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Dinitrosopentamethylenetetramine—A Potential Interference in the Detection of Explosives Traces

ABSTRACT: A strong peak was encountered in the analysis of a case sample for explosives traces by gas chromatography with chemiluminescence detection. According to the standard laboratory criteria, the peak did not coincide with any common explosive, but it lay close to pentaerythyritol (PETN) and cyclotrimethylene trinitramine (RDX). Subsequent investigation discovered that the peak was caused by dinitrosopentamethylenetetramine, a chemical blowing agent used in plastics manufacture. Details of the compound, its mass spectrum, and chromatographic responses are given.

The search for traces of high explosives such as 2,4,6-trinitrotoluene (TNT), cyclotrimethylene trinitramine (RDX), and pentaerythrityl tetranitrate (PETN) is a common forensic activity. Such traces may be sought on the debris following an explosion, on the hands, clothing and property of suspects, or in suspect vehicles and premises. Gas chromatography (GC) with selective detection is frequently used to detect and identify high explosives traces, and in recent years, the highly selective Thermo-Electric Analyser (TEA) chemiluminescence detector has become very popular in this role.

During routine casework at the forensic explosives laboratory (FEL), extracts of methyl-*tert*-butyl ether wetted cotton wool swabs taken from a soft suitcase produced strong responses when analyzed using GC/TEA. The responses took the form of sharp peaks lying close in retention to PETN and RDX. The sharp peaks did not lie sufficiently close to either explosive to be classified as positive indications of these explosives, and the case sample was properly reported as negative. Strong sharp responses of this type are, however, uncommon, and their cause was investigated further.

By the application of combined gas chromatography/mass spectrometry (GC/MS), the compound responsible for the peaks was (not without difficulty) identified and found to be dinitrosopentamethylenetetramine (DNPMT), a chemical blowing agent used in the manufacture of foamed polymers. The presence of this blowing agent was consistent with the material of the suitcase, which was a woven fabric bonded to a thin layer of foamed polymer. IR spectroscopy indicated that the polymer was some form of polyolefin rubber containing kaolin filler. This paper gives details of DNPMT, its mass spectrum, and its behavior in GC/TEA analyses.

Experimental

Materials

"UNICEL 100" was obtained from E.I. Du Pont de Nemours & Co. (Inc.), Elastomer Chemicals Department, Wilmington, Delaware, USA. The manufacturer's labeling described UNICEL 100 as dinitrosopentamethylenetetramine.

A mixed standard solution (TEA Standard) containing low concentrations of the common high explosives was used for comparison purposes. The composition was as indicated in Table 1.

A solution (mixed reference) containing 5 ng/μL each of 2-fluoro-5-nitrotoluene (FNT) and the fragrance Musk Tibetine (MT, 2,6-dinitro-3,4,5-trimethyl-tert-butylbenzene) in ethyl acetate solvent was used to provide reference peaks in gas chromatographic analyses.

Apparatus

The GC/MS was a VG TS250 double-focusing magnetic sector spectrometer direct coupled by a heated line to a Carlo-Erba Mega HRGC 5300 chromatograph oven fitted with a split/splitless injection port with glass liner lightly plugged as described below. The chromatography column was a Supelco SPB-5 column of length 15 m and internal diameter 0.25 mm. The stationary phase was 5% diphenyl-dimethylsiloxane (similar to SGE BP5) of 1.0 μm thickness. The chromatograph oven initial temperature was 170°C,

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TABLE 1—*Composition of TEA standard solution.*

Explosive	Concentration (ng/μL)
ethylene glycol dinitrate (EGDN)	0.1
2-nitrotoluene	0.6
3-nitrotoluene	0.6
4-nitrotoluene	0.6
nitroglycerine (NG)	0.2
2,4-dinitrotoluene	0.4
2,6-dinitrotoluene	0.3
3,4-dinitrotoluene	0.2
2,4,6-trinitrotoluene (TNT)	0.4
PETN	0.75
RDX	0.5

the final temperature 220°C, and the ramp rate 5°C/min. Split injection was used at a split ratio of approximately 10:1. The spectrometer used electron impact ionization at 70 eV, was set for a nominal resolution of 500, and scanned over the range 25 to 200 Da. Each scan took 2 s. The instrument was controlled, and the data processed using VG OPUS software.

