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Trace analysis of explosives in water by gas chromatography–mass spectrometry with a temperature-programmed injector

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Abstract

Gas chromatography–mass spectrometry with a cooled temperature-programmable injector was used to analyze picogram amounts of explosives in water. The analyzed explosives included 2,4,6-trinitrotoluene (TNT), 2,4,6-N-tetranitro-N-methylaniline (Tetryl), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX), pentaerythritol tetranitrate (PETN) and a series of dinitrotoluene (DNT) isomers (which are ingredients of explosives). Thermal decomposition, even in the thermolabile explosives, was minimal. Traces of explosives in water in the range of 5–100 ppb could be detected and identified.

Keywords: Temperature-programmed injector; Injection methods; Water analysis; Explosives

1. Introduction

Because of the toxicity of most explosives [1], the disposal of large quantities of explosives in an environmentally acceptable manner poses serious difficulties. For many years, obsolete explosives and ammunition were disposed of by burying them in the ground or dumping them in the sea. Wastewater from explosives-manufacturing plants, containing explosives and their degradation products were discharged into rivers and streams. In order to assess the extent of the contamination of an area by explosives it is necessary to detect and analyze the explosives and their degradation products in groundwater and soil. Such analyses may reveal the degree of contamination in areas suspected to be contaminated by improper disposal of obsolete explosives or by wastewater from ammunition plants.

Although gas chromatography–mass spectrometry

(GC–MS) is a well-established technique for trace analysis of organic pollutants, including some explosives [2], it has never been recommended for the analysis of the more thermally labile explosives because of their decomposition in either the heated GC column or injector [3,4]. Several studies were published [3–6] on the analysis of various explosives by GC.

We have used GC–MS with a cooled temperature-programmable injector to analyze picogram amounts of a series of explosives and explosives' ingredients in water. The analyzed compounds included two groups: (A) 2,4,6-trinitrotoluene (TNT), 2,4,6-N-tetranitro-N-methylaniline (Tetryl), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) and pentaerythritol tetranitrate (PETN) and (B) 2,3-, 2,4-, 2,5-, 2,6- and 3,4-dinitrotoluene (DNT).

2. Experimental

The instrument used was a Varian/Saturn 3D GC–MS–ion trap equipped with a Septum programmable injector (SPI) and 4D MS–MS technology. The GC columns used were DB-1 and DB-5MS, 15 m×0.255 mm, I.D., 0.25 μm film thickness, columns (JW Scientific, Folsom, CA, USA).

For group **A** the temperature of the DB-1 column was 80°C for 2 min, programmed to 250°C at 25°C/min, with a final hold of 2 min. The temperature of the SPI was –5°C for 0.3 min, programmed from –5° to 250°C, at a rate of 200°C/min, with a final hold time of 8.4 min. The injector was cooled with liquid CO₂.

For group **(B)** the temperature of the DB-5MS column was 50°C for 2 min, programmed to 260°C,

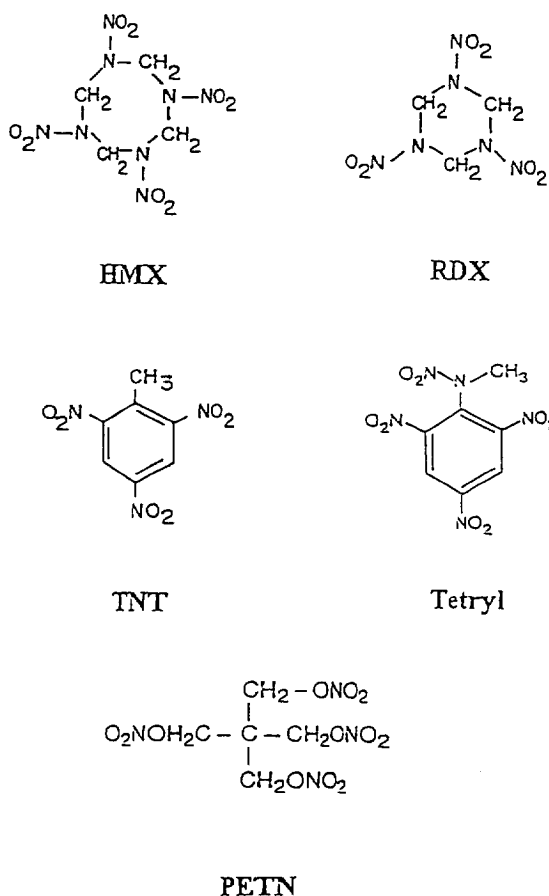
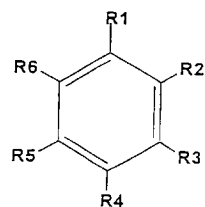


Fig. 1. Explosives of group A.



