) for 16 h.

Transfer Experiments

Two different case work consignments of 170-g (6-oz) cartridges of Eversoft Frangex® (Irish Industrial Explosives Ltd.) were used in the transfer experiments. One batch was in excellent condition, whereas the second was poorly wrapped and showed signs of "sweating," that is, droplets of liquid were visible on the cartridge exterior.

Three ways for handling explosives were investigated, and the appropriate experiments were designated as Series A, B, and C. In Series A subjects were asked to pick up a well-wrapped cartridge in the right hand, pass it to the left hand, and then put it down. This procedure (denoted a "pass") was repeated up to nine times, fresh cartridges being used in each pass and experiment. Series B experiments were similar to those in Series A, except that the cartridges were in poor condition. In Series C the subjects kneaded raw explosive. The palms, inner surfaces of the fingers (and thumbs), and the nail crevices of the subjects hands were analyzed separately in the transfer experiments so that the distribution of explosives over the hand could be determined.

Persistence Experiments

In the persistence experiments an appropriate amount of NG (in 100 μL of toluene) was applied to the hands with a dispensing pipet and spread as evenly as possible over the palm area. After the appropriate delay, the palms and inner surfaces of the fingers and thumbs were swabbed with one swabbing solution.

Hand Swabbing Procedure

The cotton wool used for swabbing was of a coarse, uncombed grade and was normally used without prior treatment. However, when very low levels of NG (< 100 ng) were expected to be recovered, as in the persistence study, the cotton wool was placed in a Soxhlet extractor with acetone for several hours prior to use.

Swabbing of the hands was performed using pea-sized pieces of cotton wool ($\simeq 30$ mg)

held in tweezers. The cotton wool swab was dipped in 2 mL of acetone and rubbed over the appropriate area of the hand. The swab was then rinsed in the solvent and the whole process repeated until the required areas had been covered three times. In the transfer experiments the areas under the nails were swabbed as before, but a piece of cotton wool that had been twisted around a small wooden stick was used.

Preparation of Hand Swab Extracts

Normally, the acetone solutions from hand swabbing were simply evaporated to a small volume at or just above room temperature prior to analysis. However, for the smallest recoveries of NG (<100 ng) the extract was applied to the baseline of a TLC plate, over its full width of 1.5 cm, and developed as described below. A band of silica gel, 1 cm in height, was scraped from the region on the plate centered on the established R_f value for nitroglycerine (typically 0.20). The silica gel was extracted twice with 200 μL of acetone in a small tube and the solution evaporated as described previously.

Analytical Methods

Thin-Layer Chromatography—Plastic-backed silica TLC plates, 20 cm square (Chromagram® 13179, Eastman Kodak Co., Rochester, NY), were eluted in ethanol overnight and dried, and the top 2 cm was removed. The plate was then cut into 36 equal strips, 6.7 by 1.5 cm, and parallel lines were drawn in pencil 5 cm apart across the strips. Solutions were spotted or hand swab extracts applied linearly (as above) to one line, which served as the origin, and the plates were developed to the other line, using a mixture of cyclohexane and toluene (70:30 by volume) under chamber-saturated conditions. Spots were initially visualized using several different reagents, with the one providing the optimum combination of selectivity and sensitivity chosen for use in subsequent analyses.

Two categories of reagent were examined. One group, consisting of diphenylamine and diphenylbenzidine reagents (50 and 20 mg, respectively, in 10 mL of 70% sulfuric acid [*6*]), were found to be sensitive to all oxidizing agents and hence could be applied directly to the plate. The other group were nitrite-specific and required hydrolysis and disproportionation of the NG prior to detection. Reagents in this category were those described by Sawicki and Scaringelli [*7*] and a commercial Griess Ilosvays reagent (Product Nos. 19062 and 19063, BDH Ltd., Poole, England) premixed in equal volumes.

Gas Chromatography—The chromatograph used was a Pye 104 (Pye Unicam Ltd., York Street, Cambridge, England) fitted with a 7-mCi ^{63}Ni electron capture detector (Pye Unicam), operated at 275°C in the pulsed mode (pulse width 0.75 μs, pulse space 150 μs). The columns consisted of 305-mm (12-in.) lengths of polytetrafluoroethylene (PTFE) tubing, 2.36-mm (0.093-in.) outer diameter and 1.22-mm (0.048-in.) inner diameter (PTFE Fabricators, Port Vale, Hertford, England), packed with 10% Silar 10C on Gas Chrom Q (Field Instruments Ltd., Twickenham, Middx., England). Nitrogen was used as carrier and quench gas (60 mL/min in each case). The column was operated at 160°C, and quantitation was achieved by comparing peak areas from the samples with those of standard solutions prepared by diluting the stock solution with acetone.