GC/TEA analysis was based upon the technique described by Douse (1). Instruments consisted of Fisons/Carlo-Erba ovens of types Mega HRGC 5300, or Mega HRGC 5300-HT, fitted with split/splitless injection ports operated with both split valves continuously closed. The glass injection port liners were lightly plugged at the midpoint with deactivated silica wool. The chromatographic columns were of three types as detailed in Table 2. The injection port temperatures were 175°C, and oven temperature programs were as given in Table 3.

In each case, the chromatographic column was joined within the oven to a short length of internally uncoated silica tube having a similar diameter to that of the column. The tube passed out of the oven through a pyrolysis furnace (supplied as part of the detector) held at 750°C, and was directly connected into the reaction chamber of a Thermedics TEA Model 610 chemiluminescence detector. Ozonized oxygen, generated by the ozonizer provided within the detector, passed into the reaction chamber through a second uncoated silica tube. The resulting detector signals were processed using Hewlett-Packard "3365 Chemstation" hardware and software.

Thin-layer chromatography (TLC) was carried out using 200 mm square Polygram SIL G/UV$_{254}$ plates (CAMLAB, Cambridge, UK) of 0.25-mm layer thickness.

Procedure

In 100 mL of a mixture of ethyl acetate and methyl-*tert*-butyl ether (MTBE), 50 mg of UNICEL 100 was dissolved without further dilution, 1 μL of this solution was analysed by GC/MS.

TABLE 2—*Details of chromatographic columns.*

Column	Details
BP1	SGE type 12AQ2/BP1 0.25. 12-m polyimide-clad silica, 0.22 mm i.d., 0.33 mm o.d., coated with bonded dimethylsiloxane 0.25 μm film thickness.
BP5	SGE type 12QC2/BP5 0.25. 12-m polyimide-clad silica, 0.22-mm i.d., 0.33-mm o.d., coated with bonded 5% diphenyl-dimethylsiloxane 0.25-μm film thickness.
CP-Sil-19CB	Chrompack catalogue no. 7712, 4-m cut from 25-m polyimideclad silica, 0.25-mm i.d., 0.39-mm o.d., coated with bonded 7% cyanopropyl-7% phenyl-1% vinyl-dimethylsiloxane 0.2-μm film thickness.

TABLE 3—*Oven temperature programs.*

Column type	Carrier press kPa	Initial temp. °C	Ramp Rate °C/min	Final Temp. °C
BP1	250	80	20	200
BP5	250	80	20	200
CPSIL-19	70	70	20	250

For GC/TEA analysis, 2 μL of the solution were diluted into 1 mL of ethyl acetate to give a solution containing approximately 1 ng/μL of DNPMT, 0.8 μL of TEA standard solution, together with 0.2 μL of mixed reference solution, was injected into the GC/TEA instrument, and the resulting chromatogram checked for satisfactory response to all explosives in the standard. Again, with added mixed reference, 0.8 μL of 1 ng/μL DNPMT solution was then injected. GC/TEA analyses were carried out using all three column types.

For TLC analysis, a solution containing approximately 1 μg/μL of DNPMT (UNICEL 100) in ethyl acetate was prepared, and 1, 2, and 5 μL spots applied to a line 20 mm from the TLC plate edge, 1 μg spots of the explosives, RDX, PETN, TNT, and nitroglycerine were also applied. The plate was eluted with 90% toluene/10% ethyl acetate, a distance of 100 mm from the application line and allowed to dry. After viewing under ultraviolet light, the plate was sprayed with molar sodium hydroxide solution, heated at 140°C in an oven for 10 min and sprayed with Griess reagent consisting of 4 g sulfanilamide, 0.4 g naphthylethylenediamine dihydrochloride and 8 mL of 85% orthophosphoric acid all dissolved in 100 mL of water.