	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆
1. 2,3-DNT	CH ₃	NO ₂	NO ₂	H	H	H
2. 2,4-DNT	CH ₃	NO ₂	H	NO ₂	H	H
3. 2,5-DNT	CH ₃	NO ₂	H	H	NO ₂	H
4. 2,6-DNT	CH ₃	NO ₂	H	H	H	NO ₂
5. 3,4-DNT	CH ₃	H	NO ₂	NO ₂	H	H

Fig. 2. Explosives of group B.

at a rate of 25°C/min, with a final hold time of 2 min. The temperature of the SPI injector was 45°C for 0.5 min, programmed to 260°C, at a rate of 150°C/min. Helium flow-rate was 1 ml/min.

The ionization mode used was electron ionization (EI). Chemical ionization (CI), with isobutane as reagent, was used for comparison purposes. Ion trap temperature was 170°C. Analyzed samples were prepared by spiking water with a mixture of explosives at various concentrations. Explosives were then extracted from water by liquid–liquid extraction with methylene chloride. After adding methanol, the methanol-dissolved extract was concentrated by a factor of 100 and injected onto the GC system.

Explosives of group **A** (Fig. 1) were obtained in pure form from the Analytical Laboratory of the Israeli Police. Explosives of group **B** (Fig. 2) were purchased from commercial sources (2,3-, 2,4-, 2,6- and 3,4-DNT from Aldrich, Milwaukee, WI, USA and 2,5-DNT from Pfaltz and Bauer, Flushing, NY, USA).

3. Results and discussion

Fig. 3 shows the mass chromatograms and mass spectrum of TNT. We see a typical EI mass spectrum of TNT with a base peak at m/z 210 due to the loss

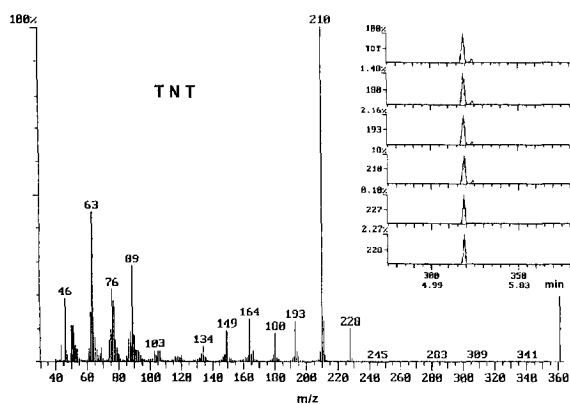


Fig. 3. Mass chromatograms and mass spectrum of TNT.

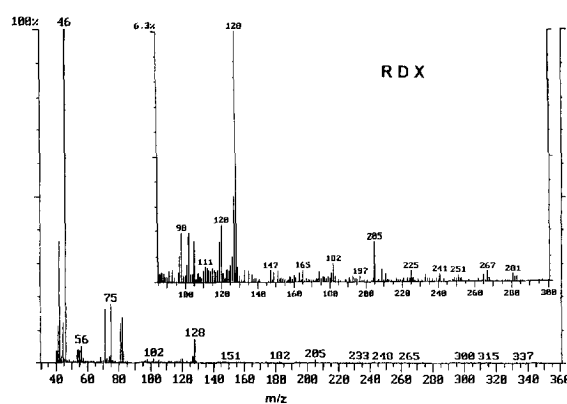


Fig. 6. Mass spectrum of RDX.

of OH from the molecular ion [7]. Figs. 4 and 5 show the mass chromatograms of RDX and HMX, respectively. While the mass spectrum of RDX (Fig. 6) is quite similar to the one previously obtained with a solid probe in the EI mode [8], the mass

spectrum of HMX (Fig. 7) is similar to the one obtained with a solid probe in the chemical ionization-methane mode [8].

Major ions in the mass spectrum of RDX are at m/z 128, due to $[M-2HNO_2]^+$, at m/z 75, due to $CH_3NNO_2^+$ and at m/z 46, due to NO_2^+ . Major ions in the mass spectrum of HMX are at m/z 205, due to $C_3H_5N_6O_5^+$ [9] and at m/z 149, due to $[M+H-2CH_2NNO_2]^+$. These characteristic ions can be used for the identification of RDX and HMX.