Gas Chromatography Mass Spectrometry—A chromatograph and column similar to those described previously were used, linked by an all-glass jet separator to a VG Micromass 12B mass spectrometer (VG Micromass Ltd., Altrincham, Cheshire, England). The column and separator were maintained at 165°C, and helium was used as carrier gas (30 mL/min). The ionizing voltage of the electron impact instrument was 70 eV, the source temperature was 200°C, and simultaneous chart recorder plots (multiple ion detection) were obtained of the intensities of the most prominent fragment ions of NG (*m/e* 46 and 30).

Results and Discussion

Techniques

Thin-Layer Chromatography—Diphenylamine and diphenylbenzidine were slightly more sensitive than the nitrite-specific reagents for visualizing pure NG standards on the plates; however, their sensitivity to any oxidizing agent and the brown char produced by the acid on co-extracted material rendered them of little use for hand swab extracts. The procedure finally adopted was to apply 0.1*M* sodium hydroxide solution carefully to the plate by capillary action from a pipet and to heat the plate to 100°C for 6 min. Visualization was then achieved by spray (or drop) application of the following Griess reagent [*7*]: sulfanilamide (0.4 g) and *N*-(1-naphthyl)ethylenediamine (0.02 g) dissolved in 85% phosphoric acid (1 mL) and then made up to 10 mL with distilled water. The hydrolysis conditions selected were found to produce optimum amounts of nitrite on the neutral silica of the Chromagram plate; however, for other silica plates a stronger alkali would be necessary to overcome the inherent acidity of the silica [*2*].

It was found necessary to line the extract across the entire width of the plate in the purification procedure to ensure that the solvent eluted through, not around, the applied material. Such elution around a spot (where the pores are blocked by the oily material) undoubtedly is responsible for the poor chromatograhic separation of extracts applied spotwise, causing reduced R_f values, extensive tailing, and hence reduced detectability. Purification will inevitably cause losses of NG; however, tests at the 10- to 25-ng level established that with care losses could be limited to about 10%.

Gas Chromatography—Although GC-ECD gave detection limits in the picogram region for pure NG standards, such sensitivity could not be achieved with hand swab extracts because of the greatly increased background. Not only was the response of the instrument to co-injected NG reduced when concentrated hand swab extracts were injected, but the response to subsequently injected NG standards was also reduced by up to an order of magnitude, indicating more general column or detector contamination.

Use of the TLC procedure gave an order-of-magnitude improvement in detecting NG in hand swab extracts and reduced the contamination problems, thereby reducing the frequency with which the system required purging. These problems are not encountered with higher concentrations of NG, as the extract may be injected without preconcentration and correspondingly less contamination is introduced.

Gas Chromatography/Mass Spectrometry—Problems similar to those described for the GC-ECD analysis of hand swab extracts were also encountered with GC/MS. To obtain detection limits in the nanogram region, monitoring had to be limited to only two fragment ions (*m/e* 46 and 30). Thus, complete specificity could not be obtained. (Later analyses by chemical ionization mass spectrometry using isobutane revealed that the sensitivity was inadequate for the levels typically encountered in hand swabs.)

Detection Limits

The detection limits for the three analytical techniques were determined for pure solutions, raw hand swab extracts, and partially purified hand swab extracts. Although representative mean results are shown in Table 1, it must be emphasized that such results are likely to be variable in the case of hand swab extracts. The variation is due to differences in the amounts and types of secreted skin oils and to coincidental contamination (see, for example, the results from a larger study [*1*]). As GC-ECD provided adequate specificity, the best detection limits, and a precision of about 10% in 3- to 4-min analysis (retention time for NG about 2 min), this method (with TLC purification as required) was used in the main study of transfer and persistence.

TABLE 1—*Detection limits for nitroglycerine using three different analytical techniques.*

Technique	Detection Limits,[a] ng		
	Pure Solution	Hand Swab Extract[b]	Partially Purified Hand Swab Extract[b]
TLC	2	10	5
GC-ECD	0.001	5	0.5
GC/MS	1	12	2

[a] Estimated as three times background for GC methods; subjectively determined for TLC (acetone solutions).

[b] Estimated detection limits in the total hand swab extract, that is, minimum detectable level on hands.

