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Note

Reversed-phase gradient high-performance liquid chromatography of nitramine munitions and characterization of munitions process samples by gas chromatography–mass spectrometry

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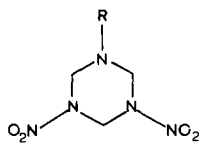
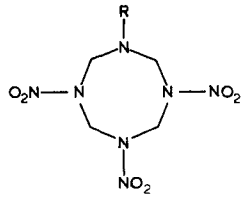
Interest in the separation and identification of organic explosives has remained at a high level for more than a decade, due to environmental and occupational health concerns as well as forensic applications, and a number of analytical methods have been published[1]. While thin-layer chromatographic[2,3] and gas chromatographic (GC)–electron-capture detection[4] procedures have been described, high-performance liquid chromatography (HPLC), with a variety of detectors[5–10] including chemical ionization (CI) mass spectrometry (MS)[11–13], has proven most versatile, sensitive, and widely useful, especially for the more thermally labile munitions compounds. The mass spectra of certain explosives, notably hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)[11–16], octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)[11–14,16], and 2,4,6-trinitrotoluene[11–13,16,17], have been extensively studied in electron impact (EI), CI, field desorption and MS–MS modes, and the fragmentation pathways are well documented.

In the past, nitramine munitions RDX (1a) and HMX (2a), each containing the respective by-products 1-acetylhexahydro-3,5-dinitro-1,3,5-triazine (TAX, 1b) and 1-acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine (SEX, 2b), were purified by batch process recrystallizations from acetone and/or cyclohexanone. The use of dimethyl sulfoxide (DMSO) in a continuous process involving recovery and re-use of the solvent proved to be more efficient and cost effective, but provoked concern over possible health hazards to workers due to the known rapid absorption of the solvent (along with the dissolved nitramines and any other trace organics present) into body tissues.





1a, R = NO_2
1b, R = $OCOCH_3$

2a, R = NO_2
2b, R = $OCOCH_3$

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Previously reported reversed-phase HPLC separations of explosives have utilized isocratic methanol–water[7,12,13] or acetonitrile–water[9,12,13] mixtures. For application to samples from the DMSO munitions recrystallization process we have developed a reversed-phase gradient elution method which provided optimum separation for quantitative determination of RDX, HMX, TAX and SEX, and which is the first open literature method published for the latter two compounds. Since separation and identification of possible munitions transformation products and/or adventitious trace organics was also important, the recrystallization process samples were also extracted and analyzed qualitatively by GC–MS.

EXPERIMENTAL

HPLC analyses

A Waters liquid chromatographic system (Waters Assoc., Milford, MA, U.S.A.) consisted of the following components: two Model 6000A solvent delivery systems, a Model 721 programmable systems controller, a Model 730 data module, a Lambda-max Model 480 LC spectrophotometer, and a Model 710B Waters intelligent sample processor (WISP). A Zorbax C_8 reversed-phase stainless-steel column (25 cm × 4.6 mm I.D., particle size 6 μm, DuPont Instruments, Wilmington, DE, U.S.A.) was used. The nitramines were eluted using a linear gradient program in which pump A contained methanol–water (1:4) and pump B contained methanol–water (4:1), and the methanol–water composition was changed from A–B (95:5) to A–B (50:50) in 25 min at a flow-rate of 1.2 ml/min. The effluent was monitored at 254 nm, 0.05 absorbance units full scale (a.u.f.s.). Standards of 2.0, 1.0, 0.4, and 0.2 mg/l were prepared by dilution of 100 mg/l stock solutions.

GC–MS analyses

GC–MS analyses were performed with a Hewlett-Packard 5985B system in the EI mode equipped with a 25 m × 0.2 mm I.D. fused-silica capillary column (cross-linked OV-1, 0.11 μm thick) interfaced directly to the source (source temperature 200°C). Injection temperature was 150 or 250°C, and the GC oven was programmed from 60 to 250°C at 20°C/min with an initial hold of 1 min. Under these conditions the presence of nitramines did not interfere with analysis of trace organics; mass spectra of the former were not observed.

Sample preparation

For HPLC analyses, 1 ml of liquid was made up to 100 ml in distilled deionized water; further dilutions were made when necessary. A 4-ml portion of each solution was passed through a 0.45-μm Millex-SR filter into a WISP sample vial. Weighed amounts of solid samples were dissolved in acetonitrile (5 ml) and made up to 100 ml in distilled deionized water and treated as above.

For GC–MS analyses, liquid samples containing DMSO and munitions compounds (5 ml) were diluted with water (10–50 ml), filtered when necessary to remove any precipitated munitions compounds, and extracted with methylene chloride (5–10 ml). The methylene chloride extracts were washed with three 25- to 50-ml portions of water, dried (magnesium sulfate), and evaporated, and the residues were dissolved in acetone (10 μl) for injection. River water samples (100–200 ml) were extracted with methylene chloride and the extracts were dried, evaporated, and treated as above.

