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## Note

# Trace analysis of explosives by capillary supercritical fluid chromatography with thermal energy analysis detection

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The thermal energy analyser is a very useful chromatographic detector for the forensic trace analysis of explosives[1–3]. Its high sensitivity and selectivity for nitro compounds allows the rapid screening of contaminated extracts for traces of explosives, the majority of which contain nitro groups[4–6], with the minimum likelihood of false positive results. This ability to screen samples for explosives is important because criminals increasingly use rare and difficult-to-analyse explosives in an attempt to escape detection[7–9].

Application of the thermal energy analyser to explosives screening is at present limited by the chromatographic techniques used to effect separation. Thus capillary column gas chromatography with thermal energy analysis detection (GC–TEA) is restricted to the analysis of thermally stable, volatile explosives, while high-performance liquid chromatography with TEA detection (HPLC–TEA) is limited to the analysis of nitrate esters and nitramines unless a photolytic reactor is used prior to the TEA pyrolysis unit[3]. HPLC–TEA additionally requires a cryogenic trap to prevent solvent from contaminating the detector, which makes the system difficult to operate and to maintain[10].

Capillary supercritical fluid chromatography (SFC) is an alternative chromatographic technique for which commercial equipment is now available[11]. Capillary SFC combines the useful features of HPLC and capillary GC and its use with sensitive GC detectors for the analysis of involatile or thermally unstable compounds has been demonstrated[11–13].

This paper describes the coupling of capillary SFC to TEA (capillary SFC–TEA), and application of the system to sub-nanogram detection of nitramines, nitrate esters, and nitroaromatics containing up to six nitro groups per molecule. Some of these compounds are thermally unstable or involatile and their analysis is difficult with HPLC–TEA or capillary GC–TEA. In addition, the detection of explosives on handswabs was briefly studied and the analysis of several nitroaromatic drugs was demonstrated.

## EXPERIMENTAL

Nitroglycerine (NG), ethyleneglycol dinitrate (EGDN), pentaerythritol tetranitrate (PETN), mannitol hexanitrate (MHN), diisopropyl nitramine (DIPNA), cy-

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clotrimethylene trinitrosamine (CTMTNA), dioxyethylnitramine dinitrate (DINA), hexogen (RDX), octogen (HMX), 2,4,6-trinitrotoluene (TNT), tetryl, hexanitrobibenzyl (NHBB), dipicryl sulphide (DPS), trinitro-*m*-xylene (TNX), 4-nitrodiphenylamine (4-NDPA), and hexanitrodiphenylamine (HNDPA) were obtained from the Propellants Explosives and Rocket Motors Establishment (PERME, Waltham Abbey, U.K.). 2-Nitrotoluene (2-NT), and nitrobenzene (NB) were obtained from Aldrich (Gillingham, U.K.). 2,4,6-Trinitrophenol (picric acid), 1-nitronaphthalene (1-NN), 1,5-dinitronaphthalene (1,5-DNN), 1,3,8-trinitronaphthalene (1,3,8-TNN), and 2,4-dinitrotoluene (2,4-DNT) were obtained from Fluka (Glossop, U.K.). Flunitrazepam, nitrazepam, and clonazepam were obtained from Roche (Welwyn Garden City, U.K.). Musk xylene was obtained from Givaudin (Whyteleaf, U.K.). All solvents used were pesticide grade (Fisons, Loughborough, U.K.) except for methyl *tert.*-butyl ether which was HPLC grade (Rathburn, Walkerburn, U.K.).

*Sample preparation*

Pure compounds were dissolved in ethyl acetate and analysed directly. Hand-swab extracts were prepared for analysis as described previously[1]. Very dirty hand-swab extracts were prepared as described in Results and discussion.

