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# CLEAN-UP PROCEDURES FOR THE EXAMINATION OF SWABS FOR EXPLOSIVES TRACES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL DETECTION AT A PENDENT MERCURY DROP ELECTRODE

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## SUMMARY

A microfilter extraction assembly containing a mixture of alumina and octadecylsilylsilica is used in the preparation of small volumes of cleaned-up extracts from handswabs for their screening for explosives components by high-performance liquid chromatography at a pendent mercury drop electrode. Apart from the removal of lipids and lipophilic materials likely to degrade chromatographic performance, the adsorbent removes highly polar electroactive compounds, and traps out volatile explosives components when the swabbing solvent is removed. From used handswabs, including grossly soiled swabs, the recovery values of fourteen compounds in the range 1–50 ng per swab are given. Also are presented the results of a survey of 98 handswabs, the majority of which were collected from people occupied in heavy manual work. From these results, the sensitivity limits are on the order of 1–10 ng per used swab, which is subject to variation by the origin of the swab and by the identity of the compound of interest. Examples are given of the application of the technique to people who had handled explosives and a firearm, and to the use of the extraction assembly in a headspace sampling of bomb debris.

## INTRODUCTION

A recently described high-performance liquid chromatography (HPLC) technique, with detection at a pendent mercury drop electrode (PMDE) gave detection limits in the range 7–49 pg for fourteen representative organic explosives components in 20-$\mu$l samples[1]. The technique is amongst the most sensitive now available, and offers particular advantages in its ease of use and its freedom from problems due to the thermal lability of many explosives. To date, the development of the technique has been especially directed to the general screening of samples for a variety of common explosives components. This application to handswabs, which are frequently submitted to forensic science laboratories for an examination for explosives traces, is the main topic of the present paper.

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In a related paper, Bratin *et al.*[2] have described the use of their thin-layer electrode–HPLC technique in the examination, without prior clean-up, of some handswab extracts for firearms discharge traces. Douse[3] has developed a clean-up procedure based on Amberlite XAD-7 resin, which is appropriate to his silica capillary column gas chromatography (GC) electron-capture detector (ECD) technique[4]; Twibell *et al.*[5] for their GC–ECD technique used a thin-layer chromatography clean-up on silica gel; and for their HPLC–ECD work on explosion debris Krull *et al.*[6] also used silica gel. Earlier references are given by these authors. Although no clean-up procedure may be necessary when relatively high amounts of explosives are present, as in the application of Bratin *et al.*[2], for the multi-sample screening of swabs for low nanogram amounts some degree of clean-up is required, not only to remove compounds interfering in the detection of those of interest, but simply as a protection of both the separation and the detection systems against fouling by any materials strongly retained on them. Earlier results in the present research[1] indicated that this is just as true for the thin-layer electrode technique as for the GC techniques referred to; and although the PMDE is relatively unaffected by fouling, because it is instantly renewable, for its effective routine use at high sensitivities sample clean-up is obligatory.

## EXPERIMENTAL

### *Chromatography*

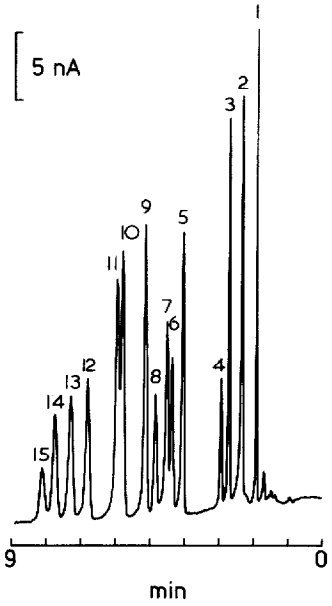
The details have been given before[1], they are summarized here. The separations are made on 150 × 4.5 mm columns of 3-μm ODS-Hypersil, in methanol–aqueous potassium phosphate (100:86, v/v) with a flow-rate of 1.0 ml $min^{-1}$. The aqueous component is 0.025 *M* orthophosphoric acid adjusted to pH 3.0 with potassium carbonate. To eliminate oxygen, the contents of the eluent reservoir are maintained under reflux. When heavily soiled swabs are being processed regularly, the column is purged, *e.g.*, weekly, with methanol followed by ethyl acetate to preserve resolution. Samples are deoxygenated, prior to injection, in a modified syringe[7]. Usually, the injection volumes are 20 μl, but slightly higher resolution is obtained with 10-μl volumes. Detection is at a PMDE normally operated at −1.0 V *vs.* Ag/AgCl.

### *Explosives components*

With the addition of 2,6-dinitrotoluene in some experiments, these are the same as before[1]. The abbreviations used are given in the caption to Fig. 1, which is of a chromatogram of a standard mixture.

