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TRACE ANALYSIS OF EXPLOSIVES AT THE LOW NANOGRAM LEVEL IN HANDSWAB EXTRACTS USING COLUMNS OF AMBERLITE XAD-7 POROUS POLYMER BEADS AND SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH THERMAL ENERGY ANALYSIS AND ELECTRON-CAPTURE DETECTION

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SUMMARY

Thermal energy analysis (TEA) was compared with electron-capture detection (ECD) for the analysis of explosives both as pure compounds and in spiked handswabs by silica capillary column gas chromatography. TEA was shown to approach the sensitivity of ECD but was more selective, enabling low nanogram levels of explosives in handswabs to be detected. Use of TEA in the nitrogen mode for drug analysis was also briefly studied.

INTRODUCTION

The trace analysis of low nanogram levels of explosives in heavily contaminated extracts from handswabs and post explosion debris is important in forensic science[1–3]. Gas chromatography (GC) is suitable for this type of analysis because the sensitivity of the method is high and the equipment is easy to operate and maintain in the long term.

Electron capture detection (ECD) is the most widely used GC detection method for explosives analysis because of its excellent sensitivity[1]. It was found, however, to be insufficiently selective to allow the detection of less than 10–50 ng of explosive per handswab since interfering coextractives are present even after a clean-up procedure[1].

Thermal energy analysis (TEA) is a promising detection method for explosives with detection limits for pure compounds approaching those of ECD[4–6], but with a greatly enhanced selectivity as demonstrated by the analysis of nitroaromatics in biosludge[7].

Previous application of TEA to the analysis of explosives in handswabs was limited to the study of relatively high levels and offered no comparison with other GC modes of detection[5,6].

The present study compares TEA and ECD for the trace analysis of explosives at the low nanogram level in handswabs. Small columns of Amberlite XAD-7 porous

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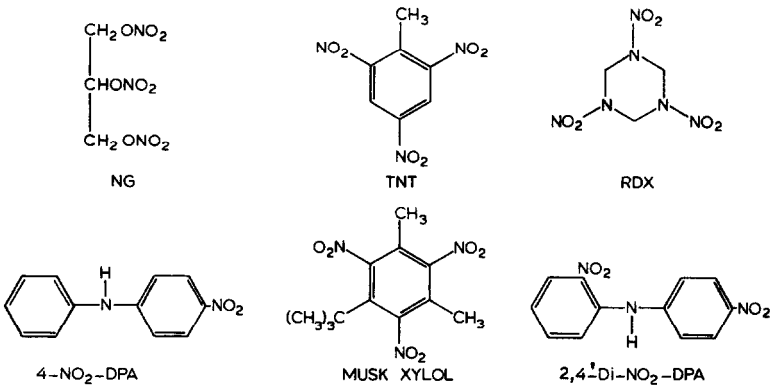


Fig. 1. Examples of explosives, polynitrodiphenylamines and a nitromusk of forensic interest.

polymer beads were used to clean up the extracts and provided improvements over the technique previously used[1]. The analysis of a wide range of explosives, three polynitrodiphenylamines (minor components of propellants[8]) and two nitromusks (potential interferences found in cosmetic products[9]) is described. Examples are given in Fig. 1. A brief study of the trace analysis of drugs using TEA in the nitrogen specific mode is also presented.

EXPERIMENTAL

Reagents

The explosives studied were: ethylene glycol dinitrate (EGDN), nitroglycerine (NG), butane-1,2,4-triol trinitrate (BTT), 2,4,6-trinitrotoluene (TNT), RDX and Tetryl (PERME, Waltham Abbey, U.K.), nitrobenzene (NB) (Aldrich, Gillingham, U.K.), trinitrobenzene (TNB) (BDH, Poole, U.K.), and 2,4-dinitrotoluene (2,4-DNT) (Fluka, Glossop, U.K.).

The polynitrodiphenylamines studied were: 2-nitrodiphenylamine (2-NO_2-DPA), 4-nitrodiphenylamine (4-NO_2-DPA) (Aldrich), and 2,4'-dinitrodiphenylamine (2,4'-diNO_2-DPA) (PERME).

The nitromusks studied were: musk xylol and musk moskene (Givaudan, Whyteleafe, U.K.).

The drugs studied were amphetamine (Riker, Loughborough, U.K.). and medazepam (Roche, Welwyn Garden City, U.K.).

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

Methyl *tert.*-butyl ether (HPLC grade; Rathburn, Walkerburn, U.K.) contains no additives and was therefore used in preference to diethyl ether. All other solvents were Distol grade (Fisons, Loughborough, U.K.).