*Capillary SFC–TEA configuration*

A Lee Scientific (Salt Lake City, UT, U.S.A.) Series Model 600 supercritical fluid chromatograph was used with supercritical carbon dioxide (high purity grade with dip tube; Air Products, Southampton, U.K.) as eluent. The chromatographic column was a 6.8 m × 0.05 mm I.D. SB Octyl 50 Superbond cross-linked flexible silica (Flexsil) capillary with a stationary phase film thickness of 0.25 μm. The injection solvent was ethyl acetate and the injection loop volume was 0.2 μl.

A ceramic frit restrictor (Lee Scientific) was joined to the detector end of the flexsil column with a butt connector incorporating a Flexsil liner and graphite ferrules (Lee Scientific). The restrictor was inserted 20 cm into an uncoated length of flexible silica capillary column (0.22 mm I.D.) (SGE, Milton Keynes, U.K.) used as the TEA pyrolysis tube[1] and the joint sealed with silicone gum (Silastic, Dow Corning, London, U.K.). The restrictor penetrated 11.5 cm into the TEA pyroliser interface block.

The thermal energy analyser (Thermoelectron, Waltham, MA, U.S.A.) was operated as previously described[1] but using an Edwards Model ES 200A high vacuum pump. The pyrolysis temperature was 625°C, the reaction chamber pressure was 0.55 mm of mercury, and the ozone flow-rate was 11.1 ml/min.

When different operating conditions were used they are detailed in the text.

*SFC density and temperature programmes*

The SFC density and temperature programmes operated simultaneously. The carbon dioxide density was held at 0.15 g/ml for 1 min and then programmed at a rate of 0.065 g $ml^{-1}$ $min^{-1}$ to 0.6 g $ml^{-1}$ where it was held for 3 min.

The oven temperature programme was held at 100°C for 4 min, then programmed at a rate of 10°C/min to 160°C and held for 1 min. The injection time was 1 s. An interface temperature of 350°C was used.

Other temperature and density programmes were used for specific applications and are described in the Results and discussion section.