Results and Discussion

GC/MS identification

Initial analyses of the casework sample yielded a good quality mass spectrum, which was computer searched against the US National Institute of Standards and Technology (NIST) mass spectral libraries, totaling approximately 75,000 spectra. No good matches were found, but after much of the structure of the unknown had been worked out by other means, a chance search of the older printed mass spectral library known as the Eight Peak Index (2), located two very good matches to the compound 3,7-dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane, (CAS Registry No. 101-25-7), which is more commonly known as DNPMT (Fig. 1).

A sample of this compound, in the form of the Du Pont product UNICEL 100, was obtained and its mass spectrum acquired as described above. Under the GC/MS conditions used, a single sharp chromatographic peak was observed that had the mass spectrum shown in Fig. 2. This closely matched the spectrum of the casework unknown, and the two spectra listed in the Eight Peak Index. Subsequent reexamination of the NIST spectral library revealed that a spectrum labeled as 3,7-dinitroso-1,3,5,7-tetraazabicyclo [3.3.1]nonane was present as NIST: 69665, but that this spectrum differed markedly both from the Eight Peak Index spectra and the spectrum shown in Fig. 2.

GC/TEA Analyses

Chromatograms of the DNPMT solution, compared in each case with a chromatogram of TEA standard, are given in Figs. 3, 4,
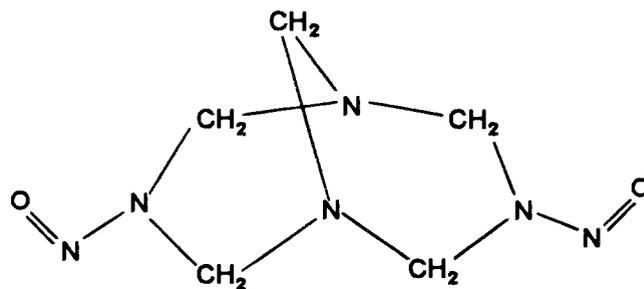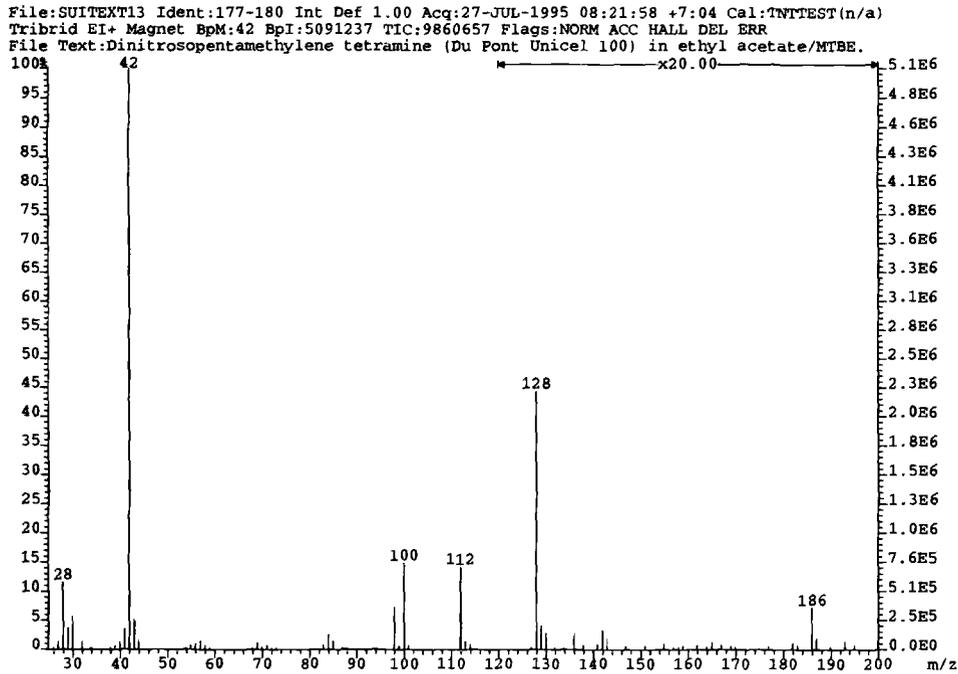