All glassware was silanised as described previously[10] and was thoroughly rinsed with methyl *tert.*-butyl ether and dried before use.

Preparation of Amberlite XAD-7 extraction columns

A soda glass tube (14 cm × 5.6 mm O.D. × 2.5 mm I.D.) was silanised and

plugged at its lower end with silanised glass wool (Phase Separations, Queensferry, U.K.). Approximately 18 mg of Amberlite XAD-7 Beads (100–200 μm diameter) were poured into the tube to form a 1-cm column. The column was washed sequentially with 2 ml ethyl acetate and 3 ml pentane just prior to use, causing the beads to swell and increasing the column-bed to about 1.5 cm. Slight pressure was required to initiate the flow of ethyl acetate through the dry column.

Sample preparation of handswab extracts[4]

Handswabs were obtained by repeatedly scrubbing the upper surface[11] of one hand using a cotton wool swab (10 mg) moistened with methyl *tert.*-butyl ether.

Spiked handswabs were prepared by swabbing a blank hand and then distributing standard solutions of explosives throughout the used swab by means of a syringe.

Swabs were extracted by washing with small portions of methyl *tert.*-butyl ether (total volume 3 ml per swab) in a beaker using a glass rod. The combined extracts were centrifuged to remove traces of skin debris and the clear supernatant decanted into a silanised conical tube.

Pooled handswab extracts were prepared by combining the ether extracts of 25 swabs of the palms and lower surfaces of the fingers[11] of the hands of males who had not handled explosives or recently used any toiletry products other than soap, and storing at 4°C until required for use. Volumes corresponding to one handswab extract were used in experiments.

Pooled handswab extracts were spiked by adding small volumes of solutions of explosives prior to evaporation and clean-up.

Clean-up of handswab extracts

Handswab extracts were evaporated to near dryness (5–10 μl) using a current of nitrogen, and the last traces of ether were allowed to evaporate at room temperature.

The residue from each extract was moistened with 10 μl of methyl *tert.*-butyl ether, dissolved in pentane (0.5 ml), passed through the XAD-7 extraction column and discarded. Additional pentane (0.5 ml) was used to ensure quantitative transfer of the extract to the column. The column was then washed with pentane (2 ml) which was discarded. Explosives were eluted by two 200-μl washings with ethyl acetate allowing 1 min between each. The combined ethyl acetate extracts were concentrated to 30 μl under a stream of nitrogen at room temperature and 1 μl was analysed by GC.

GC–ECD

A Carlo Erba 2150 gas chromatograph (Erba Science, Swindon, U.K.) with an HT-25 ^{63}Ni electron-capture detector and a Model 251 electron-capture detector control module was used. The injector was operated in the splitless mode at 175°C as described previously[10]. A 12 m × 0.25 mm BP-1 fused-silica capillary column (SGE, Milton Keynes, U.K.) was used. The temperature was held at 60°C for 1 min then programmed at 39.9°C/min to 260°C and held for 2 min. The carrier gas was helium at a flow-rate of 17.6 ml/min (25°C). The electron-capture detector was operated at a temperature of 250°C. with all other conditions as described previously[10].

The injection port liner was cleaned as described previously[10] at the end of each working day.

GC-TEA

A Carlo Erba 4160 gas chromatograph (Erba Science) was coupled to a Model 610 thermal energy analyser (Thermoelectron Corporation, Waltham, MA, U.S.A.). The GC conditions were as described above except for the carrier gas flow-rate which was 8.8 ml/min (25°C) and the temperature programme for drug analysis in the nitrogen specific mode which was 30°C/min. The outlet end of the BP-1 column passed through the side of the instrument via an interface heated to 140°C. The junction between the capillary and the ceramic pyrolysis tube was a 1/4 to 1/16 in. Swagelock reducing union with 2 cm of 1/16 in. O.D. stainless-steel tube silver soldered into the smaller aperture. The wider end of the union was attached to the end of the pyrolysis tube using a graphite ferrule, and the capillary passed through the stainless-steel tube and terminated 4.5 cm inside the pyrolysis tube. Silicone gum (Silastic, 732 RTV,