Transfer Experiments

Details of the various handling experiments performed, the total explosive found on each hand, and the proportions present on the palms and fingers and beneath the fingernails are shown in Table 2. The handling of a single well-wrapped cartridge of explosive in experiments A1 and A2 transferred about 60 ng of NG to each hand. When nine different cartridges were handled, between 1 and 32 μg of NG were found (A3 and A4); thus, the average amoung of NG transferred from each cartridge was considerably higher than in the previous experiments. This probably reflects the fact that the wrappers from a batch of cartridges in good condition are not uniformly contaminated with NG. For the experiments in Series A, about 60% of the explosive transferred was found to be present on the fingers, 30% on the palms, and 10% under the fingernails.

The handling of single, poorly wrapped cartridges in experiments B1 and B4 transferred between 25 and 83 μg of NG to each hand. The distribution of explosive in the Series B experiments was similar to that in Series A, about 50% being on the fingers, 40% on the palms, and 10% under the fingernails.

The kneading of raw explosives transferred 20 mg of NG to a subject's right hand (C1). In Experiment C2 the subject washed with soap and water immediately after kneading the explosive as his hands were sticky and he felt a natural desire to do so. About 2 mg of NG was then found on each hand, 60% of which was present on the fingers, 30% on the palms, and 10% under the fingernails. Ten minutes after a subject had kneaded the raw explosive with his fingers only and then immediately washed his hands, 14 μg of NG were found on the right hand.

As the distribution of NG over the hand was characteristically different in only one experiment (C3R), different hand areas were not examined in the persistence study.

Persistence Study

The quantities of NG recovered from eight volunteers who did not wash their hands during the 3-h period after application of 1 mg, 100 μg, and 1 μg of NG in toluene solution are shown in Fig. 1. Fivefold replication of some experiments revealed that although the within-subject variation usually was 10%, it was occasionally much higher. The variation between subjects averaged about 50%. A very rapid loss of NG was observed in the first 15 min, and the subsequent rate of loss was much slower. It was noticed that, as the amount of NG applied to the hand was reduced, the proportion lost in the first 15 min increased.

The persistence study was extended to cover a typical day's activity for a group of

TABLE 2—*Amounts of NG recovered and its distribution over the hands 10 min after contact with explosives.*

Experiment[a]	Handling Description	Total NG recovered, μg	Distribution, %		
			Palm	Fingers	Nails
	A (FRANGEX IN GOOD CONDITION)				
1R	one pass	0.062	25	75	0
2L	one pass	0.070	34	44	22
Mean		0.066	...	...	...
3L	nine passes	4.1	21	72	7
3R	nine passes	32.0	14	76	10
4R	nine passes	1.4	44	55	1
Mean		12.5	...	...	...
	B (FRANGEX IN POOR CONDITION)				
1L	one pass	40	45	52	3
1R	one pass	25	42	51	7
2L	one pass	32	53	43	4
2R	one pass	38	34	50	16
3R	one pass	62	22	72	6
4L	one pass	83	45	51	4
4R	one pass	60	42	51	7
Mean		48.5	...	...	...
	C (KNEADING UNWRAPPED FRANGEX)				
1R	in hand	20 000	39	NM[b]	NM
2L	in hand followed by immediate wash	2 100	29	57	14
2R	in hand followed by immediate wash	2 600	28	58	14
3R	kneading in fingers followed by wash	14	2	60	38

[a] R = right hand, L = left hand.
[b] NM = not measured.

laboratory workers. As it was anticipated that washing would remove some of the NG, the subjects were asked not to wash. On their arrival at the laboratory, 1 mg of NG was applied to each of the workers' hands. Swabbing took place about 7 h later. The results are shown in Fig. 2 and have been used to extend the mean persistence curve obtained earlier (Fig. 1). Figure 2 also shows the results obtained from longer persistence experiments in which the subjects were allowed to wash. Although some individuals washed their hands as many as three times, NG was still detectable after about 14 h. That NG would remain on the hands for longer periods when the initial contamination was greater was verified by swabbing the subject from transfer experiment C2 on the day after he had kneaded the raw explosive. Over 20 h later, 170 and 41 ng of NG were found on his left and right hands, respectively, despite his having washed his hands six times and been swabbed twice.

