Journal of Chromatography, 208 (1981) 83–88
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,572

Note

Trace analysis of explosives at the low picogram level by silica capillary column gas–liquid chromatography with electron-capture detection

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(Received December 9th, 1980)

The trace analysis of explosives is of importance in forensic science and analytical problems encountered in this field involve the detection of nanogram quantities of explosives in extracts obtained from handswabs and post-explosion residues[1]. The most sensitive and specific routine analytical technique at present available for performing these analyses is gas chromatography with electron-capture detection. In principle this method is capable of detecting explosives at the picogram level[2]. However the thermal instability and highly polar character of the explosives has prevented previous workers from analysing explosives by gas chromatography at levels below several nanograms thus severely limiting the use of this technique for trace analysis[3–5]. Priming of packed columns by repeated injections of explosives[6] is a method for extending the working range for some explosives below the nanogram level, but in forensic work the use of this type of procedure is highly questionable.

Attempts to analyse explosives by high-performance liquid chromatography[5] have only had limited success because the most sensitive of the commonly used detectors, the ultra-violet absorbance detector, lacks specificity at the low wavelengths where non-aromatic explosives can be detected and a more selective detector such as the thermal energy analyser[4,7] does not have sufficient sensitivity for trace analysis when used in this mode.

In this paper a method for analysing mixtures of the important commercial and military explosives at the low picogram level by gas chromatography using silica capillary columns with electron-capture detection is described. Clean-up techniques suitable for use with the analytical system are currently under development and the results will be reported in a future publication.

EXPERIMENTAL

Gas chromatographs

A Varian Model 1800 gas chromatograph equipped with a ^{3}H electron-capture detector was used. The detector was operated in the direct current mode at a potential of 90 V. The detector base was modified so that the capillary column terminated in the make up gas stream close to the entrance to the detector chamber. The high thermal capacity detector oven was maintained at a temperature of 200°C.

A home-made glass-lined splitter similar to that supplied commercially

0021-9673/81/0000–0000/$02.50

(Column Technology, Newcastle, Great Britain) was used in the splitless mode. The injector was cleaned and treated with hexamethyldisilazane (HMDS) (Phase Separations, Queensferry, Great Britain) at 280°C and baked out before use. Gas-tight seals, for connecting the column to the injector and the detector, suitable for use at pressures up to 150 p.s.i. were prepared using silicone rubber (Silicoset 151; I.C.I., London, Great Britain).

A computing integrator Model 308 (Laboratory Data Control, Stone, Great Britain) was used to measure peak areas.

Analytical conditions

The following conditions were used: column, 25 m × 0.25 mm I.D.; injection port temperature, 165°C; detector oven temperature, 200°C; temperature programme, 50°C for 1.5 min then programmed at 40°C/min to 240°C, cooldown time 1.5 min; stationary phase film thickness, approximately 0.1 μm; carrier gas, helium; carrier gas flow-rate, 28 ml/min (25°C); make-up gas, methane–argon (1:99); make-up gas flow-rate, 13 ml/min; injection solvent, ethyl acetate; stationary phase, OV-101.

Capillary columns

Soda glass capillary columns were prepared by published methods[8] and were 25 m × 0.25 mm I.D. Flexible silica capillary columns[9] (Phase Separations, Queensferry, Great Britain) were 25 m long with an internal diameter of 0.25 mm and were sheathed externally in either silicone rubber or polyimide. The sheaths were removed from the lengths of capillary column protruding into the injection port.

The columns were coated by the mercury plug dynamic method using a 10% solution of OV-101 (Phase Separations) in toluene (Aristar grade; BDH, Poole, Great Britain) at a velocity of 2.5 cm/sec. Observation of the capillary columns under the scanning electron microscope showed that the stationary phase film thickness was of the order of 0.1 μm. However this thickness could not be measured accurately because even at the limit of magnification of the instrument (× 10,000) the film could only just be detected on the surface of the silica.

Reagents

Ethyl acetate was pesticide grade (Fisons, Loughborough, Great Britain).

The explosives ethylene glycol dinitrate (EGDN), nitroglycerine (NG), 2,4,6-trinitrotoluene (TNT), hexogen (RDX), pentaerythritol tetranitrate (PETN), tetryl, and octogen (HMX) were specially purified for use as standards (Propellants, Explosives and Rocket Motors Establishment, Waltham Abbey, Great Britain). 2,6-Dinitrotoluene (2,6-DNT), 2,3-dinitrotoluene, 3,4-dinitrotoluene, 2,4-dinitrotoluene (Fluka, Buchs, Switzerland) and nitrobenzene (NB) (Aldrich, Gillingham, Great Britain) were commercial samples. All of the explosives gave a single peak when analysed by capillary column gas chromatography with electron-capture detection. The structures of the important explosives are shown in Fig. 1.