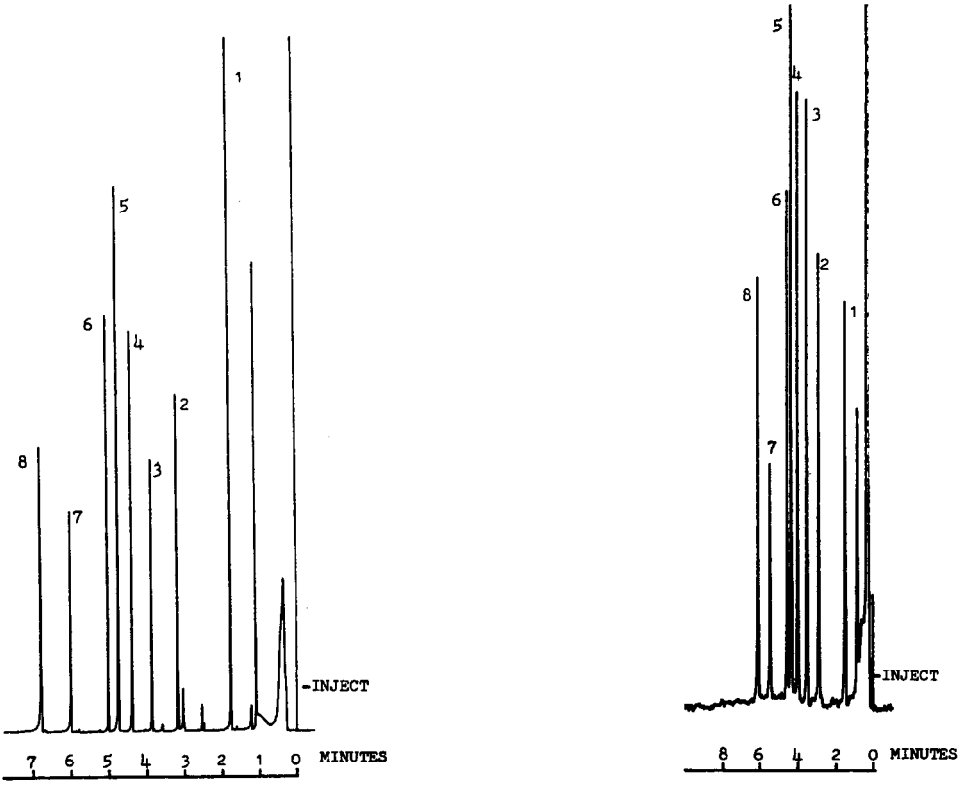


Fig. 2. Analysis of a mixture of explosives containing 300 pg each of EGDN (1), NG (2), 2,4-DNT (3), TNT (4), RDX (5), musk xylol (6), 4-NO_2-DPA (7), and 2,4'-di-NO_2-DPA (8) by capillary column GC–ECD (attenuation, ×128).

Fig. 3. Analysis of a mixture of explosives containing 500 pg each of EGDN (1), NG (2), 2,4-DNT (3), TNT (4), RDX (5), musk xylol (6), 4-NO_2-DPA (7), and 2,4'-di-NO_2-DPA (8) by capillary GC–TEA (nitroso mode; attenuation, ×8). Pyrolysis temperature: 800°C. Cold trap temperature: 25°C. Demonstrating peak broadening due to detector dead volume.

Dow Corning, London, U.K.) was used to seal the capillary column into the stainless-steel tube.

The cold trap between the pyrolysis tube and the thermal energy analyser was an 1/8-in. O.D. stainless-steel U-tube (18 cm × 2.5 cm) submerged to a depth of 8 cm in *n*-pentane in a thin walled glass tube (15.5 cm × 3 cm I.D.) cooled with liquid nitrogen.

The thermal energy analyser was modified by coupling the entry port of the instrument directly to the reaction chamber using the minimum possible length of blackened 1/8-in. PTFE tubing.

A nitrosamine-specific ceramic pyrolysis tube was used when the thermal energy analyser was operated in the nitroso mode, with a vacuum of 1.15 mmHg (oven temperature: 60°C), a pyrolysis oven temperature of 550–900°C (see text) and an ozone flow-rate of 0.018 ml/min.