General Discussion

By repeatedly swabbing the same pair of NG-contaminated hands at 2-min intervals, the swabbing procedure was shown to be about 70% efficient. The results reported in this paper are actual recoveries and have not been corrected for swabbing losses. Similarly, the recoveries quoted after TLC purification have not been corrected for losses during this pro-

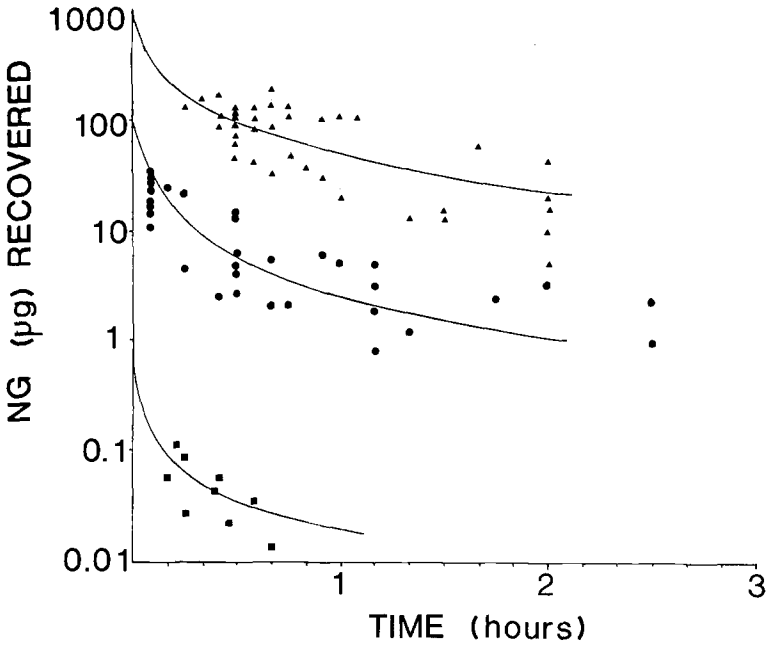

FIG. 1—*Recoveries of NG at various times after application in solution of 1 μg (■), 100 μg (●), and 1000 μg (▲) to the palms of subjects' hands.*

cedure, which are small compared to natural sources of variation. Although results were not examined in any detail, it was estimated that washing the hands removed the same amount of NG as swabbing. (Use of aqueous detergent solutions for swabbing hands is discussed in the accompanying paper [*8*].)

The amounts of NG transferred to the hands during various types of handling can be estimated from Table 2, and the persistence from Fig. 2. As the persistence curves for 100 μg and 1 mg (Fig. 1) are roughly parallel, the basic decay curve of Fig. 2 appears to hold for different levels of initial contamination. Hence, by adjusting the curve along the abscissa to a level typifying the type of handling involved, rough estimates of persistence can be obtained. To check this model against the actual handling situation, some delays were incorporated into the handling experiments. The mean level found 10 min after handling was used as the starting point. With the curve set at the 10-min delay position, the amounts predicted were compared with the actual levels found. Table 3 shows that, despite all possible sources of variation, there seems to be reasonable agreement between the values. Thus, there is no reason to believe that the results from solution simulation are grossly unrealistic.

The initial sensitivity experiments suggest that, although the GC-ECD procedure can detect lower levels, about 10 ng must be present for adequate confirmation. Using this level as a realistic limit, suitable adjustment of the curve to allow for the type of handling allows a rough estimate to be made of the time over which NG will remain detectable. Suitable displacement of the curve will also allow for the effects of washing. Such adjustments predict that it is unlikely that NG will remain detectable for more than a few hours after handling well-wrapped cartridges or for more than about 12 h after handling sweating ones. After heavy contamination with raw explosives, however, detection may be possible for over 30 h.