### *Processing of handswabs*

*Materials.* Methanol is HPLC grade (Rathburn); the other chemicals are AristaR grade (BDH). BP-quality cotton wool is Soxhlet-extracted in methanol for 8 h. Aqueous potassium phosphate, 0.061 *M*, is prepared by the addition of potassium carbonate to 3.5 g of orthophosphoric acid (86%) dissolved in 500 ml of water to give a pH of 3.0. Sulphamic acid solution (5%, w/v) is prepared (when required for the removal of nitrite) from 0.5 g of the acid dissolved in 5 ml of water, and made up to 10 ml with methanol. This solution is filtered through a 0.2-μm polytetrafluoroethylene membrane. The adsorbent suspension is a mixture of 2.5 g of Spherisorb ODS-silica,



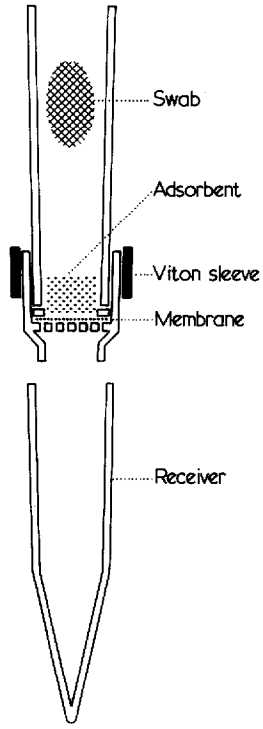




Fig. 1. Chromatogram of standard compounds (0.5 ng each in 10 $\mu$l) run on 150 × 4.5 mm ODS-Hypersil, 3 $\mu$m, in deoxygenated methanol–aqueous potassium phosphate (0.025 *M*, pH 3.0) (100:86, v/v) at 1 ml $min^{-1}$, with detection at a PMDE (−1.0 V *vs.* Ag/AgCl). The compounds are: 1 = octogen (HMX); 2 = picric acid (PA); 3 = hexogen (RDX); 4 = ethyleneglycol dinitrate (EGDN); 5 = 1,3-dinitrobenzene (DNB); 6 = tetryl (TET); 7 = nitrobenzene (NB); 8 = nitroglycerine (NG); 9 = 2,4,6-trinitrotoluene (TNT); 10 = 2,6-dinitrotoluene (26DNT); 11 = 2,4-dinitrotoluene (24DNT); 12 = 2-nitrotoluene (2NT); 13 = 4-nitrotoluene (4NT); 14 = 3-nitrotoluene; (3NT); 15 = pentaerythritol tetranitrate (PETN).

Fig. 2. Cross-sectional diagram of a centrifugal microfilter (Bioanalytical Systems) prepared for use as a clean-up extraction assembly.

10 $\mu$m, and 2.5 g of Spherisorb alumina, 10 $\mu$m (Phase Separations), in 50 ml of ethanol. A glass-sleeved magnetic stirrer bar is kept in the mixture's storage vessel.

*Extraction assemblies.* These are made from centrifugal microfilters (Bioanalytical Systems). Prior to its use, each dismantled filter is soaked overnight in methanol containing 2% (w/v) sodium hydroxide, 0.2% ethylenediaminetetraacetic acid and 0.2% thiourea. Explosives components in particular are rapidly degraded by the mixture (the thiourea acts as a source of sulphide); even so, microfilters that have come into contact with explosives are not used subsequently for trace analysis. After they have been rinsed in water, methanol and dried (50°C), each microfilter is fitted with a 0.2-$\mu$m cellulose membrane, and assembled with a piece of Viton sleeving (Soxhlet-extracted in methanol) pushed over the membrane holder (see Fig. 2) to enable the holder itself later to be sleeved by an inlet of a vacuum manifold.

To each assembled microfilter is added 1 ml of the adsorbent suspension, transferred by means of a wide-bore dropping pipette from the vigorously stirred

mixture. The adsorbent is then centrifuged down at 1850 *g* onto the filter membrane. The assemblies are stored in a sealed container, in the absence of ethanol, until they are required for use, when they are washed through at the centrifuge with 1 ml of ethanol. Fig. 2 shows the completed assembly.

*Clean-up procedure.* The following is used for swabs consisting of 90–110 mg of cotton wool and *ca.* 200 µl of ethanol. This volume of solvent is left after a swab holding 500 µl has been rubbed thoroughly over a hand.

A swab is inserted loosely into the top of a prepared microfilter assembly, from which the receiving tube has been removed. The assembly is attached to a vacuum manifold so that a stream of air can be sucked through the swab and then through the adsorbent. A silica desiccant trap (made from a 5-ml glass hypodermic syringe, the cone of which is pushed through a hole made in a microfilter cap) is attached to the entrance of the filter. With an air flow of 75 ml $min^{-1}$, once the bulk of the ethanol has evaporated from the adsorbent, the solvent is removed completely (mass loss less than 1 mg $min^{-1}$) within 30 min at an ambient temperature of about 20°C.

The outlet tip of the microfilter is washed with acetone, shaken dry and fitted with a tared receiver tube. The swab is packed down tightly onto the adsorbent bed, treated with 250 µl of methanol–water (100:35, v/v) and centrifuged for 5 min at 460 *g* and then at 1850 *g* for 10 min. The volume collected, *ca.* 160 µl, is calculated from the mass collected on the assumption that the eluate's density is 0.86 g $ml^{-1}$. For chromatography, a 0.37-volume ratio of the aqueous 0.061 *M* phosphate is added either to the whole of the eluate, or to an aliquot when the presence of phosphate could interfere in other work on the eluate. If nitrite is to be removed (see below), 1 µl of the sulphamic acid solution is added per 20 µl of the diluted eluate.