FIG. 1—*Structure of DNPMT.*

File:SUITEXT13 Ident:177-180 Int Def 1.00 Acq:27-JUL-1995 08:21:58 +7:04 Cal:TNTTEST(n/a)
Tribrid EI+ Magnet BpM:42 BpI:5091237 TIC:9860657 Flags:NORM ACC HALL DEL ERR
File Text:Dinitrosopentamethylene tetramine (Du Pont Unicel 100) in ethyl acetate/MTBE.

FIG. 2—*Mass spectrum of DNPMT obtained by GC/MS.*

and 5. The strong sharp peaks produced by DNPMT are apparent in each chromatogram. The detector response per nanogram of DNPMT was of the same order as that produced by explosives, as is to be expected from the presence of two nitrosamine groups in the molecule. The observed retention times of DNPMT, PETN, and RDX, measured relative to the retention time of the Musk Tibetine reference peak, are given in Table 4.

The FEL standard method for explosives trace identification by GC/TEA requires that the relative retention times of the suspect explosive peak and standard explosive peak agree within ± 0.5%. DNPMT did not coincide sufficiently well with PETN or RDX to meet this criterion, but it should be noted that the BP1 column

placed DNPMT before PETN, whereas the BP5 column placed it after PETN. These two column types do not differ greatly in polarity, and there is a strong possibility that other columns of about this polarity might place DNPMT sufficiently close to PETN for misidentification to occur if reliance were to be placed on a single analysis. (FEL always carries out analyses using three column types to eliminate such a misidentification.) The proximity of RDX suggests that confusion with this explosive could also arise.

TLC Analyses

After spraying with Griess reagent, the four common high explosives produced, as expected, magenta spots at the Rf values given
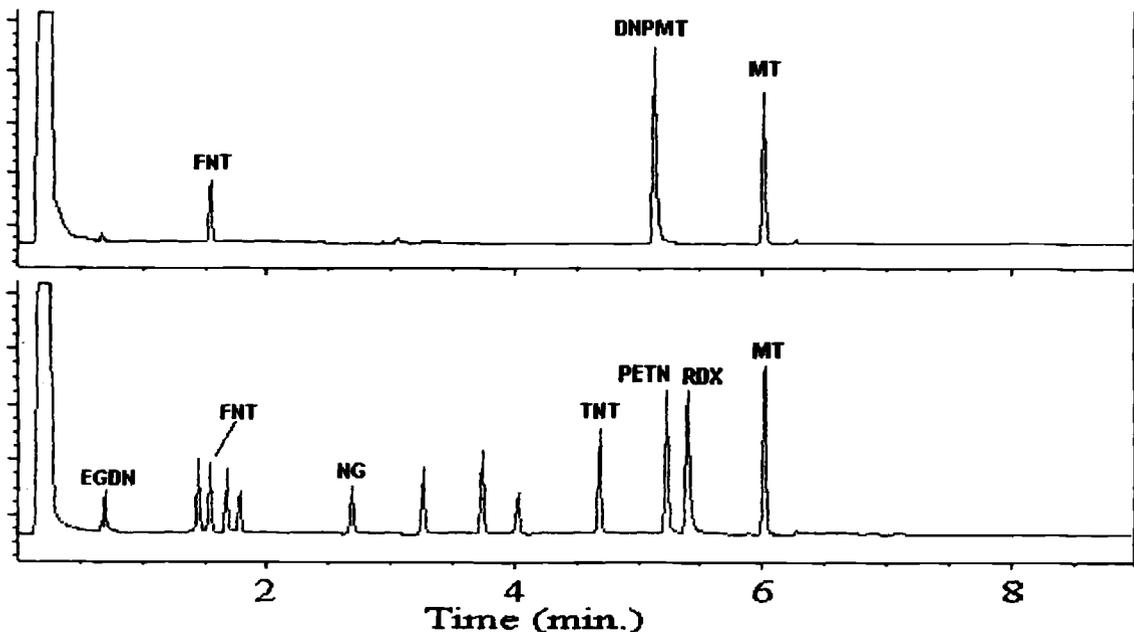