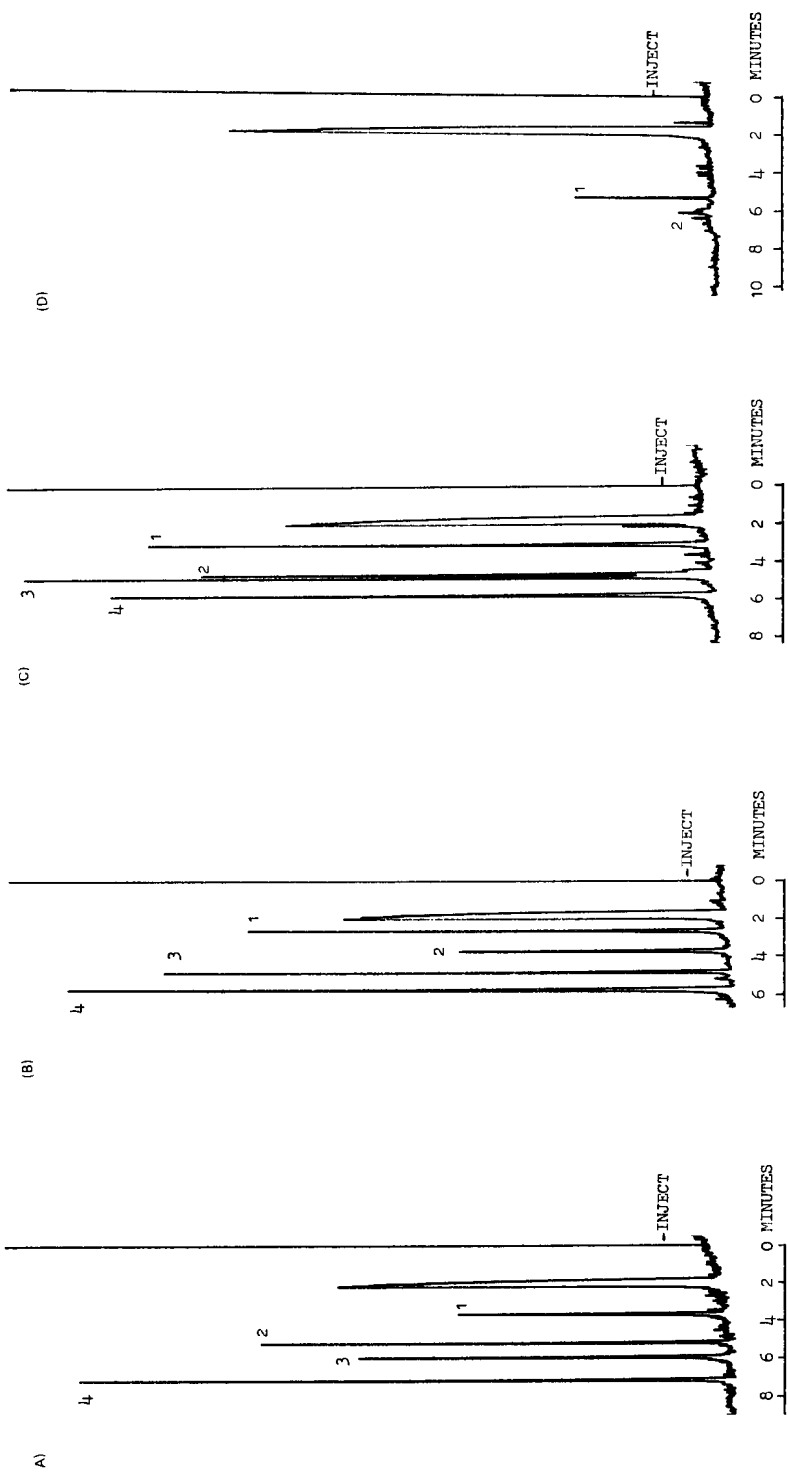


Fig. 1. Capillary SFC–TEA analysis of explosives using a TEA ozone flow-rate of 1.3 ml/min, an attenuation of 20 mV and a pyrolysis temperature of 625°C. (A) 5.5 ng of 2-NT (1). 1 ng of TNT (2), 1 ng of tetryl (3), and 2 ng of HNBB (4). (B) 266 pg of EGDN (1), 456 pg of NG (2), 744 pg of PETN (3), and 1.3 ng of RDX (4). (C) 1.1 ng of DIPNA (1), 504 pg of CTMTNA (2), 680 pg of DINA (3), and 1.2 ng of RDX (4). (D) 840 pg of MHN (1), showing also MHN hydrolysis products (2). The programme conditions are described in the Experimental section.

## RESULTS

*Explosives (pure standards)*

Capillary SFC–TEA with the operating conditions described above permitted the analysis of many nitramine, nitrate ester, and nitroaromatic explosives at sub-nanogram levels with good peak shapes and a maximum elution time of 6–8 min (Fig. 1). Other nitroaromatics not shown in Fig. 1 such as NB, MNN, DNN, TNN, musk xylol, TNX and DPS were also successfully analysed. The responses and peak shapes of the longer retained explosives such as HNBB were significantly improved by a faster temperature programming rate (30°C/min) and a longer hold at 160°C (3 min).

The minimum detectable levels ranged from 20 to 60 pg injected for a representative group of compounds (NG: 23 pg; PETN: 40 pg; tetryl: 60 pg; HNBB: 55 pg), and the relative standard deviation ($n = 5$) at the sub-nanogram level ranged from 2 to 5% [EGDN (266 pg), 2.8%; NG (456 pg), 4.5%; PETN (744 pg), 2.2%; RDX (1.27 ng), 2.0%; tetryl (600 pg), 4.1%; HNBB (1.1 ng), 4.1%].

Compounds containing very polar groups, *e.g.* amino (polynitrodiphenylamines and nitroguanidine) and hydroxy (picric acid, styphnic acid and nitrocellulose) could not be analysed. In addition HMX had a poor peak shape, probably due to its low solubility in supercritical carbon dioxide which is approximately equivalent in solvent power to methylene chloride[11]. Low percentages of organic additives or a more polar supercritical fluid might improve the analysis of these compounds[11].

