

## TECHNICAL NOTE

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### The Efficient Extraction of Some Common Organic Explosives from Hand Swabs for Analysis by Gas Liquid and Thin-Layer Chromatography

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**ABSTRACT:** A comparison of the relative efficiencies of several established techniques for extracting some common explosives from swabs has been made. Two methods were found to be of a reproducibly high efficiency while a third was much more variable. In an endeavor to reduce the amount of solvent required for extraction, and hence the problems resulting from concentrating the extracts, a new microfilter centrifuge extraction technique was also investigated.

**KEYWORDS:** criminalistics, explosives, extraction, chromatographic analysis

There are several ways of extracting explosives from hand or scene swabs for analysis by thin-layer chromatography (TLC) or gas chromatography with electron capture detection (GC-ECD). Whichever approach is chosen, the aim must be to maximize the recovery of the explosives using a minimum of solvent. Excessive amounts of solvent should be avoided because of: problems resulting from concentrating the sample, impurities present in the solvent, and losses of the more volatile explosives during concentration.

Most of the early work at the Central Research Establishment, Home Office Forensic Science Service used small cotton wool swabs (about 30 mg in weight) which could be easily extracted by dipping, squeezing, and rinsing them in 1 to 2 mL of solvent. Although the recovery efficiency of this technique for nitroglycerine (NG) was better than 90% at the 50-ng level<sup>3</sup> other explosives were not investigated. More recently Douse [1] described ex-

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<sup>3</sup>J. D. Twibell, unpublished work, 1975.

traction of similar sized swabs (40 mg) by washing them repeatedly with small volumes of ether. A total volume of extract of 12 mL was obtained which was then evaporated to less than 10  $\mu$ L. Such a large extraction volume appears to be undesirable: although impurities present in the solvent may be removed in the subsequent cleanup, the recovery of the more volatile species must be reduced considerably.

Since the introduction of the National Hand Test Kit for explosives in January 1980, which is exclusively used in England, Wales, and Scotland (containing gloves, swabs, forceps, ethanol, nail scrapers, instructions, and packaging materials), much larger swabs (300 to 500 mg) have been employed. Hence any recovered explosives will be distributed over about ten times more swab material than before. A much larger volume of solvent would therefore be necessary for efficient extraction by the above methods. An alternative method for extracting the larger swabs was devised at the Birmingham Forensic Science Laboratory several years ago and the procedure is now widely used. A swab is tightly compressed into a drawn down test tube which has a hole in the bottom (similar to a large pasteur pipette) and is then extracted by eluting it with a solvent.

Recently one of us (Lloyd [2]) has developed an extraction and cleanup technique to provide samples for a reverse-phase high performance liquid chromatographic (HPLC) method for explosives analysis using a Pendant Mercury Drop Electrode (PMDE). Although incorporated into the cleanup procedure, the extraction step involves adding 200 to 300  $\mu$ L of an aqueous methanol eluent to a small swab (100 mg approximately) and centrifuging the swab in a microfilter tube. The overall procedure can give virtually complete extraction of 13 organic explosives species, but the extract may be unsuitable for GC-ECD analysis because the eluent contains water. The use of an organic solvent such as ethanol as an alternative would prevent the cleanup stage in Lloyd's method [2] from working. However, if the technique were modified by using small volumes of organic solvents, it might then allow concentrated extracts to be prepared for GC-ECD or TLC analysis. Ideally, a case swab when received for examination should be moist with solvent with the majority of any explosive in solution. In these circumstances the swab could be centrifuged to provide a relatively concentrated sample for analysis. More solvent could be added and the sample centrifuged again if necessary.

A brief study of the efficiency of extraction using the centrifugal microfilter procedure was therefore undertaken and its performance compared with those of three established methods of extraction. For simplicity only the three explosives most likely to be encountered in case-work (NG, trinitrotoluene [TNT], and cyclonite [RDX]) were studied. These species also provided a broad span of volatility, polarity, and solubility. Although it cannot be assumed automatically that a procedure giving efficient extraction of these three compounds will work equally well for all other organic explosives, recent work [2] suggests that this will occur for most.

### Experimental Procedure

Purified samples of NG, TNT, and RDX (Propellants, Explosives and Rocket Motors Establishment, Waltham Abbey, Essex, England) were dissolved (10 mg/mL) in toluene (NG and TNT) or acetone (RDX) and used to prepare analytical standards in ethanol for quantification and for application to swabs. Fresh diluted solutions were prepared at each stage of the work.