Solutions of explosives were freshly prepared in ethyl acetate and were stored at 0°C in the dark.

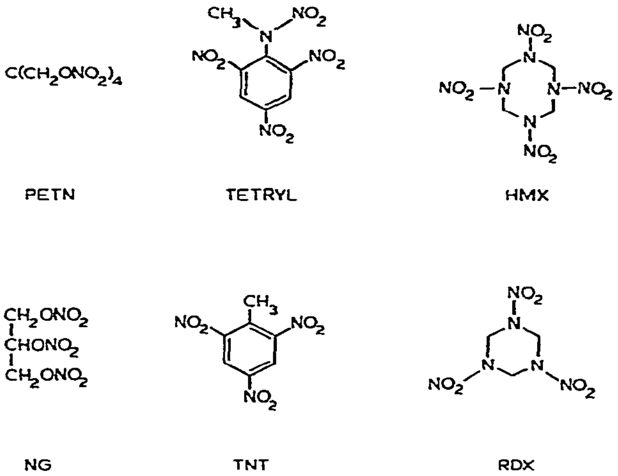


Fig. 1. Important commercial and military explosives of forensic interest.

RESULTS AND DISCUSSION

As mentioned in the introduction the detection of subnanogram levels of explosives using packed column GC is very difficult, and therefore capillary columns with their superior characteristics of resolution, sensitivity, and inertness[8], were used in this work.

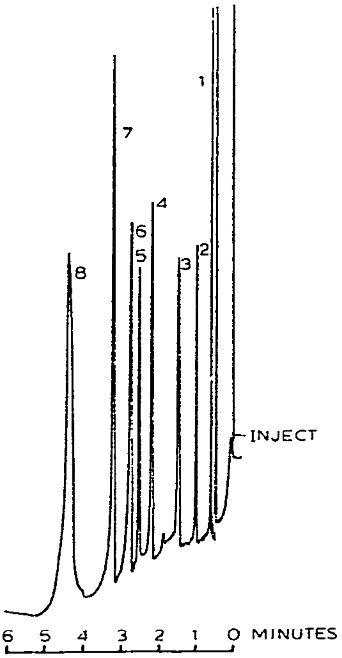
Attempts to analyse mixtures of explosives at the 100 picogram level on leached persilylated soda glass[8], barium carbonate coated soda glass[8] and untreated soda glass capillary columns coated with non-polar stationary phases were unsuccessful. On each glass type one or more explosives were irreversibly adsorbed rendering the methods unsuitable for use as a general analytical technique.

All of the explosives were, however, successfully analysed at the low picogram level using silica capillary columns coated with OV-101. Deactivation of the silica capillary columns with HMDS at 150°C prior to coating with OV-101 did not affect the activity of the column towards explosives.

The explosives shown in Fig. 1 differ markedly in their volatility[10] and in attempting to develop a screening method applicable to all of the explosives it was necessary to make a compromise between column length, column diameter, temperature programme rate, carrier gas flow-rate, and stationary phase film thickness. It was thus found possible to analyse standard solutions of all of the explosives in one chromatographic run and a typical analysis is shown in Fig. 2.

Under carefully optimised conditions and using a more efficient capillary column however it was possible to improve the peak shape of the explosives and hence the overall sensitivity of the method (Fig. 3).

To achieve these separations it was found necessary to use high helium carrier gas flow-rates of the order of 30 ml/min; without this it was not found possible to achieve the highest sensitivity for the longer retained compounds and it is assumed that this may be related to the flow-rate minimizing the residence time in the injection port, reducing decomposition of the less volatile explosives. The response for these



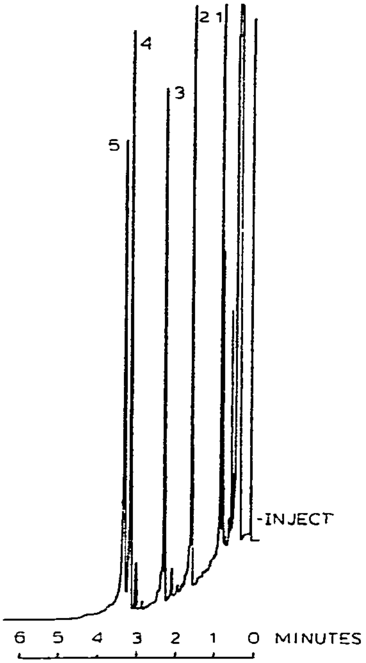


Fig. 2. Mixture of explosives containing 150 pg EGDN (1), 300 pg NG (2), injection port contaminant (3), 800 pg each of TNT (4), PETN (5), RDX (6), 3 ng tetryl (7), 8 ng HMX (8), analysed under standard conditions described under Experimental.