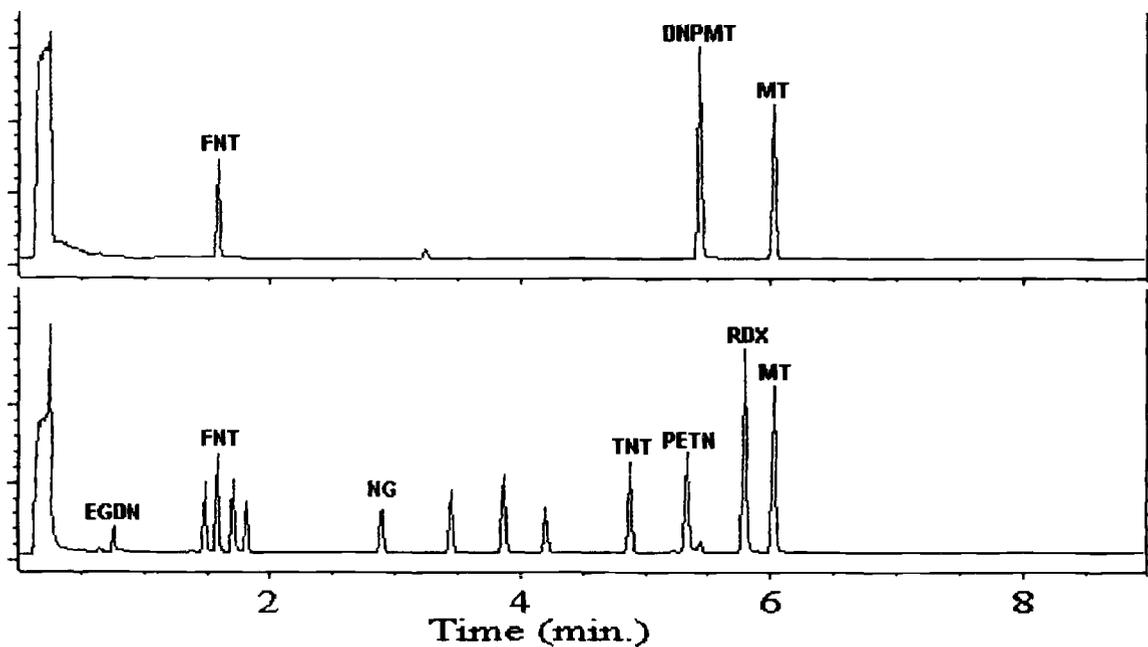FIG. 3—*GC/TEA chromatograms of DNPMT and TEA standard—BP1 column.*