Cotton wool, viscose wool (Smith and Nephew Ltd, Welwyn Garden City, England), and Acrilan<sup>®</sup> wool (Home Office Forensic Science Laboratory, Nottingham, England) were used to form swabs of approximately 300 to 500 mg in weight. In the later microfilter experiments, ready-made swabs (Vernaïd Small Cotton Wool Balls, Vernon Carus Ltd, Preston, Lancs, England) were used (370 to 530 mg). Swabs were Soxhlet extracted for several days with ethanol/ethyl acetate (1:1) before use and placed in glass vials (10 mL) with polythene closures (FBG Trident, Temple Cloud, Avon, England) as used in the Explosives Hand Test

Kits. Swabs were then doped with 500  $\mu\text{L}$  of an ethanol solution of the appropriate explosive(s) and stored in the sealed vials for up to eight days. The quantity of ethanol used (500  $\mu\text{L}$ ) was an average value for the amount of solvent retained on a correctly used swab. Applying the explosives in solution ensured that they were uniformly distributed throughout the swab.

#### Extraction Methods

*Constricted Tube Technique*—Test tubes (approximately 12.7 by 1.25 cm) were drawn down to produce extraction tubes as shown in Fig. 1. The “doped” swab was placed in the tube and tightly compressed into the base using a glass rod. (Any solution forced out at this stage was collected and became all or part of the first collected fraction). Initially 250  $\mu\text{L}$  of the appropriate solvent was used for elution and the fractions were collected for analysis. In later experiments 1.5-mL quantities were used.

*“Squeegee” Method*—Ethanol (2.5 mL) was added to the swab in the storage vial and the swab was squeezed and pressed against the inside walls of the vial using forceps. Finally as much liquid as possible was removed by squeezing the swab on the inside of the vial neck. The recovered solvent was transferred to another vessel using a 5-mL glass syringe. Further solvent was then removed from the swab using the syringe while the swab was being squeezed with forceps. This procedure was repeated with another 2.5 mL of solvent to produce a total extract volume of approximately 5 mL.

*Syringe Elution*—The swab was compressed into the base of a 5-mL glass syringe and the plunger pressed down hard to expel any solvent, which was collected. Ethanol (approximately 2.5 mL) was then drawn up into the syringe and forced out through the swab, which was again compressed. This procedure was repeated and the extracts pooled to give a total volume of about 5 mL.

*Centrifugal Microfilter Extraction*—BAS MF1 Microfilters (Bioanalytical Systems Inc., West Lafayette, Ind., USA) were used (Fig. 2) after Soxhlet extraction for two days with a

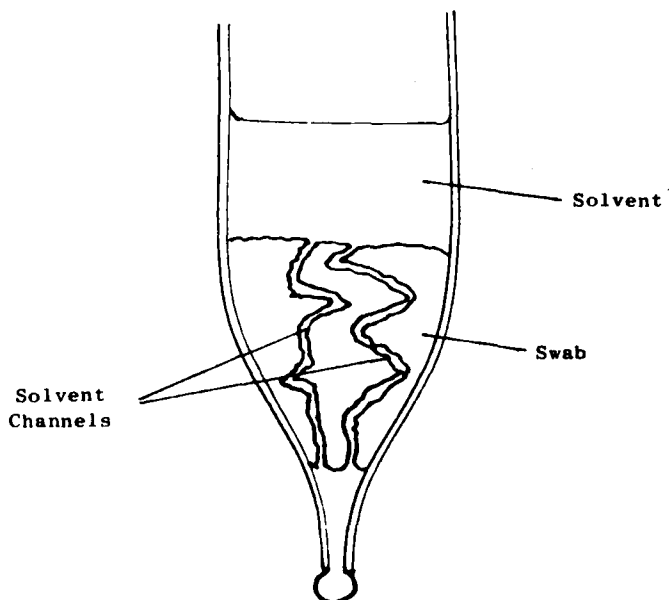


FIG. 1—Constricted tube extraction technique showing (schematic) channelling of eluting solvent resulting from nonuniform packing of the swab.

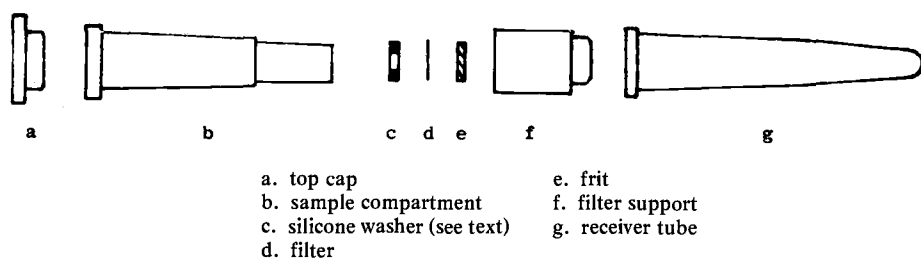


FIG. 2.—Centrifugal microfilter tubes (Anachem Ltd., Luton, England).