For drug analysis, the thermal energy analyser was operated in the nitrogen mode using a nitrogen mode ceramic pyrolysis tube. In this mode, oxygen from the

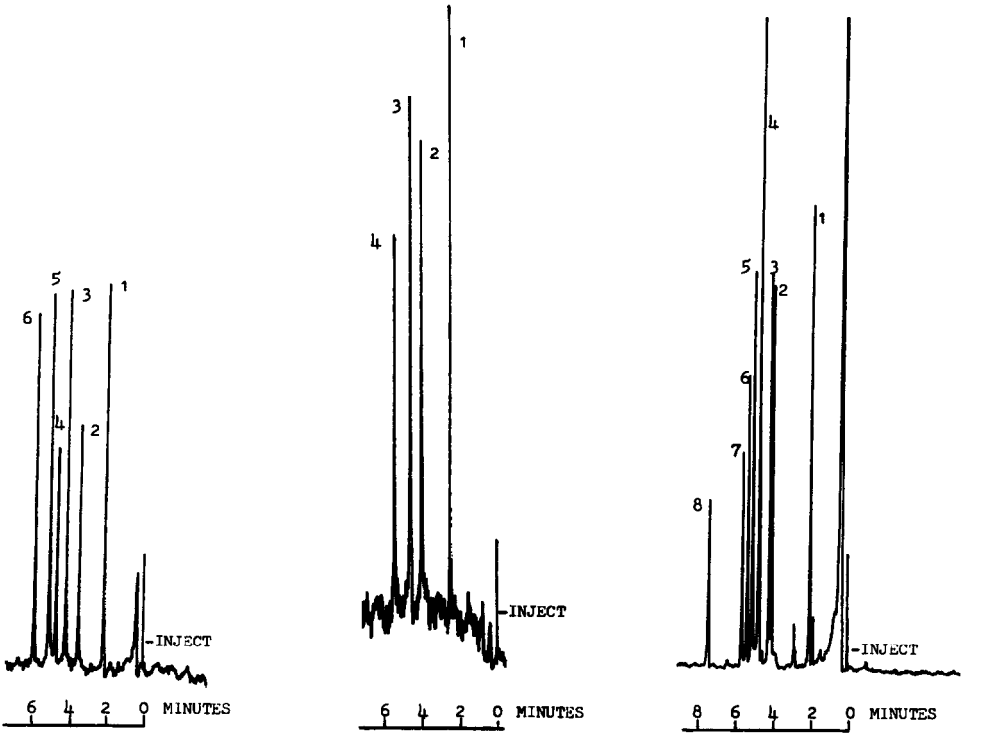


Fig. 4. Analysis of a mixture of explosives containing 250 pg each of EGDN (1), NG (2), 2,4-DNT (3), 150 pg of TNT (4), 250 pg of RDX (5), and 500 pg of Tetryl (6) by capillary GC–TEA (nitroso mode; attenuation ×8). Pyrolysis temperature: 900°C.

Fig. 5. Analysis of a mixture of explosives containing 100 pg each of NB (1), BTT (2), TNB (3), and musk moskene (4) by capillary GC–TEA (nitroso mode; attenuation, ×2; pyrolysis temperature 900°C).

Fig. 6. Analysis of a mixture of explosives containing 500 pg each of EGDN (1), BTT (2), 2,4-DNT (3), TNB (4), RDX (5), musk xylol (6), 2-NO_2-DPA (7), and 2,4'-di-NO_2-DPA (8) by capillary GC–TEA (nitroso mode; attenuation ×16; pyrolysis temperature, 900°C).

thermal energy analyser was passed into the pyrolysis tube via a stainless-steel T-piece coupled to the 1/16-in. O.D. tube described above. The end of the silica capillary column passed through the T-piece and the 1/16-in. O.D. tube before entering the pyrolysis chamber and was sealed in place with silicone gum. The flow-rate of both oxygen and ozone was 0.02 ml/min and the vacuum was 1.8 mmHg (oven temperature: 60°C). The pyrolysis oven temperature was 700°C.

RESULTS AND DISCUSSION

A mild selective clean-up involving adsorption of explosives on to Amberlite XAD-7 porous polymer beads has been reported previously[1].

The present paper describes an improved method using small columns of finely divided Amberlite XAD-7 porous polymer beads, which resulted in a faster clean-up procedure, considerably less sample manipulation and higher recoveries of a range of explosives and other nitro compounds.