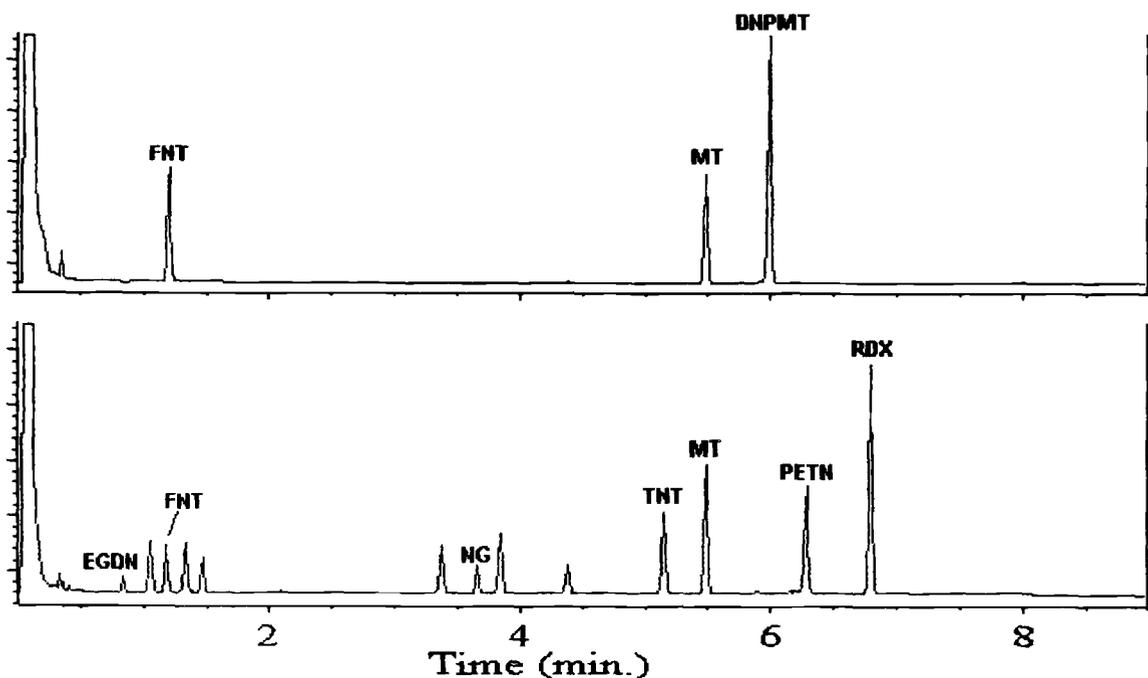FIG. 4—GC/TEA chromatograms of DNPMT and TEA standard—BP5 column.

FIG. 5—GC/TEA chromatograms of DNPMT and TEA standard—CPSIL-19 column.

TABLE 4—Retention times of DNPMT, PETN and RDX, measured relative to Musk Tibetine peak.

	BP1 column	BP5 column	CPSIL-19 column
DNPMT	0.8533	0.9022	1.0921
PETN	0.8696	0.8857	1.1450
RDX	0.8966	0.9610	1.2384

in Table 5. The DNPMT solution produced no visible spots after spraying with Griess reagent, but ultraviolet absorbing spots were observed before spraying at an Rf value of 0.02.

Uses of DNPMT

According to Brydson (3) DNPMT is widely used as a chemical blowing agent in natural and synthetic rubbers, a view that was supported by a search of the patent literature. Its structure is of course quite similar to that of explosives (particularly RDX), but Urbanski (4) does not report that it has explosive properties. When

TABLE 5—*Rf values of explosives.*

Explosive	Rf value
RDX	0.11
NG	0.63
PETN	0.74
TNT	0.88

heated, DNPMT releases a mixture of gases including nitrogen, and its oxides which foam the polymer. Although, the foaming process presumably consumes most DNPMT, it is likely that traces sufficient for detection by GC/TEA would remain.

Conclusions

DNPMT, a compound widely used as a chemical blowing agent, produces a strong response in GC/TEA analyses that might incorrectly be taken as indicative of the presence of PETN or RDX. A similar problem could arise in other instruments using the same nitric oxide/ozone chemiluminescence detection mechanism as the TEA. DNPMT solution produced no spots on a TLC plate after visualization with sodium hydroxide/Griess reagent, a system commonly used for the detection of explosives traces (5).

The NIST library spectrum of 3,7-dinitroso-1,3,5,7-tetraazabi-cyclo[3.3.1]nonane (DNPMT) differs considerably from two spectra given in the Eight Peak Index and the spectrum in this paper, and is thus incorrect.

References

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(4) Urbanski T. Chemistry and technology of explosives. 1st English ed. Oxford, United Kingdom: Pergamon Press, 1967;3:124.
(5) Jenkins R, Yallop HJ. The identification of explosives in trace quantities on objects near an explosion. Explosivstoffe 1970; 18:139–41.

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