mixture of ethanol and ethyl acetate (1 : 1). Because the O-rings normally fitted to the filter produced interferences on GC-ECD analysis even after prolonged extraction, the microfilters were used without them by pressing the sample tubes (60- by 8-mm maximum diameter) very firmly onto the filters in the bases. Each microfilter was assembled as in Fig. 2 (using RC58 regenerated cellulose filters) and the swab was teased out and gently inserted into the sample compartment. The assembly was then centrifuged at 4000 rpm for 5 min in an MSE Superminor centrifuge to remove as much solvent from the swab as possible. This was collected as the first fraction. Two or three subsequent centrifuge fractions were collected after adding further quantities (200  $\mu$ L) of ethanol.

### Analysis

A Pye 104 gas chromatograph with an electron capture detector (10 mCi Ni63) operated at 275°C was used with a short support-coated open-tubular (SCOT) column (13 m) coated with SP2100. Nitrogen was used both as carrier gas (2 mL/min) and makeup gas (45 mL/min). The column was operated isothermally at 140°C for NG and 160°C for TNT and RDX. Splitless injection was used with injection volumes of 0.5 or 1  $\mu$ L. The concentrations of explosives in swab extracts were determined by comparison of peak areas with calibration graphs produced from injected standards. Total recoveries were calculated from these concentrations and accurate measurement of the total extract volume. With concentrations of 300 ng of explosives in 3 mL or more of solvent it was necessary to concentrate extracts, before analysis, to about 1 mL using a water bath at 90°C and a moderate air jet.

### Results and Discussion

In initial extraction tests constricted tubes with ethanol moist swabs which had been doped with NG (500 ng) the previous day were used. The results are shown in Table 1. Irre-

TABLE 1—Extraction of NG (500 ng) from ethanol moist (500- $\mu$ L) swabs (doped previous day) using the constricted tube technique.

Eluent	Experiment No.	Total Elution Volume, $\mu$ L <sup>a</sup>	Recovery of NG, %
Ethanol	1	1330	98
Ethanol	2	1040	54
Acetone	1	1530	62
Acetone	2	1440	55
Ether	1	1350	64
Ether	2	1300	92

<sup>a</sup>Total volume recovered in successive fractions before NG recovery becomes impractical. Includes any solvent expressed from swab on compression.

spective of the solvent used for extraction, between 1 and 1.5 mL was required before further elution of NG became impractical (because of the rapidly decreasing amount recovered in successive fractions). It can be seen also that recoveries varied widely, being typically around 60% and occasionally over 90%.

Similar tests using ethanol moist swabs doped with 500 ng each of TNT and RDX revealed that, although most of the RDX was recovered in the first 1.5 mL, it was necessary to use up to 3 mL to elute the TNT completely. Therefore to ensure elution of all species, a final extract volume of at least 3 mL will be produced, and the recovery efficiency will be somewhat variable.

There are two possible reasons for the highly variable recovery. The extraction technique may be nonreproducible or the explosives may be tenaciously bound to the swab. (The latter explanation is supported by the relative difficulty in eluting TNT). Alternative swabbing materials and extraction methods were therefore investigated. It was decided to use ethanol as extraction solvent in these tests because (a) it is used for swabbing in the Hand Swabbing Kits and (b) the above results indicate that the solvent has little effect on extraction efficiency.

The results in Table 2 show that the material used to prepare the swab had little effect on the efficiency of extraction by the constricted tube technique. As in the earlier results (Table 1) it was found that efficient extraction (over 90%) occurred in less than one third of the tests.

The results from the constricted tube procedure, albeit at slightly lower doping levels, give poorer recoveries than those from other extraction procedures (Table 3). The somewhat poor

TABLE 2—*Recovery of explosives from swabs of differing materials (doped previous day) using the constricted tube technique with ethanol.*

Doping Level	Swab Type	Recovery, %
300-ng TNT	cotton	64
	viscose	100
	Acrilan	45
300-ng RDX	cotton	58
	viscose	60
	Acrilan	61
300-ng NG	cotton	90
	viscose	60
	Acrilan	69

TABLE 3—*Recovery of explosives from swabs (doped previous day) using the "squeegee" (A) and syringe elution (B) techniques using ethanol as solvent.*

Doping Level	Swab Type	Recovery, %	
		A	B
1- $\mu$ g TNT	cotton	85	81
	viscose	99	91
	Acrilan	88	90
1- $\mu$ g RDX	cotton	98	100
	viscose	100	95
	Acrilan	57	65
1- $\mu$ g NG	cotton	86	94
	viscose	82	87
	Acrilan	100	97

result for the recovery of RDX from Acrilan may have resulted from instrumental problems. The variable performance of the constricted tube method undoubtedly results from the difficulty in compressing the swab uniformly into the tube; areas of low resistance are produced through which the solvent channels rather than eluting the whole swab matrix (Fig. 1). This effect was proved conclusively for explosives in the following manner. Ethanol (1.5 mL) was used to elute a swab doped with NG (500 ng), when a recovery of 58% was obtained. The swab was then removed from the tube, turned over, and repacked and recompressed. Subsequent elution with 1 mL of ethanol recovered a further 32% of the explosive, giving a total recovery of 90%.