For swabs of the stated composition, from which the results described here were obtained, the drying time and the volume of the collected eluate are sufficiently reproducible that it is unnecessary to weigh the microfilter and the receiver tube. This is necessary, however, in the examination of swabs collected under unstandardized conditions. In some cases solvent exudes when an over-wet swab is inserted in the microfilter. This surplus may be removed and put aside, as sufficient remains on the swab for analysis. Alternatively, the surplus is returned to the swab after the initial drying. When over-wet swabs are being dealt with, the extraction assembly is inverted during the evacuation in order to avoid any drainage of the solvent onto the adsorbent. As the dried adsorbent is loose, the assembly is set upright before the vacuum is turned off. Up to 250 mg cotton wool swab may be handled by the technique, with a proportionate increase in the volume of eluent. Aliquots are taken of larger swabs.

*Recovery experiments*

These are made with DNB as an internal standard. Known amounts of explosives components in ethanol or aqueous methanol are distributed with a syringe throughout the swab, and the swab is then processed. To the extract is added DNB in an amount comparable to the explosives components, and the recoveries are calculated from peak heights with reference to standards in the usual way.

## RESULTS AND DISCUSSION

### *Factors relevant to the swabbing solvent*

For much of the present work a relatively large injection volume, for 3-$\mu$m column packings, of 20 $\mu$l was adopted as a compromise between the requirements of resolution and sensitivity. (With reference to a 10-$\mu$l injection, as in Fig. 1, the increases in peak width and the inverse variation in peak height of a constant amount of HMX in 20- and 50-$\mu$l injections are 1.14 and 1.47, respectively.) Because of this it is important that the injection solvent must closely match the chromatography eluent in composition, otherwise disastrously distorted chromatograms are obtained. If the composition of the injection solvent is to be readily and accurately controlled, a clean-up technique must include a step in which the swabbing solvent is removed. The chromatography eluent or one of its components cannot be used as a swabbing solvent unless it is then removed, because its composition is changed uncontrollably by the effects of evaporation and by the accumulation of moisture from sweat. Neither are dry swabs practicable. Although they efficiently remove explosives from skin surfaces[8], presumably by attrition of lipid material in which the explosives may dissolve[2], the presence of a solvent is necessary to inhibit the loss of volatile compounds from the swab between the times of its use and extraction[9].

At present, ethanol is a frequently used swabbing solvent, mainly because the amounts of compounds extracted that interfere in the commonly used GC–ECD techniques are relatively low[9]. Although it does not follow that this is the case for the HPLC–PMDE technique, the present work has been conducted with ethanol-containing swabs because in the short term, at least, it is likely that they will remain in common use. However, the clean-up technique has been designed to deal with any solvent that is appreciably volatile at ambient temperatures.

### *Clean-up adsorbent*

There are three important functions performed by the mixed adsorbent (alumina plus ODS-silica) in the extraction assemblies. The first is the removal of lipids and strongly lipophilic materials, such as mineral oil, that otherwise either are thrown out of solution when the aqueous phosphate is added to the microfilter eluate, or are strongly retained on the chromatography column and degrade its performance. These materials are retained on the ODS-silica.

The second function is the removal of the large amounts of the highly polar reducible species present in some handswabs, which give rise to an intense broad peak that obscures the early part of the chromatogram, and leaves behind a disrupted baseline. An illustration is given in Fig. 3, which compares chromatograms from a pair of left and right handswabs that had been intermixed and divided. One part (A) was dried, then extracted directly with the chromatography eluant. The other (B) was cleaned-up as described. The effective adsorbent here is the alumina. Less satisfactory adsorbents examined were a cation-chelating resin. Florisil and silica.

Thirdly, the adsorbent traps out any explosives components that volatilize during the solvent removal stage, particularly if the time-to-dryness is exceeded. This is shown in Table I, where the quantities recovered separately from the adsorbent and from two unused swabs are compared after 30 ng of each compound had been added to the swabs before the solvent was removed. At 29 min the swabs had almost reached

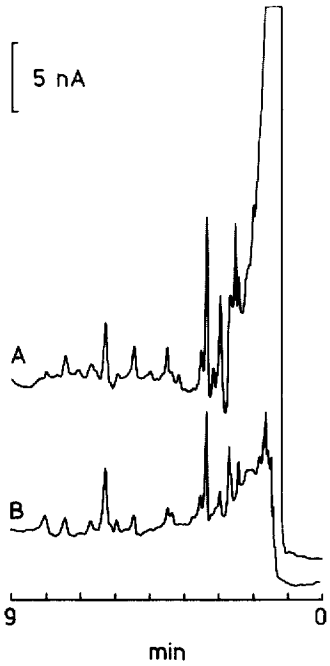



Fig. 3. Example of the effect of the clean-up procedure on handswab extracts. Sample A is from half of a bulked pair of handswabs which was extracted directly; B is an extract from the other half made by the described clean-up procedure. The chromatography conditions are as in Fig. 1.

dryness, but some transfer to the adsorbent was already occurring. On further pumping for a similar period, up to 5 ng amounts of the more volatile components were transferred, which otherwise would have been lost. Other experiments indicated that on a proportionate basis this potential loss increases as the amounts of the compounds decrease. With the prolonged pumping time in the given example, evidently some break-through occurred, *e.g.*, 7 ng of NB were lost. The retentivity of the adsorbent mixture can be increased by the use of a more heavily silylated silica, but the advantage gained in this respect is offset by the increased difficulty with which PETN can be subsequently eluted.