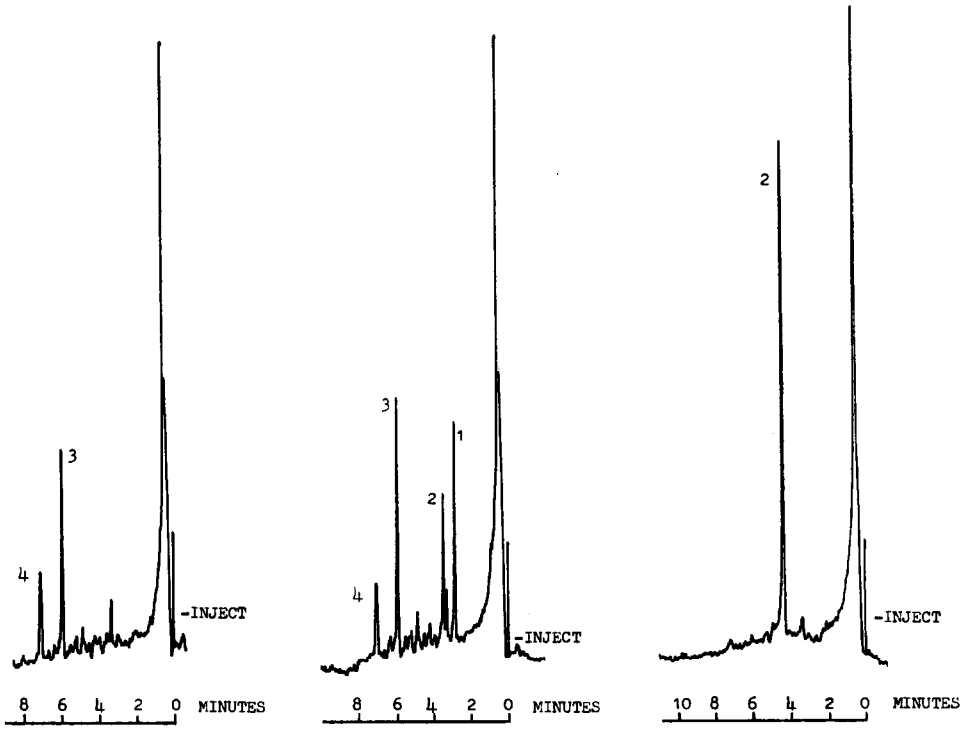


Fig. 7. Analysis of a cleaned-up extract of a blank handswab by capillary GC–TEA (nitroso mode); 3% of the sample was analysed at ×8 attenuation using a pyrolysis temperature of 800°C. For possible identification of peaks 3 and 4 see text.

Fig. 8. Analysis of a cleaned-up extract of a pooled handswab spiked with 10 ng/swab of NG (1) and 2,4-DNT (2), by capillary GC–TEA (nitroso mode); 3% of the sample was analysed at pooled attenuation of ×8 using a pyrolysis temperature of 800°C.

Fig. 9. Analysis of a cleaned-up an handswab extract spiked with 20 ng/swab of RDX (2) by capillary GC–TEA (nitroso mode); 3% of the extract was analysed at an attenuation of ×8 and with a pyrolysis temperature of 700°C.