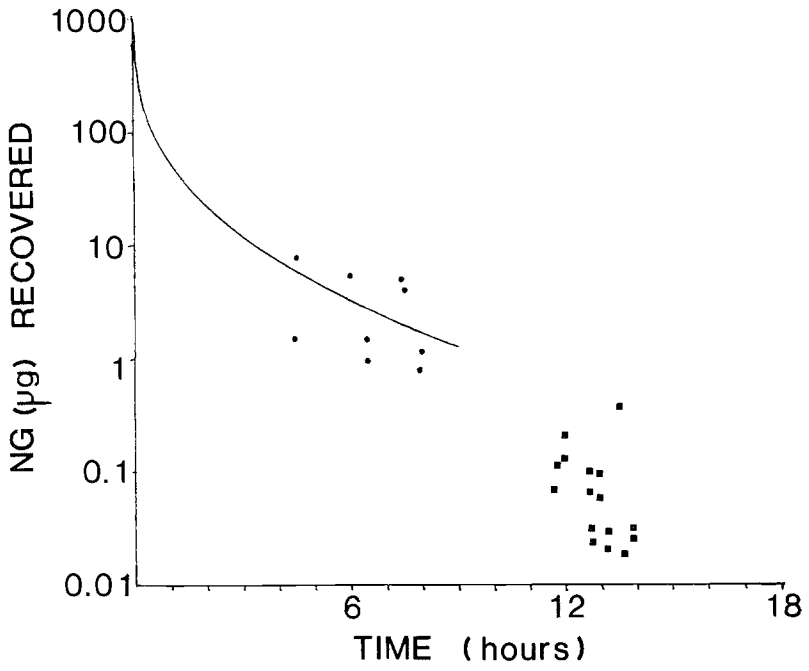

FIG. 2—*Recoveries of NG from hands after various periods without washing (●) and with two to three washes (■). (The no washing results have been used to extend the curve shown in Fig . 1.)*

TABLE 3—*Actual recoveries of NG from hands 1 h after handling compared with estimates derived from the recoveries at 10 min in similar experiments.*

Experiment	Similar Experiments	NG Recoveries, μg		
		Mean at 10 min	Predicted at 1 h	Actual at 1 h
A1L	A2L, A1R	0.066	0.012	0.023
A2R	A2L, A1R	0.066	0.012	<0.010
A4L	A3L, A3R, A4R	12.5	2.3	1.0
B3L	remainder of B series	48.5	9	26
C3L	C3R	14	2.8	0.7

Summary

The relative merits of thin-layer chromatography, gas chromatography with electron capture detection, and gas chromatography/mass spectrometry were compared for the analysis of nitroglycerine in hand swab extracts. On the basis of this preliminary study, GC-ECD was chosen to determine both the amount of nitroglycerine transferred to hands from commercial explosives and its subsequent persistence on the hands.

The detection limits for nitroglycerine using GC-ECD were typically about 5 ng per total hand extract. This could be reduced by about one order of magnitude if the extract was first purified with a TLC procedure. In case work applications about 10 ng of nitroglycerine would be the minimum that would allow confirmation by more than one method. The quan-

tities of nitroglycerine transferred to a hand ranged from 60 ng after touching a single well-wrapped cartridge to 20 mg when raw explosive was kneaded directly. The corresponding periods during which nitroglycerine could be detected were estimated to range from about 2 to more than 30 h.

References

[1] Kempe, C. R. and Tannert, W. K., "Detection of Dynamite Residues on the Hands of Bombing Suspects," *Journal of Forensic Sciences,* Vol. 17, No. 2, April 1972, pp. 323-324.

[2] Lloyd, J. B. F., "Detection of Microgram Amounts of Nitroglycerine and Related Compounds," *Journal of the Forensic Science Society,* Vol. 7, No. 4, Oct. 1967, p. 198.

[3] Jenkins, R. and Yallop, J., "The Identification of Explosives in Trace Quantities on Objects near an Explosion," *Explosivstoffe,* Vol. 6, 1970, pp. 139-141.

[4] Parker, R. G, McOwen, J. M., and Cherolis, J. A., "Analysis of Explosives and Explosive Residues. Part 2: Thin Layer Chromatography," *Journal of Forensic Sciences,* Vol. 20, No. 2, April 1975, pp. 254-256.

[5] Williams, A. F., Murray, W. J., and Gibb, B. H., "Determination of Traces of Ethylene-glycol Dinitrate (and Nitroglycerine) in Blood and Urine," *Nature* (London), Vol. 210, No. 5038, 21 May 1966, pp. 816-817.

[6] Cowan, M. E. and Purdon, P. L., "A Study of the 'Paraffin Test,'" *Journal of Forensic Sciences,* Vol. 12, No. 1, Jan. 1967, pp. 19-36.

[7] Sawicki, C. R. and Scaringelli, F. P., "Colorimetric Determination of Nitrate After Hydrazine Reduction to Nitrite," *Microchemical Journal,* Vol. 16, 1971, pp. 657-672.

[8] Twibell, J. D., Home, J. M., Smalldon, K. W., Higgs, D. G., and Hayes, T. M., "Assessment of Solvents for the Recovery of Nitroglycerine from Hands Using Cotton Swabs," *Journal of Forensic Sciences,* Vol. 27, No. 4, Oct. 1982, pp. 792-800.

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