The possible use of proprietary clean-up cartridges was examined; but because of the amounts of adsorbent they contain, and its large particle size, they are unsuitable for the recovery of samples into small volumes of solvent unless an evaporative concentration step is introduced, with consequent loss of volatile compounds: *e.g.*, when the volume of a methanol–water (100:20, v/v) solution from a cartridge was reduced to 1/3rd in a stream of nitrogen at ambient temperature, the losses of NB and EGDN were 38% and 20% respectively. A 1/5th reduction gave the respective losses of 50% and 86%. No losses due to sorption of the compounds in the plastics composing the microfilters have been encountered, in contrast to the losses reported for some organomercury compounds[10].

The microfilter clean-up technique is readily adapted for other adsorbents that are more selective for individual classes of compound, although such adsorbents are unsuitable for the comprehensive detection of all of the compounds of interest. Ex-

TABLE I

RECOVERY OF EXPLOSIVES COMPONENTS FROM UNUSED SWABS AND THE ADSORBENT AFTER SOLVENT REMOVAL IN AN EXTRACTION ASSEMBLY

The swabs contained 250 μl of ethanol and 30 ng of each compound initially.

| *Compound** | *Recoveries (ng)* | | | |
|---|---|---|---|---|
| | *Drying time 29 min* | | *Drying time 59 min* | |
| | *Swab* | *Adsorbent* | *Swab* | *Adsorbent* |
| HMX | 31 | nd** | 29 | nd |
| PA | 25 | nd | 24 | nd |
| RDX | 30 | nd | 29 | nd |
| EGDN | 28 | nd | 22 | 4.2 |
| TET | 28 | nd | 26 | nd |
| NB | 28 | 0.63 | 18 | 4.8 |
| NG | 29 | nd | 27 | 1.3 |
| TNT | 29 | nd | 27 | 0.15 |
| 26DNT | 29 | nd | 25 | 2.2 |
| 24DNT | 28 | nd | 26 | 1.4 |
| 2NT | 27 | 0.33 | 20 | 5.4 |
| 4NT | 26 | 0.48 | 22 | 4.2 |
| 3NT | 31 | 0.24 | 21 | 5.1 |
| PETN | 28 | nd | 29 | nd |

* Full names are given in the caption to Fig. 1.
** nd = None detected.

periments were made with Amberlite XAD-7 in a modified form of Douse's technique[3], with results in general agreement with his except that NB was recovered, probably because of the improved measures that can be taken to avoid the loss of volatile compounds. Selective and generally higher recoveries were obtained with LiChrosorb-$NH_2$. However, both techniques involved extra steps, because the adsorbent was additionally extracted with isopentane, and gave poor recoveries for some compounds. Where specific compounds are sought though, such adaptations could be important, and applied to the products of an initial non-selective clean-up.

*Interferences not removed in the extraction assembly*

Substantial amounts of nitrite were found in swabs taken from two lathe operators. Presumably, the nitrite was from an anticorrosion additive in cutting fluid. As Fig. 4 shows, an intense, distinctively shaped peak is produced, which is readily removed by the treatment with sulphamic acid. Because nitrite could be of significance in an explosives investigation, and because of its infrequent occurrence in amounts likely to prove a nuisance, the extracts are not routinely treated with sulphamic acid. It should be noted that apart from its reaction with nitrite, the sulphamic acid is added in amount sufficient to reduce the pH of the extract to the point where the reaction rapidly occurs. Chromatographic resolution and recoveries are unaffected.

A high level of calcium was present on two occasions in handswabs from

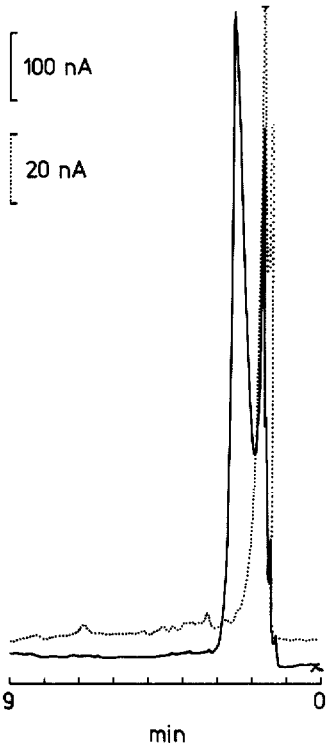



Fig. 4. Chromatograms of a handswab sample from a lathe operator, before (full line) and after (dotted line) the extract had been treated with sulphamic acid.

bricklayers, and precipitated as phosphate when the extracts were diluted. This was readily removed at the centrifuge. The effect was obvious and caused no particular difficulty, but as a precaution against column blockage a filter was subsequently installed between the injector and the column.

*Quantitative recovery experiments*

The variation of recovery, with a constant volume of varied eluent, of 10-ng amounts of explosives components from typical used swabs processed as described under Experimental is shown in Table II. For most of the compounds there is slight variation in recovery as the water–methanol ratio is increased to 35:100 (v/v). Beyond this, recoveries decrease considerably for the compounds more strongly adsorbed on ODS-silica. This could be countered by an increase in volume of the eluent, but with poorer detection limits because of the resulting dilution of the eluate. From heavily soiled handswabs, lipid-type materials are eluted when the solvent ratio is reduced below 35:100, hence this composition is adopted for general use. In the present instance the average recovery is 90%.