*Explosives (handswab extracts)*

Capillary SFC–TEA analysis of explosives in cleaned-up[1] handswab extracts gave good results with the explosives readily detected against a clean background. Examples show nitroglycerine in a handswab from a subject who had discharged a firearm (Fig. 2) and the analysis of a handswab spiked with HNBB, an involatile nitroaromatic explosive (Fig. 3). The latter compound cannot be analysed by capillary GC–TEA.

The effect of dirty extracts on column stability was also investigated. A dirty extract was prepared by pooling extracts of forty handswabs from laboratory personnel who had not handled explosives. An aliquot equivalent to four handswabs was removed, centrifuged to remove skin debris, evaporated to dryness and the lipid rich residue was dissolved in the minimum volume (30 μl) of ethyl acetate.

Such extracts were analysed about thirty times by capillary SFC–TEA (0.2-μl injections) with no initial clean-up, and the column performance was monitored by injections of pure standard mixtures in ethyl acetate. The SFC temperature programme was as described in the Experimental, but the maximum of the density programme was increased to 0.75 g/ml. It was found that the deterioration in column performance was minimal if after each injection the supercritical fluid was held at its maximum until coextractives from the dirty extract had eluted.

While the SFC capillary column was thus shown to be resistant to contamination, interference by coextractives precludes the analysis of explosives at low levels in dirty extracts without a preliminary clean-up. It should be noted that had the dirty extract been injected into a capillary GC, the column would have been permanently damaged.