#### *Centrifugal Microfilter Extraction*

Although efficient extraction can be obtained by correct manipulation of any of the methods already described, the final extract volume will be of the order of 3 to 5 mL. The centrifugal microfilter extraction method used by Lloyd [2] should, however, produce efficient extraction using much less solvent. Tests were therefore carried out with whole swabs, rather than smaller pieces used by Lloyd, to determine whether high extraction efficiency could be achieved with extraction volumes of 1 mL or less.

Preliminary tests of the centrifugal procedure revealed that 350 to 400  $\mu\text{L}$  of ethanol could be recovered from a swab which had been moistened with 500  $\mu\text{L}$  of the solvent. After adding further 200- $\mu\text{L}$  quantities of ethanol and centrifuging, 200  $\mu\text{L} \pm 10\%$  could be recovered. Table 4 shows the mean results of the extractions of four swabs doped at least one day earlier with NG, TNT, and RDX. Although the extraction was not pursued until virtually complete recovery was obtained, it is clear that over 70% of the added explosives can be extracted in about 1 mL of solvent. It is possible therefore to produce an initial extract containing three or four times the concentration of explosives than would be obtainable by conventional extraction techniques. This would then avoid an undesirable concentration stage.

It is interesting to note from Table 4 that most of the extracted explosives are recovered at the first spin, producing an initial extract about ten times more concentrated than that obtainable by conventional extraction. The 30 to 40% of the explosive remaining on the swab could be subsequently extracted if necessary. This presumes that the swab returned in the Explosives Hand Test Kit is in the correct condition (that is, just moist). Experience has shown however that police officers do not shake the swabs sufficiently to remove excess solvent prior to use, so that submitted swabs are frequently heavily loaded with solvent and will produce large volumes of initial extract. In cases where swabs are received in an almost dry condition, a preliminary spin would reveal how much solvent to add before a second spin so that the required total extract volume is obtained.

TABLE 4—Mean recoveries of explosives (500 ng each) in centrifuge fractions from four swabs after storage for at least one day.

Fraction	Mean Volume, $\mu\text{L}$	Mean Recoveries, %		
		NG	TNT	RDX
(a) First spin	420	63	43	64.5
(b) 200- $\mu\text{l}$ EtOH added, respun	219	7	10	14
(c) 200- $\mu\text{l}$ EtOH added, respun	220	0.5	7.5	8.5
(d) 200- $\mu\text{l}$ EtOH added, respun	205	0	7	6
Total	1064	70.5	67.5	93
Concentration factor <sup>a</sup>	...	2.3	1.6	1.8

<sup>a</sup>  $\left( \frac{\text{Concentration in first fraction}}{\text{Concentration in total extract}} \right)$

## Conclusions

The constricted tube extraction technique gives more variable recovery efficiency than other methods because of inconsistencies produced in packing the swab. With correct manipulation however, extraction efficiency comparable with other techniques, is possible.

Centrifugal microfilter extraction is capable of extracting explosives from swabs efficiently and with very much smaller volumes of solvent than are needed with established procedures. An extract some three or four times more concentrated is produced, thereby minimizing concentration before analysis. Modification of the procedure gives less efficient extraction but produces extracts up to ten times more concentrated than those possible from other techniques. More explosives residues can be recovered later if required.

The use of centrifugal microfilters gives extraction volumes less than 1 mL thereby reducing the amounts of solvent impurities which will be concentrated prior to analysis. The technique will therefore diminish losses of the more volatile explosives on evaporation.

## References

- [1] Douse, J. M. F., "Trace Analysis of Explosives in Handswab Extracts using Amberlite XAD-7 Porous Polymer Beads, Silica Capillary Column Gas Chromatography with Electron-Capture Detection and Thin-layer Chromatography," *Journal of Chromatography*, Vol. 234, No. 2, Jan. 1982, pp. 415-425.
- [2] Lloyd, J. B. F., "High Performance Liquid Chromatography of Organic Explosive Components with Electrochemical Detection at a Pendant Mercury Drop Electrode," *Journal of Chromatography*, Vol. 257, No. 2, March 1983, pp. 227-236.

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