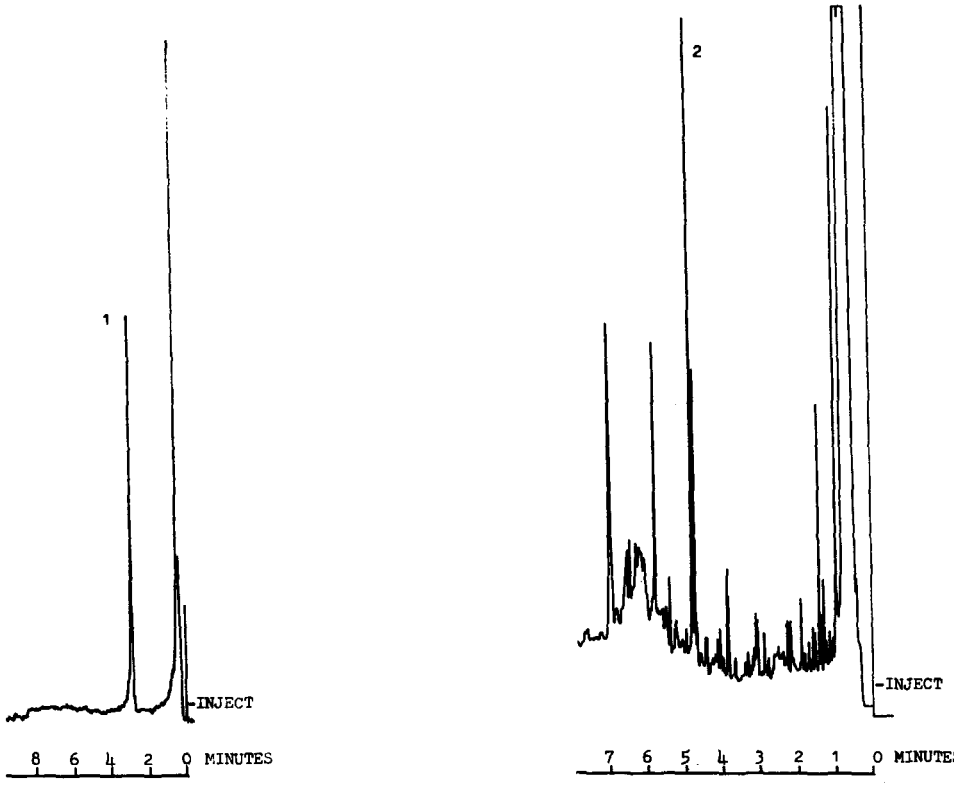


Fig. 10. Analysis of a cleaned-up pooled handswab extract spiked with 50 ng/swab of NG (1) by capillary GC–TEA (nitroso mode); 3% of the sample was analysed at an attenuation of ×8 and with pyrolysis temperature of 700°C.

Fig. 11. Analysis of a cleaned-up pooled handswab extract spiked with 20 ng/swab of RDX (2) by capillary column GC–ECD; 3% of the sample was analysed with an attenuation of ×128.

By this method 97% (w/w) of coextractives were removed in one step and the total time for the clean-up was less than 5 min. Preliminary results indicate that optimising the polarity of the washing solvent can further enhance the degree of clean-up of the extracts and this is now being investigated. This will be fully reported in a further publication.

GC analysis

Figs. 2–6 show the analysis of subnanogram amounts of explosives and related compounds using both ECD (Fig. 2) and TEA (nitroso mode) (Figs. 3–6). The peak broadening observed with TEA was probably due to the additional dead volume in the instrument compared with ECD. The thermal energy analyser was available for only a limited time which precluded complete optimisation of the experimental conditions. Elimination of dead volume in the detector and optimisation of the cold trap configuration and temperature might well have improved both the chromatography and the response.

Analysis of handswabs

The temperature of the TEA pyrolysis furnace (nitroso mode) was found to affect the selectivity of the detector and experiments were therefore carried out to optimise the pyrolysis temperature using pooled handswabs spiked with varying levels of explosives (see Experimental).

With a pyrolysis temperature of 800°C, at which all three classes of explosives (nitrate ester, nitroaromatics, and nitramines) are pyrolised, two peaks were observed (Fig. 7) in the cleaned-up blank extract having retention times longer than the majority of explosives. Peak 3 has the retention time of musk ketone while peak 4 is unidentified. Fig. 8 shows the detection of nitroglycerine and 2,4-dinitrotoluene at the 10 ng/swab level using a furnace temperature of 800°C.

Reduction of the pyrolysis temperature to 700°C gave a cleaner background suggesting that both interference peaks in Fig. 7 are nitroaromatic compounds since they are not detected at this temperature (Figs. 9 and 10). Comparison of Figs. 9 and