Fig. 3. Mixture of explosives containing 60 pg EGDN (1), 100 pg each of NG (2), TNT (3), RDX (4), and 400 pg of tetryl (5) analysed under standard conditions described under Experimental, but with a temperature programme of 25–240°C at 40°C/min. The two low retention time peaks are septum impurities.

compounds however was found to achieve an optimum value at a flow-rate of about 30 ml/min and it is believed that future improvements in the analytical technique will be achieved by optimising the stationary phase film thickness. It should also be noted that the peak shape and response for HMX was improved by using a temperature programme of 140–240°C at 40°C/min.

For the analysis of the relatively volatile explosives a lower carrier gas flow-rate and a slower programme can be used (Fig. 4).

The minimum detectable levels of the various explosives are shown in Table I.

The gas chromatographic procedure described gave satisfactory reproducibility in its quantitative aspects (Table I) and also in terms of retention time data. Care was taken to reproduce each temperature programme cycle exactly and in spite of the high temperature programme rate needed to perform the analysis the reproducibility of the retention time was better than 1 % relative standard deviation for all explosives.

Under isothermal conditions the calibration curves (peak area *versus* quantity) for both TNT and NG were found to be linear over the ranges 10–50 pg and 50–200 pg with correlation coefficients of 0.996 and 0.999, respectively.

It should be noted that all the above data were obtained using standard solutions whereas in practice with the types of samples encountered in forensic work it is

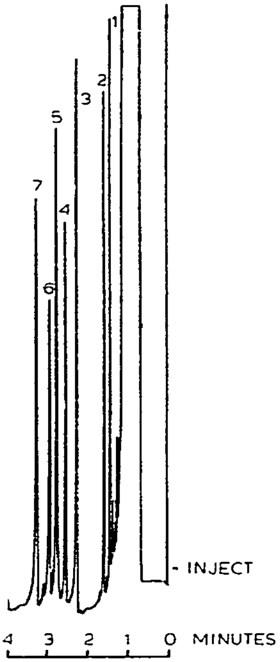


Fig. 4. Mixture of explosives containing 100 pg EGDN (1), 400 pg NB (2), 1000 pg NG (3), 100 pg each of 2,6-DNT (4), 2,3-DNT (5), 3,4-DNT (6), 200 pg of TNT (7). Standard conditions but using a capillary column deactivated with HMDS prior to coating, with a temperature programme of 25–240°C at 30°C/min, and a carrier gas flow-rate of 6 ml/min.

unlikely that the detection limits mentioned above could be routinely obtained. This is mainly due to interference from electron-capturing impurities in the sample extracts and solvents[7] and for the characterisation of explosives an effective clean-up procedure must be developed.

TABLE I

MINIMUM DETECTABLE LEVELS (MDL) AND REPRODUCIBILITY OF QUANTITATIVE ANALYSIS OF EXPLOSIVES UNDER THE STANDARD CONDITIONS DESCRIBED UNDER EXPERIMENTAL

Explosive	*Detectable levels*		*Quantitation*	
	MDL (pg)		*Level (pg) (silica column)*	*Relative standard deviation (%) (n = 10)*
	Silica column	*Silica column (deactivated with HMDS)*		
EGDN	1	5	100	3
NB	10	—	—	—
NG	5	5	100	13
2,4-DNT	10	—	—	—
TNT	5	5	100	1
PETN	30	—	500	10
RDX	10	10	100	5
Tetryl	40	40	400	5
HMX	100	—	1000	10

Two new selective detection methods applicable to explosives, the use of the thermal energy analyser[4,7] and negative specific ion monitoring[11] could well be applied with a preliminary capillary gas chromatography separation of the type described and would no doubt reduce the clean-up requirements of the routine method.

CONCLUSIONS

This paper describes a general method for analysing explosives reproducibly by gas chromatography at the low picogram level. It appears that the use of fused silica capillary columns has been responsible for achieving these new detection limits.

The high cost of the commercial flexible silica capillary columns has prevented us from rigorously investigating all aspects of this analytical technique. However the results we have obtained indicate that this line of research merits further investigation.

ACKNOWLEDGEMENTS

I wish to thank I. Jane and B. B. Wheals for their guidance and advice.

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