The similarities between the mass spectra obtained with a solid probe and with GC-MS show that there is little or no decomposition of RDX and HMX in the GC. Tetryl has been shown to form N-methylpicramide in the ion source before ionization [10]. The mass chromatograms and mass spectrum of Tetryl (Fig. 8 and Fig. 9, respectively) show indeed a mass spectrum typical of N-methylpicramide and do not show any additional decomposition. Major ions in

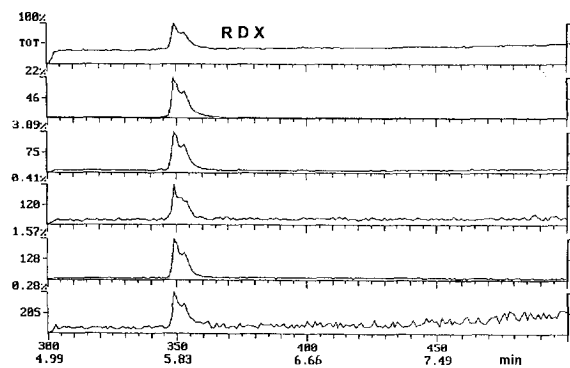


Fig. 4. Mass chromatograms of RDX.

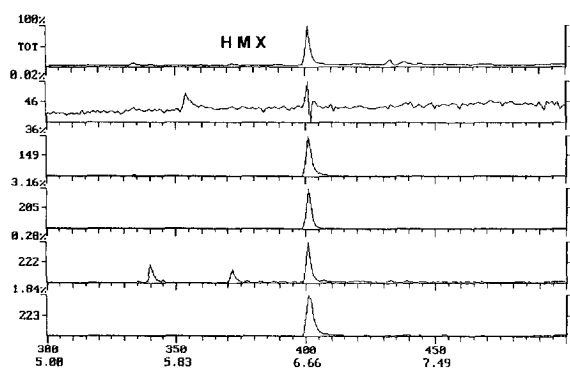


Fig. 5. Mass chromatograms of HMX.

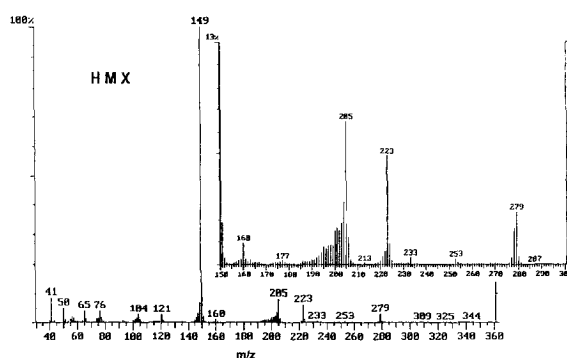


Fig. 7. Mass spectrum of HMX.

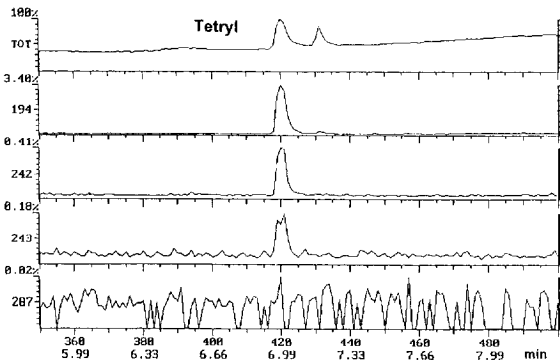


Fig. 8. Mass chromatograms of Tetryl.

the mass spectrum of Tetryl were therefore found to be at m/z 242, due to M^+ of N-methylpicramide, at m/z 224, due to $[M-H_2O]^+$ and at m/z 194, due to $[M-H_2O-NO]^+$. These ions can be used for the identification of Tetryl. Fig. 10 shows the mass chromatograms of a mixture of explosives in water containing 10 ppb of each one of the investigated explosives of group A, with the exception of PETN. Each of the explosives can be identified by at least one typical ion. PETN produced a mass spectrum containing one single ion at m/z 46 and could be identified, at a minimal amount of 100 ppb, by starting the GC run at 50°C (Fig. 11).

