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Note

Trace analysis of explosives at the low picogram level using silica capillary column gas chromatography with thermal energy analyser detection

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A previous publication from this Laboratory described a routine method for the trace analysis of explosives in handswab extracts using silica capillary column gas chromatography with electron-capture detection[1]. Although pure explosives could be detected at the low picogram level using this method, the minimum detectable levels in handswabs were limited to the 10–50 ng per swab range even after extensive clean-up because of the poor selectivity of the electron-capture detector.

During recent studies on the deposition of explosive residues from the firing of handguns it was found that sometimes only 10–20 ng of nitroglycerine were transferred to the hands. These initial levels decay rapidly with time and in order to successfully detect nitroglycerine several hours after the firing of such a weapon it will probably be necessary to monitor levels of nitroglycerine in the 0.5–1 ng per swab range. Only by using a very sensitive and selective detector would it be possible to detect explosive residues at such low levels.

The thermal energy analyser (TEA) has been demonstrated to be potentially a very selective detector for explosive analysis[2–4]. However, the reported sensitivity of this detector when used in combination with high-performance liquid chromatography (HPLC) or packed column gas chromatography (GC) is only in the low nanogram range for many explosives. In contrast, the sensitivity reported for nitrosamines is in the low picogram range[5]; this discrepancy is believed to be due to problems of adsorption of the very polar explosives on the packed columns used for GC analysis and in the transfer lines of the TEA.

A method using silica capillary column GC[1] overcame such adsorption problems and this paper describes a successful attempt at detecting low picogram levels of explosives by linking such columns with a TEA.

EXPERIMENTAL

A Carlo Erba 2150 gas chromatograph (Erbascience, Swindon, Great Britain) was used with a Model 610 TEA (Thermo Electron Corporation, Waltham, MA, U.S.A.) operated in the nitroso mode. The $\frac{1}{4}$-in. I.D. metal tube of the pyrolyser probe was mounted vertically on the Carlo Erba electron-capture detector baseplate and the joint was sealed using silicone gum (Silastic 732 RTV; Dow Corning, London, Great

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Britain). A 25 m × 0.3 mm OV-101 flexible fused silica capillary column[1] was used and was mounted so that it protruded into the hot region of the ceramic tube of the pyrolyser.

The GC conditions were as follows: injection port temperature, 200°C; temperature programme, 40°C for 1 min, then programmed at 39.9°C/min to 240°C and held at this temperature for 1 min; splitless injection; no septum purge; carrier gas, helium; injection port pressure, 1.5 kg/cm^2; carrier gas flow-rate 11 ml/min (25°C, and atmospheric pressure at the outlet).

The TEA conditions were as follows: transfer line temperature, 200°C; pyrolyser oven temperature, 1000°C; oxygen flow-rate to ozonizer, 0.018 ml/min; vacuum pressure, 1.7 mmHg (oven temperature 40°C); attenuation, ×2 or ×4. All other reagents and conditions were as described previously[1].

RESULTS AND DISCUSSION

Explosives were successfully analysed at the sub-nanogram level by silica capillary column gas chromatography with TEA detection using a Carlo Erba gas chromatograph under operating conditions similar to those described previously[1]. The silica capillary column was passed from the gas chromatograph through a heated transfer line and was inserted deep into the heated zone of the pyrolysis tube so as to

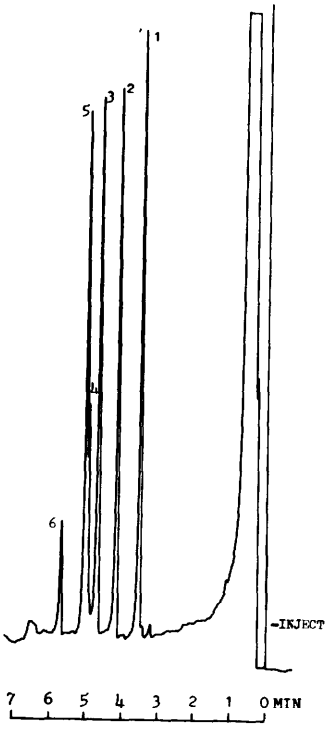

Fig. 1. Mixture of explosives containing 1 ng each of nitroglycerine (1), 2,4-dinitrotoluene (2), TNT (3), PETN (4), RDX (5) and tetryl (6) analysed by silica capillary column GC with TEA detection using the conditions described under Experimental with an attenuation of ×8.