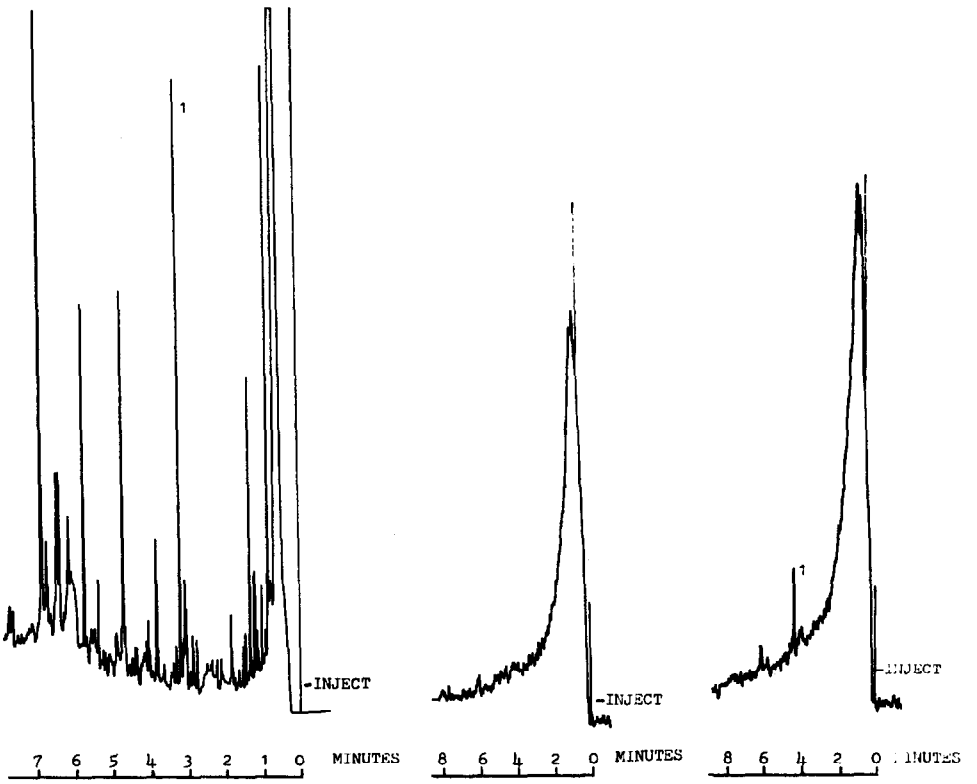


Fig. 12. Analysis of a cleaned-up pooled handswab spiked with 20 ng/swab of NG (1) by capillary GC–ECD; 1.5% of the sample was analysed with an attenuation of ×64.

Fig. 13. Analysis of a cleaned-up extract of a blank single handswab by capillary GC–TEA (nitroso mode); 13% of the cleaned-up sample was analysed with an attenuation of ×4 and a pyrolysis temperature of 550°C. (The small peak having a retention time of 6 min is a syringe artefact.)

Fig. 14. Analysis of 13% of a cleaned-up extract of a single handswab spiked with 2 ng/swab of RDX (1). The analytical conditions were the same as in Fig. 13.

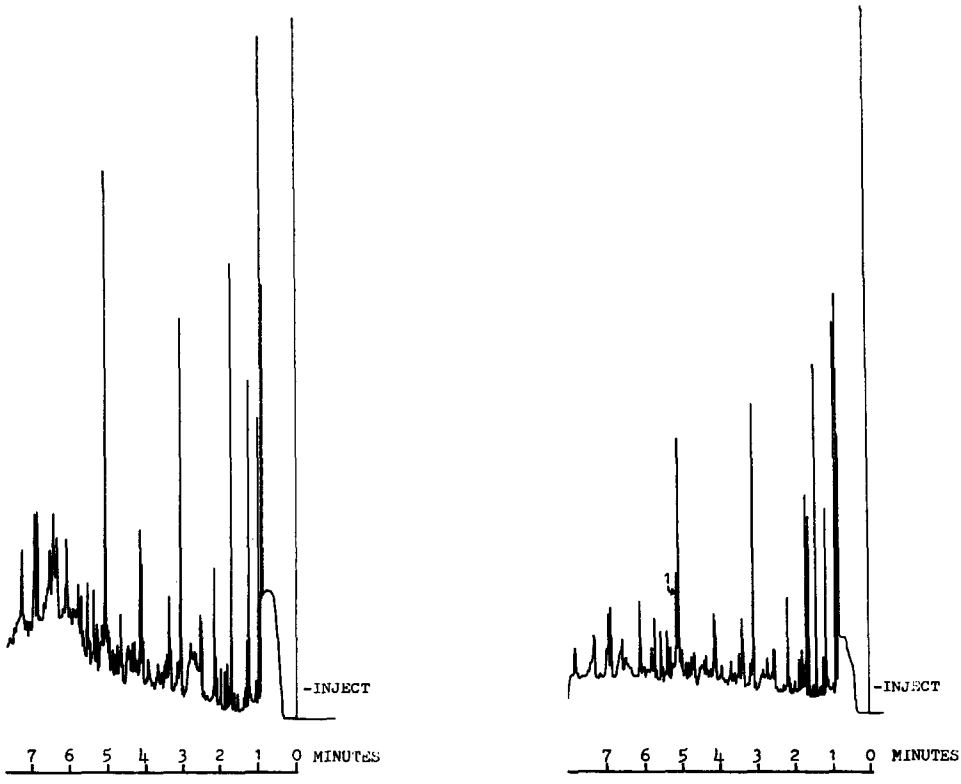


Fig. 15. Analysis of a cleaned-up extract of a blank single handswab by capillary column GC–ECD; 3% of the sample was analysed with an attenuation of ×64.

Fig. 16. Analysis of a cleaned-up extract of a single handswab spiked with 2 ng/swab of RDX (1) by capillary GC–ECD; 3% of the sample was analysed with an attenuation of ×128.

10 (TEA) with Figs. 11 and 12 (ECD) clearly shows the superior selectivity of TEA.