The presence of large amounts of lipid and mineral oil on a swab do to some extent retard the elution, but the effect is fairly small. Recovery data from some exceptionally soiled handswabs are given in Table III. These, which were collected from five garage mechanics, contained large quantities of mineral oil and other

TABLE II

COMPOSITION OF CLEAN-UP ELUENT: RECOVERIES OF EXPLOSIVES COMPONENTS FROM USED HANDSWABS

The amount of each compound was 10 ng; the volume of eluent, 250 μl.

| *Compound* | *Recoveries (%)* | | | |
|---|---|---|---|---|
| | *Volumes of water per 100 volumes of methanol* | | | |
| | *25* | *35* | *45* | *55* |
| HMX | 85 | 88 | 81 | 82 |
| PA | 75 | 88 | 70 | 80 |
| RDX | 94 | 96 | 86 | 82 |
| EGDN | 94 | 103 | 90 | 86 |
| TET | 74 | 78 | 64 | 55 |
| NB | 92 | 95 | 79 | 68 |
| NG | 99 | 97 | 87 | 73 |
| TNT | 83 | 86 | 68 | 54 |
| 24DNT | 83 | 88 | 65 | 43 |
| 2NT | 90 | 93 | 72 | 51 |
| 4NT | 84 | 90 | 64 | 41 |
| 3NT | 85 | 89 | 65 | 37 |
| PETN | 90 | 84 | 70 | 47 |
| Mean | 86.8 | 90.4 | 73.9 | 61.5 |

TABLE III

RECOVERIES OF 50-ng AMOUNTS OF EXPLOSIVES COMPOUNDS FROM FIVE HEAVILY SOILED GARAGE MECHANICS HANDSWABS: EFFECT OF ELUTION VOLUME DURING CLEAN-UP

| *Compound* | *Recoveries (%)* | | | |
|---|---|---|---|---|
| | *Elution volume, 250 μl* | | *Elution volume, 450 μl* | |
| | *Mean* | *Range* | *Mean* | *Range* |
| HMX | 64 | 41–80 | 85 | 68–99 |
| PA | 66 | 38–88 | 93 | 88–96 |
| RDX | 76 | 49–95 | 92 | 85–98 |
| EGDN | 91 | 84–102 | 98 | 87–105 |
| TET | 73 | 45–89 | 84 | 75–91 |
| NB | 80 | 71–86 | 88 | 86–90 |
| NG | 79 | 56–94 | 93 | 89–98 |
| TNT | 68 | 44–87 | 84 | 73–91 |
| 24DNT | 62 | 37–86 | 80 | 58–93 |
| 2NT | 75 | 65–90 | 85 | 73–96 |
| 4NT | 67 | 53–84 | 80 | 66–87 |
| 3NT | 72 | 63–86 | 86 | 78–90 |
| PETN | 72 | 45–91 | 87 | 79–96 |

TABLE IV

RECOVERIES OF 10-ng AMOUNTS OF EXPLOSIVES COMPOUNDS FROM FIVE HEAVILY SOILED GARAGE MECHANICS HANDSWABS

The extraction assembly was eluted with 250 $\mu$l in each case.

| *Compound* | *Recovery (%)* | |
|---|---|---|
| | *Mean* | *Range* |
| HMX | 73 | 62–78 |
| PA | 80 | 68–88 |
| RDX | 90 | 82–94 |
| EGDN | 86 | 76–97 |
| TET | 68 | 44–82 |
| NB | 65 | 44–84 |
| NG | 80* | 78–89 |
| TNT | 70 | 39–82 |
| 24DNT | 64 | 34–80 |
| 2NT | 71 | 62–80 |
| 4NT | 77* | 72–82 |
| 3NT | 79 | 51–93 |
| PETN | 72 | 60–81 |

* Only four results, the peak in the other samples was obscured.

debris, and were far more soiled than any that have been encountered in case work in this laboratory. The swabs were spiked with 50-ng amounts of the compounds, and yielded the results shown for 250-$\mu$l and 450-$\mu$l elution volumes. On average the increase in recovery due to the larger volume of eluent is from 73% to 87%. Even for the poorest single recovery in the smaller elution volume (24DNT, 37%), which is remedied in the larger one (81% in this particular sample), the increase in concentration of the compound in the approximately doubled volume of eluate is negligible. However, if a high recovery must be assured the larger elution volume is used with this type of sample. Alternatively, a second elution of the extraction assembly is made if a positive result is given by a first 250-$\mu$l elution.

Further recovery data from five other garage mechanics' handswabs spiked with 10-ng quantities are given in Table IV, and data from a set of swabs taken to represent a more usual level of soiling and spiked with 1-ng quantities are given in Table V. The latter data are in the region of the sensitivity limits, given swabs of this type, as discussed later. Above this level, the average recovery under the standard conditions from Tables II–IV is 75.8%. The associated variation, which also is a function of the soiling present on the swab, on average is $\pm 15\%$. This, from the results in Table III, is reduced to $\pm 8.5\%$ by an increased elution volume.