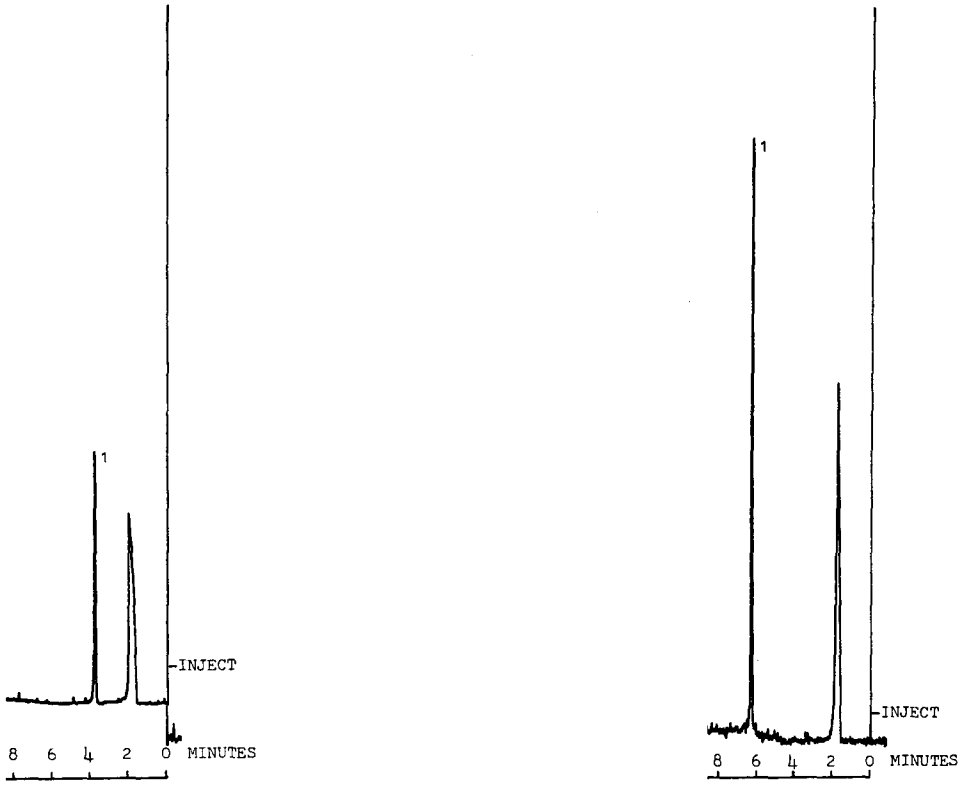


Fig. 2. Capillary SFC–TEA analysis of NG (1) in a handswab from a subject who had fired three rounds of Winchester Super X ammunition from a Smith and Wesson Model 19 revolver. The handswab extract contained about 180 ng of NG (1), and was cleaned-up using the Amberlite XAD-7 method with pentane–MTBE (50:50) as eluent. The TEA ozone flow-rate was 11.1 ml/min, the attenuation was 50 mV, and the pyrolysis temperature was 625°C.

Fig. 3. Capillary SFC–TEA analysis of a handswab spiked with 50 ng of HNBB (1). The handswab extract was cleaned-up using the Amberlite XAD-7 method with MTBE as solvent. The SFC oven temperature was held at 100°C for 4 min, programmed at 30°C/min to 160°C and then held for 3 min. The TEA ozone flow-rate was 11.1 ml/min, the attenuation was 20 mV and the pyrolysis temperature was 625°C.

*Nitroaromatic benzodiazepine drugs*

The nitroaromatic benzodiazepine drugs, flunitrazepam and clonazepam (Fig. 4) and nitrazepam (which coelutes with clonazepam under the conditions used) were analysed by capillary SFC–TEA with good peak shapes and responses. Maximum sensitivity was obtained with a TEA pyrolysis temperature of 850°C.

## DISCUSSION

The supercritical fluid chromatograph was easily coupled to the thermal energy analyser and the response stabilised after a short period of equilibration. The performance was maintained for the month during which this study was undertaken. The results showed that capillary SFC–TEA has considerable potential for explosives

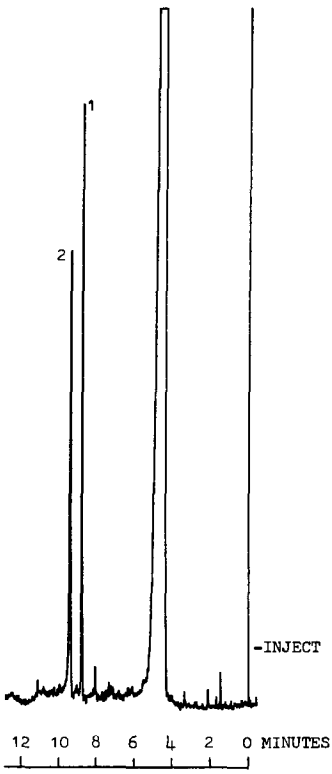


Fig. 4. Capillary SFC–TEA analysis of 564 pg of flunitrazepam (1), and 960 pg of clonazepam (2). The TEA ozone flow-rate was 1.3 ml/min, the attenuation was 20 mV, and the pyrolysis temperature was 850°C. An old partially blocked ceramic frit restrictor was used for this analysis and was found to be the cause of the increased solvent retention time.

analysis since it is sensitive, selective, rapid, simple to operate and maintain, and resistant to coextractives in the samples.

Some explosives which cannot be analysed by capillary GC due to their involatility or instability were readily analysed by capillary SFC. These were HNBB which has a low vapour pressure[15], tetryl which decomposes to N-methylpicramide[16], and PETN which requires a clean GC system to prevent decomposition. In addition, capillary SFC–TEA is more resistant than capillary GC–TEA to contamination by coextractives.

Capillary SFC–TEA could be a useful method for drug analysis. This was briefly demonstrated by the analysis of nitroaromatic benzodiazepines. Few drugs contain nitro groups but most contain nitrogen and so operation of the thermal energy analyser in the nitrogen specific rather than nitroso (explosive) mode would enable a great many drugs to be detected while the resistance of the SFC capillary column to contamination could be an advantage in forensic toxicology. Further work on the application of capillary SFC–TEA to drug analysis and toxicology is planned.

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