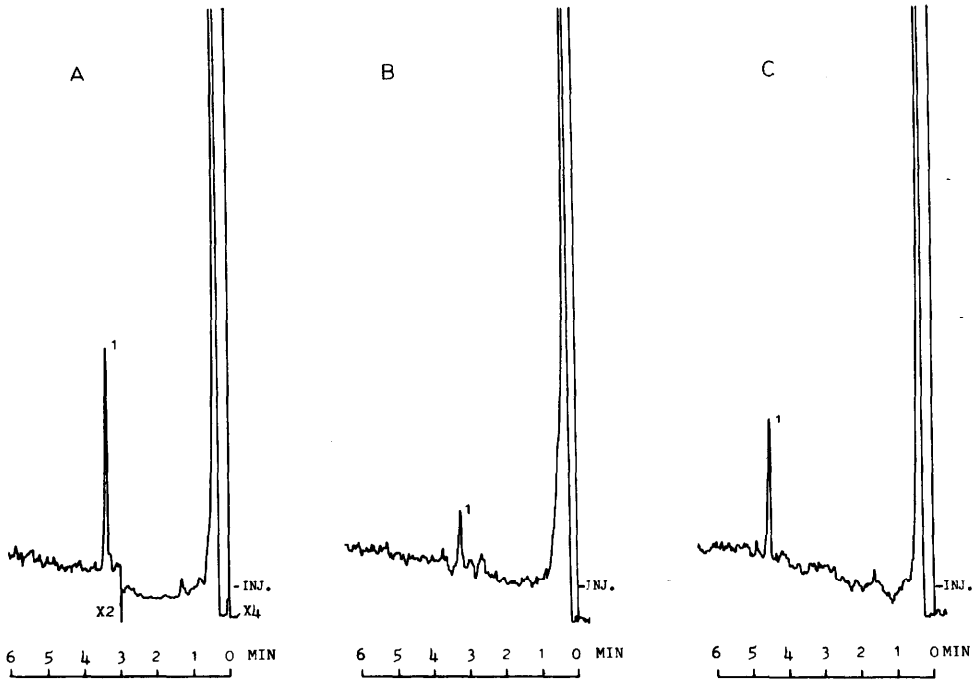

Fig. 2. Analysis of low picogram levels of explosives using silica capillary column gas chromatography with TEA detection using the conditions described under Experimental and an attenuation of × 2. (A) 100 pg of nitroglycerine (1); (B) 20 pg of nitroglycerine (1); (C) 50 pg of TNT (1).

avoid losses of the very polar explosives due to adsorption. This aspect of the interface was critical as sensitivity was limited to the low nanogram level if the column protruded only into the transfer line or the cool zone of the pyrolysis tube.

An analysis of a range of explosives at the nanogram level using this system is shown in Fig. 1. It should be noted that the poor response for tetryl and PETN has subsequently been found to be due to the use of a capillary column coated with too thick a layer of stationary phase, which is believed to have resulted in a loss of response of these compounds through thermal decomposition. The analysis of low

TABLE I

MINIMUM DETECTABLE LEVELS OF EXPLOSIVES OBTAINED USING THE THERMAL ENERGY ANALYSER (TEA) AND THE ELECTRON-CAPTURE DETECTOR (ECD)

Explosive	*Minimum detectable level (pg)*			
	HPLC–TEA	*GC–TEA*		*GC–ECD: Capillary column*
		Packed column	*Capillary column*	
Nitroglycerine	500 (ref. 4)	–	15	5 (ref. 1)
TNT	–	< 200 (ref. 3)	10	5 (ref. 1)
RDX	1000 (ref. 2)	–	< 200	10 (ref. 1)

picogram levels of nitroglycerine and TNT are shown in Fig. 2. Toluene was used as the injection solvent for these analyses as it caused less baseline disturbance when the detector was operated at high sensitivity. The minimum detectable levels of these compounds are shown in Table I and are similar to those obtained using the electron-capture detector. The sensitivity is an improvement on methods described previously using HPLC or packed column GC in combination with the TEA.

The method also appears to be of general application as the explosives ethylene glycol dinitrate, nitrobenzene, 2,4-dinitrotoluene, RDX and 2-nitrodiphenylamine were successfully analysed with good response at the 200 pg level.

Owing to the limited period of time that the TEA was available to us for use, the results presented in this paper were not exhaustively tested and hence are only preliminary. However, we were able to show that the improved sensitivity of the TEA combined with its high selectivity has the potential to allow the detection of explosives in contaminated samples such as handswabs at lower levels and with fewer interferences than was previously possible using the electron-capture detector. It is probable that the use of this more selective detector will obviate the need for clean-up procedures for certain types of sample such as porous polymer headspace traps. However, samples heavily contaminated with involatile materials such as handswab extracts will still require clean-up prior to GC analysis in order to protect the column and the detector from contamination.

CONCLUSION

A general method has been described for the trace analysis of explosives at the low picogram level using gas chromatography with TEA detection. It appears that the use of fused silica capillary column GC is responsible for enabling these lower detection limits to be achieved by eliminating adsorption of explosives when analysed at the sub-nanogram level.

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