*Detection limits and interferences on handswabs*

As the sensitivity of detection is increased, explosives-free handswabs increasingly yield a number of chromatographic peaks that sometimes appear at positions corresponding to explosives components, or, if they are not coincident, overlap these positions. Consequently, minor amounts of explosives components may be obscured. An extensive quantitative variation in such peaks occurs between handswabs, al-

TABLE V

RECOVERIES OF 1-ng AMOUNTS OF EXPLOSIVES COMPOUNDS FROM FIVE MODERATELY-SOILED HANDSWABS

The extraction assembly was eluted with 250 μl in each case.

| *Compound* | *Recovery (%)* | | *No. of results** |
|---|---|---|---|
| | *Mean* | *Range* | |
| HMX | | | 0 |
| PA | 79 | 74–84 | 2 |
| RDX | 84 | 62–98 | 4 |
| EGDN | 80 | 71–90 | 2 |
| TET | 38 | | 1 |
| NB | 69 | 54–79 | 3 |
| NG | 78 | 73–84 | 3 |
| TNT | 70 | 51–89 | 5 |
| 26DNT | 71 | 70–73 | 2 |
| 24DNT | 52 | 48–57 | 2 |
| 2NT | 76 | 57–95 | 2 |
| 4NT | | | 0 |
| 3NT | | | 0 |
| PETN | | | 0 |

* Successful analyses could be made only in a restricted number of cases. In others the peaks were obscured.

though the qualitative variation is inconsiderable: some peaks are common to many samples but vary widely in amplitude. For example, the strong peaks shown in Fig. 3 at 3.4 and 6.3 min are particularly common and normally the most intense apart from the unretained peak. They are not, however, coincident with explosives components, but usefully indicate the level of interference to be expected in other parts of the chromatograms. The amounts of explosives that can be seen against this type of background is indicated by the results in Tables IV and V. With the heavily soiled garage mechanics' handswabs (Table IV), 10-ng additions of NG and 4NT to the whole swabs were obscured in one out of the five swabs used. In the other set of less-soiled swabs (Table V) 1-ng additions could not be determined in many instances.

Further examples are given in Figs. 5 and 6. Fig. 5 shows chromatograms from explosives-free handswabs exhibiting the most intense peaks encountered in this work. Superimposed (dotted line) is a chromatogram representing 1-ng amounts of the standard compounds, which is equivalent to the contribution expected from the complete recovery from the swabs of 11 ng of each compound. Fig. 6 is an example from a more characteristically soiled swab with a superimposed contribution expected from 1 ng of each explosives compound per swab.

These examples are taken from the examination of a collection of 98 different swabs. Of these, 25 were from members of the general public; the remainder were from groups of people occupied largely in manual work, the majority of whose swabs were extensively soiled. Of the latter, 12 were collected from garage mechanics, 8 at a steel fabrication plant, 14 at a light engineering works, 22 at a building site, 15 at a rail terminal and 2 from laboratory staff. One swab from each person, generally from the

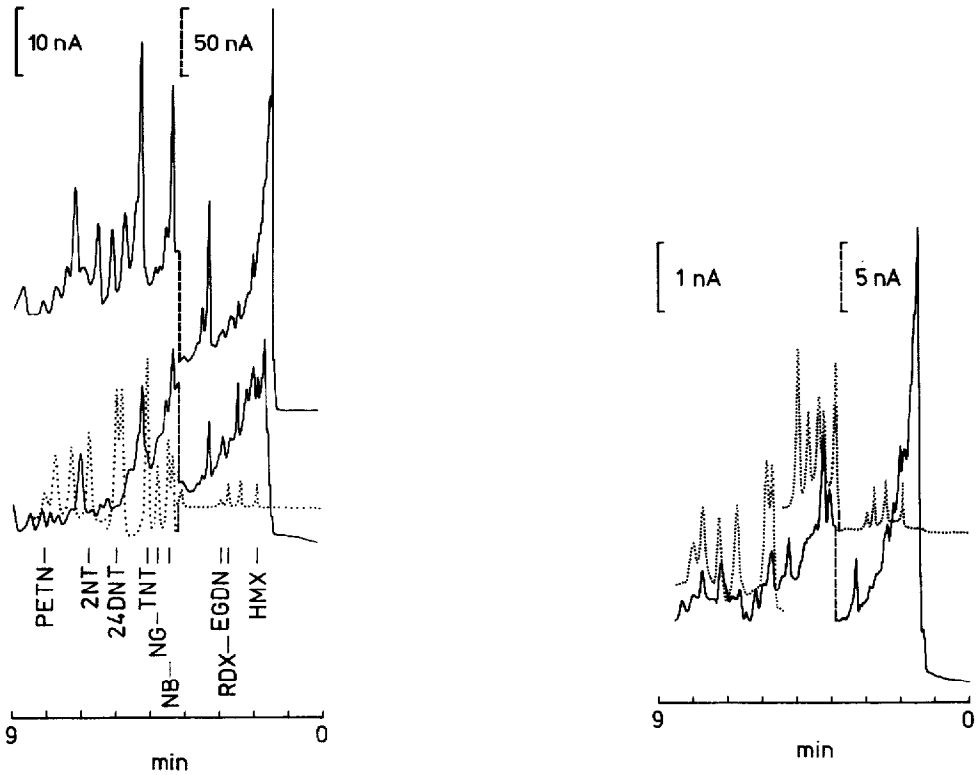



Fig. 5. Chromatograms from two heavily soiled, explosives-free handswabs (full lines), and 1 ng of each of the standard compounds (dotted line), of which some of the more important are labelled. The abbreviations are identified in the caption to Fig. 1. The chromatography conditions are as in Fig. 1, except the injection volume is 20 $\mu$l.