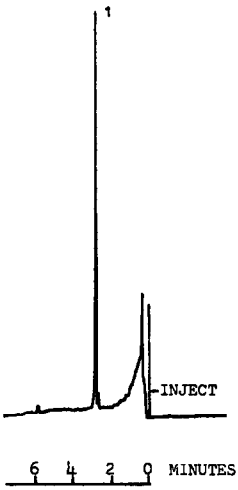
Reduction of the pyrolysis temperature from 700°C to 550°C further demonstrated the selectivity of TEA (Figs. 13–16), but this is offset to some extent by a partial loss of response for all explosives. It was found, however, that the selectivity of TEA using a pyrolysis temperature of 550°C was such that as much as 13% of the sample could be analysed with little effect on the background (Figs. 13–16).

The analysis of a handswab of a subject who had just fired a 9-mm pistol is shown in Fig. 17, peak 1 corresponding to approximately 100 ng/swab of nitroglycerin.

Analysis of drugs by GC–TEA (nitrogen mode)

The detection of single dose levels of unknown nitrogen containing drugs in small blood samples is frequently required in forensic toxicology. A number of drugs have peak single dose therapeutic levels in the low ng/ml range (*e.g.*, amphetamine 35 ng/ml) and so a very sensitive and selective detector is required.

The most widely used specific detector for nitrogen containing drugs is the thermionic nitrogen-phosphorus detector. It does not, however respond well to pri-



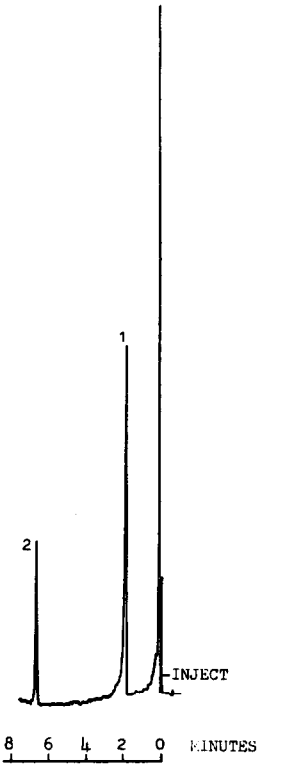


Fig. 17. Analysis by capillary GC–TEA (nitroso mode) of a cleaned-up extract of a handswab obtained from the back of the hand of a subject who had just fired a 9-mm handgun, showing NG (1); 1.5% of the sample was analysed with an attenuation of × 16 and a pyrolysis temperature of 550°C. (The peak having a retention time of 6 min is a syringe artefact.)

Fig. 18. Analysis of a mixture containing 1 ng each of amphetamine (1) and medazepam (2) by capillary GC–TEA using the nitrogen mode, an attenuation of × 8 and a pyrolysis temperature of 700°C.

mary amines such as amphetamine and it lacks the sensitivity and selectivity to detect very low levels of drugs.

In contrast, the thermal energy analyser can function as a nitrogen specific detector with excellent selectivity and low picogram sensitivity for nitrogen containing compounds. This was demonstrated by the analysis of amphetamine and medazepam, drugs that are detected with poor sensitivity by the nitrogen-phosphorus detector and electron-capture detector, respectively. Both drugs were successfully analysed by GC–TEA in the nitrogen mode at the nanogram level (Fig. 18).

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REFERENCES

1 J. M. F. Douse, *J. Chromatogr.*, 234 (1982) 415, and references cited therein.
2 J. B. F. Lloyd, *J. Chromatogr.*, 261 (1983) 391, and references cited therein.
3 D. F. Wardleworth and S. A. Ancient, *Proc. Symp. Anal. Detect. Explosives, Quantico VA, 1983*, NTIS, Springfield, VA, p. 405.
4 J. M. F. Douse, *J. Chromatogr.*, 256 (1983) 359.
5 E. U. Goff, W. C. Yu and D. H. Fine, *Proc. Symp. Anal. Detect. Explosives, Quantico, VA, 1983*, NTIS, Springfield, VA, p. 159.
6 E. U. Goff, W. C. Yu and D. H. Fine, *Proc. Symp. Anal. Detect. Explosives, Quantico, VA, 1983*, NTIS, Springfield, VA, p. 169.
7 J. H. Phillips, R. J. Coraor and S. R. Prescott, *Anal. Chem.*, 55 (1983) 889.
8 J. B. Apatoff, *Frankford Arsenal Report (AD-783499)*, NTIS, Springfield, VA, 1973.
9 T. J. Betts, G. M. Tai and R. A. Turner, *J. Chromatogr.*, 244 (1982) 381.
10 J. M. F. Douse, *J. Chromatogr.*, 301 (1984) 137.
11 A. Maehly and L. Stromberg, *Chemical Criminalistics*, Springer Verlag, New York, 1981, p. 187.