The GC-EI-MS analysis of a mixture of isomers of DNT (group B) is shown in Fig. 12. Each one of the isomers is characterized by one or two typical ions as follows: 2,3-DNT by the ions at m/z 135 $[M-OH-NO]^+$ and at m/z 165 $[M-OH]^+$, 2,4-DNT by the ions at m/z 165 and m/z 119 $[M-OH-$

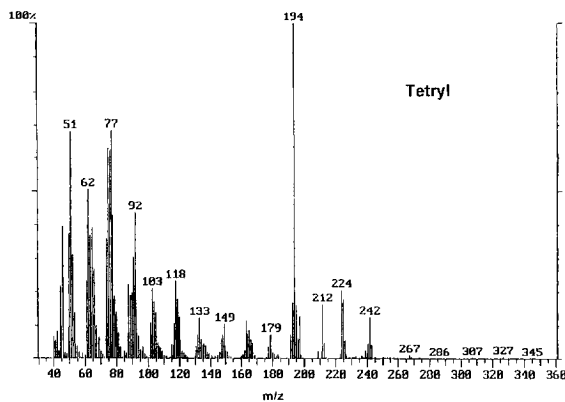


Fig. 9. Mass spectrum of Tetryl.

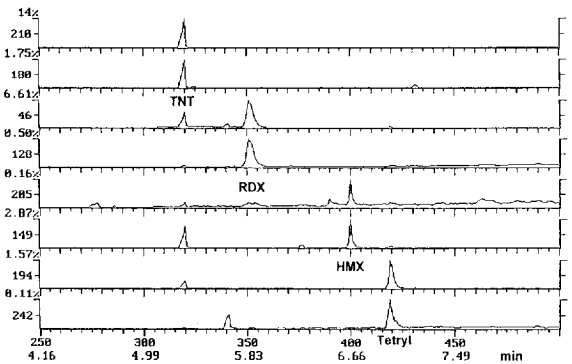
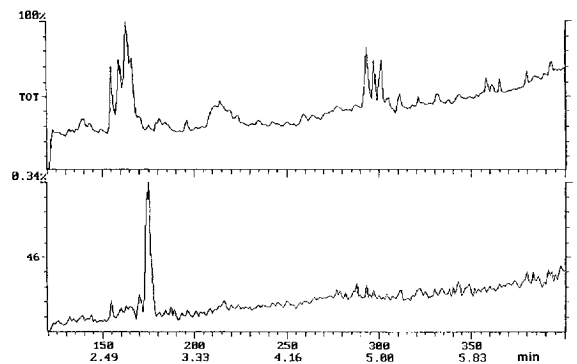
Fig. 10. Mass chromatograms of a mixture of explosives (10 ppb each) extracted from water by liquid-liquid extraction (concentration $\times 100$).

Fig. 11. Mass chromatogram of PETN from a mixture of explosives in water containing 100 ppb PETN.

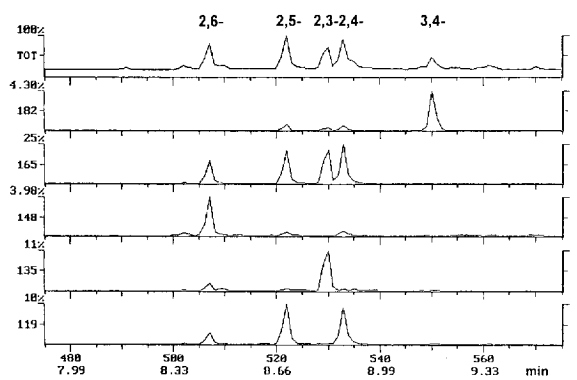


Fig. 12. Mass chromatograms of a mixture of DNT isomers on a DB-5 column.

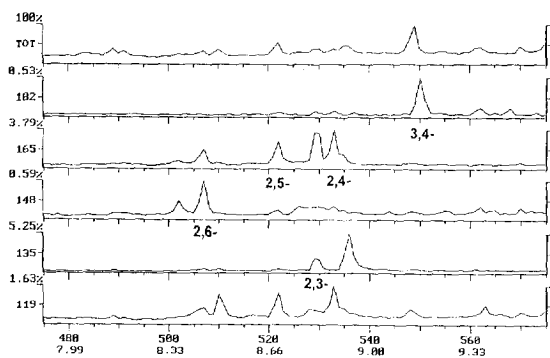


Fig. 13. Mass chromatograms of a mixture of DNT isomers (5 ppb each) extracted from water with a DB-5 column.

NO_2^+ , 2,5-DNT by the ions at m/z 165 and m/z 119, 2,6-DNT by the ions at m/z 165 and m/z 148 $[\text{M}-2\text{OH}]^+$ and 3,4-DNT by the molecular ion M^+ at m/z 182.

Fig. 13 shows the mass chromatograms of the mixture of DNT isomers in water, containing 5 ppb of each one of the isomers.

4. Conclusions

GC-MS with a 15-m column and a temperature-programmed injector can be used for the identification of traces of explosives at ppb levels. Analyzed explosives included thermally labile explosives such as RDX and HMX. Identification was based on typical fragment ions for each one of the explosives.

Acknowledgments

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