Fig. 6. Chromatogram from a typically soiled, explosives-free handswab (full line) with a superimposed chromatogram of 91-pg amounts of the standards, equivalent to 1-ng amounts in the swab. The chromatography conditions are as before, with an injection volume of 20 $\mu$l.

right hand, was examined for the presence of chromatographic peaks coincident with the explosives components run consecutively to each swab sample. Coincidence was taken to be an agreement in retention times of within 1 % (the maximum variation in retention time detectable between any pair of compounds in ten consecutive standard chromatograms was 0.6 %). The results expressed in terms of the number of swabs giving a response within different concentration ranges (on the assumption that losses during recovery were insignificant in the context of the ranges used) are summarized in Table VI. From these results it is apparent that for most of the compounds there is usually little interference at levels above 1 ng per swab. Major exceptions commonly seen in the 1–10 ng interference range are at the 3NT position, which is unimportant because this compound only occurs as an explosives trace as a minor component of the nitrotoluenes mixture, and at the TET position, which compound is of rare occurrence. Lesser exceptions are RDX and PETN. The RDX coincidence typically occurs in heavily soiled swabs, the other is more generally distributed but readily

TABLE VI

INTERFERENCE PEAKS IN A COLLECTION OF 98 USED HANDSWABS

Any interfering peak is allotted to the concentration range of the corresponding explosives component.

| *Compound* | *Number of swabs in the indicated range* | | |
|---|---|---|---|
| | *Less than 1 ng per swab* | *Between 1 and 10 ng per swab* | *Greater than 10 ng per swab* |
| HMX | 93 | 5 | 0 |
| PA | 95 | 2 | 1 |
| RDX | 86 | 12 | 0 |
| EGDN | 95 | 2 | 1 |
| DNB | 98 | 0 | 0 |
| TET | 70 | 20 | 8 |
| NB | 95 | 3 | 0 |
| NG | 95 | 3 | 0 |
| TNT | 97 | 1 | 0 |
| 26DNT | 97 | 1 | 0 |
| 24DNT | 94 | 3 | 1 |
| 2NT | 95 | 3 | 0 |
| 4NT | 92 | 6 | 0 |
| 3NT | 41 | 53 | 4 |
| PETN | 88 | 8 | 2 |

distinguished from PETN voltammetrically (see below). In general, from the data given in Tables II–VI, the sensitivity limits of the present technique applied to used handswabs are on the order of 1–10 ng per 100-mg swab.

*Voltammetric selectivity*

The chemical identities of the interference peaks are at present unknown, but in

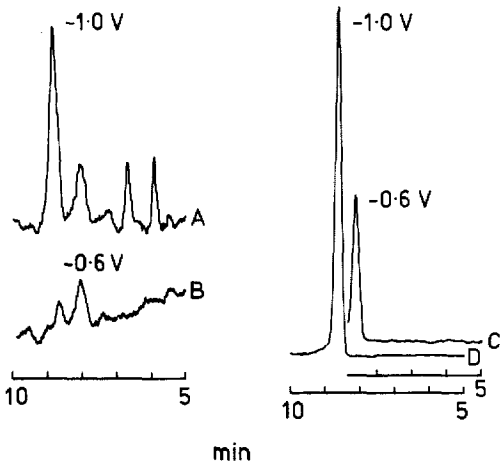



Fig. 7. Sections of the PETN region of chromatograms of a handswab extract (A and B) and a PETN standard (C and D) with the PMDE potential set at −1.0 V (A and D) and −0.6 V (B and C) *vs.* Ag/AgCl. The same sensitivity setting was used for both chromatograms of each sample. Other chromatography conditions are as in Fig. 1.

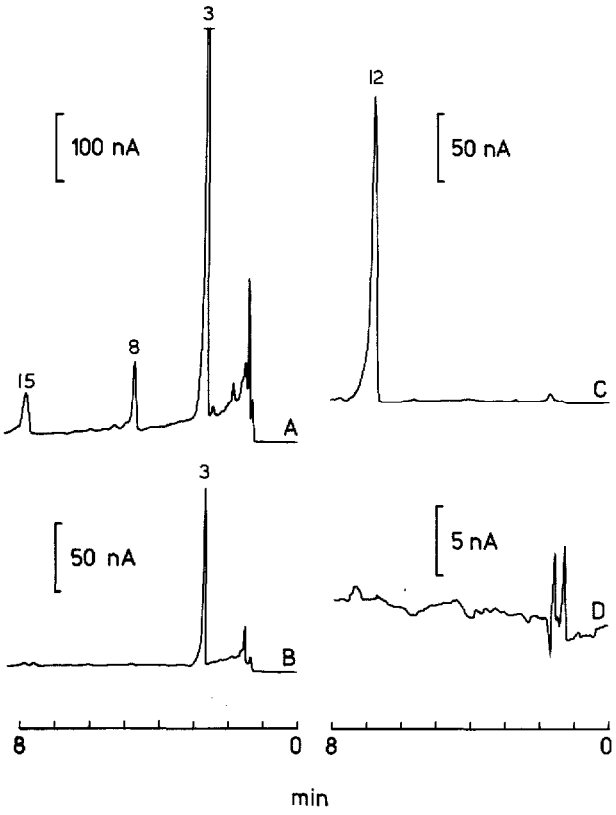



Fig. 8. Chromatograms of various samples: (A) handswab collected after a brief handling of explosives 3 h before sampling, and an unknown number of hand washes in the interim; (B) a swab collected from a beer glass used by a person who had handled an RDX-based explosive 2.5 h before sampling, and had subsequently washed his hands; (C) an extract from an extraction assembly used to vapour-sample the debris remaining after the explosion, 1 day previously, of a device containing 2NT; (D) a blank handswab. The peaks are labelled as in Fig. 1. The chromatography conditions are as in Fig. 1, with 20-$\mu$l injection volumes.

some cases, at least, it is possible to distinguish the peaks from explosives components voltammetrically, if not by modified chromatography conditions. Thus, PETN is readily distinguished when the potential of the PMDE is raised to $-0.6$ V. An example is shown in Fig. 7. For the handswab material (chromatograms A and B) the reduction in the response of the peak at the PETN position is by a factor of 0.12 when the potential is changed from $-1.0$ to $-0.6$ V, whereas for PETN (C and D) the factor is 0.41. As the coefficients of variation of the peaks are in the region of 3%[1], PETN and the handswab compound are completely differentiated.

*Examples of various applications*

In Fig. 8, chromatogram A shows the result from a handswab of a person who had briefly handled wrapped sticks of two explosives and some Cordtex detonating fuse 3 h before the sample was taken, during which time the hands had been washed at least once. The numbered peaks correspond to RDX (289 ng per swab), NG (108

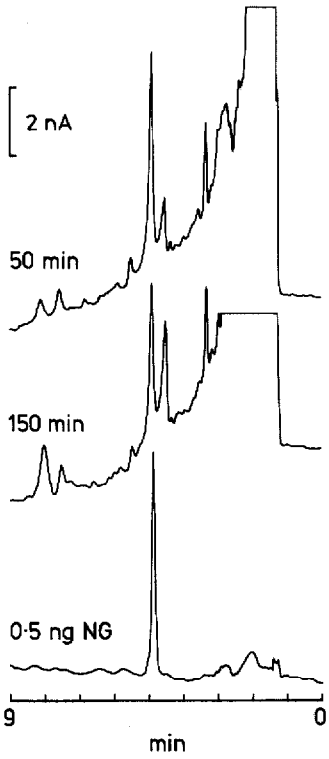



Fig. 9. Handswab chromatograms from two experiments in each of which two shots were fired from a Smith and Wesson Model 10, .38 Special revolver before the indicated sampling times. From each extract 10 μl were injected representing *ca.* 5% of the material on the swabs. The chromatography conditions are as in Fig. 1.

ng per swab) and PETN (141 ng per swab), which are the major components of each of the explosives. The NG-containing explosive also contained EGDN, which is probably responsible for the weak shoulder present in the tail of the intense RDX peak. Chromatogram B is from a swabbed drinking glass used by a person who had handled an RDX-based explosive 2.5 h previously, and subsequently washed his hands: the peak corresponds to 28 ng per swab of RDX. Chromatogram C is of the eluate from an extraction assembly through which the headspace over the debris from a device containing 2NT, exploded 24 h earlier, had been sampled. This was done at ambient temperature for 20 min with the outlet of the extraction assembly attached to a filter pump whilst the inlet collected the headspace within the Polythene bag containing the debris. A twenty-fold dilution of the eluate was necessary to obtain the 2NT peak in the chromatogram. A direct solvent extraction of the debris gave a similar peak, but with much higher levels of background. A result from a blank swab is shown at D.

Fig. 9 shows the chromatograms from handswabs taken 50 and 150 min after two rounds on each occasion had been discharged in a Smith and Wesson Model 10, .38 Special revolver. The NG peaks seen, from injections representing 5% of the recovered material, correspond to 9.1 and 5.8 ng per swab, respectively. Two other

experiments yielded *ca.* 1 ng per swab of NG. This amount of potentially available explosive is well within the sensitivity range of the chromatography system, but a satisfactory characterization requires clean-up techniques more specific than the relatively non-selective one presented here.

## CONCLUSIONS

Other recently reported results for the detection of explosives traces in hand-swabs include GC–ECD techniques giving limits of 0.5 ng per swab[5] and 10 ng per swab[3] for NG, and 10–50 ng per swab for six other compounds[3]. GC–mass spectrometry, for NG, gives 2 ng per swab[5]. The earlier introduced thin-layer chromatography for NG[11] gives, with sample clean-up, 5 ng per swab[5] and 20 ng per swab[3]. Because of the variations in the samples used, in the specificity of the techniques, and in the criteria applied in the assessment of these results, close comparison cannot be made between them and the limits in the region of 1–10 ng per swab obtained with the present technique. Even so, the conclusion seems to be justified that for all of the compounds examined the HPLC–PMDE technique is amongst the most sensitive that have been developed to date. The technique is not subject to operating difficulties analogous to those characteristic of GC–ECD techniques, *e.g.*, detector fouling cannot occur because the detector electrode is replaceable for or during each chromatogram; the only routine maintenance work required is the periodic solvent-purge of the column; and the technique is robust to the multiple analysis of contaminated samples.

Although the clean-up technique has been designed as a general-purpose screening technique for use with HPLC–PMDE, it could be readily modified to suit other detection systems, or to vary its selectivity, by means of other adsorbents and solvents. Probably, slight modification will be needed for its use in the recovery of inorganic explosives components and of nitrocellulose.

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