RESULTS AND DISCUSSION

The samples, obtained at several stages in the munitions recrystallization and recovery of the DMSO, were composites from both the RDX and HMX processes. Quantitative analyses for the nitramines, determined by peak areas, are summarized in Table I. A typical HPLC separation of nitramine standards is shown in Fig. 1, and a typical analysis of a munitions process sample (4) is depicted in Fig. 2. Precision and accuracy of the method have been documented earlier[18] and the ranges of coefficients of variation are listed in Table I. While there was variation among individual compounds, total nitramine content was 5000–10 000 ppm in four of five samples.

TABLE I

HPLC ANALYSES OF MUNITIONS FROM DMSO RECRYSTALLIZATION PROCESS SAMPLES

Compound	*Coefficient of variation**	*Amount (ppm)*			
		*Sample***			
		2	*3*	*4*	*5*
SEX	0.42–11.6	64	66	150	412
HMX	0.45–8.3	1750	1940	3500	41 900
TAX	2.0–12.2	2400	2540	580	648
RDX	0.36–9.5	403	410	5500	39 900

* Inversely proportional to concentration. Detection limit below 100 ng.

** Sample 1 was not precisely determined, but relative amounts were TAX > RDX ⩾ HMX > SEX, total amount *ca.* 5000 ppm.

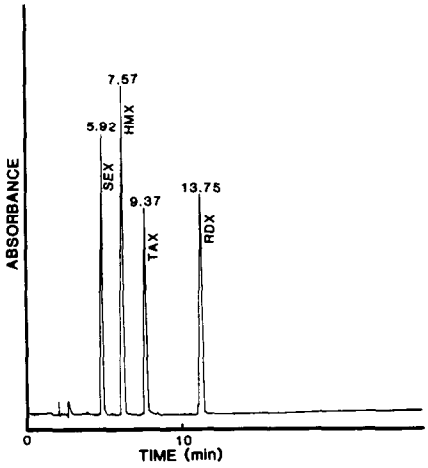


Fig. 1. HPLC separation of nitramine munitions standards (250 ng each).

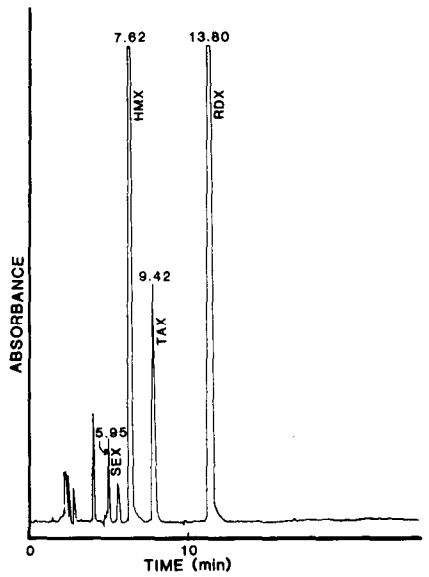


Fig. 2. HPLC analysis of munitions process sample 4.

TABLE II

GC–MS ANALYSES OF TRACE ORGANICS IN DMSO RECRYSTALLIZATION PROCESS SAMPLES

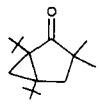
Phthalates were present in all samples.

Identity	*Retention time (min)*	*Found in sample(s)*
Diacetone alcohol*	2.5	1, 2, 5, 6, 7
1,4-Dithiane	2.6	2
trans-4-Chlorocyclohexanol**	3.4	2, 5
Dimethyl sulfone	4.1	4
Benzothiazole	4.9	1, 2, 4, 5
p-Hydroxyacetanilide	6.4	7
1,5-Di-*tert.*-butyl-3,3-dimethylbicyclo[3.1.0]hexan-2-one**	6.8	2, 4, 5
2,6-Di-*tert.*-butyl-4-methylphenol (BHT)	7.0	2, 5, 6
Diphenyloxazole***	7.3	7
Unidentified, mol.wt. 213	7.6	7
3,4'-Dimethyldiphenylmethane**	7.7	6
N-Butylbenzenesulfonamide**	8.9	6
Acetyl-tri-*n*-butyl citrate§	10.9	3
Octadecanamide	12.1	6

* Not detected in sample 4 because of DMSO interference.
** Not a commercial product.
*** Mass spectrum indicated 4,5-isomer rather than the commercially available 2,5-isomer.
§ Citroflex A, citrate plasticizer.

Sample 6 was DMSO which had been distilled for recovery and contained no detectable nitramines. The reason for the tenfold increase in RDX and HMX content of sample 5 is not understood but may be attributed to sampling error.

The trace organic content of samples 1–6 is summarized in Table II. Diacetone alcohol, found in four of the five samples in which trace organics (in addition to the ubiquitous plasticizers) were found, was probably present in all five, but was not detected in sample 4 because of DMSO interference. Benzothiazole was found in four of five samples, and BHT and 1,5-di-*tert.*-butyl-3,3-dimethylbicyclo[3.1.0]hexan-2-one (3) in three of five. No trace organics were found in the DMSO before use. It is clear that, with the obvious exception of dimethylsulfone (present in sample 4), none of the trace organics observed can be attributed to breakdown or transformation of the nitramines or the solvent. This observation suggested water from the Holston River (Kingsport, TN, U.S.A.), which had been used in the process, as the probable source of the trace organics, and prompted an investigation of river water samples. Diacetone alcohol was indeed present in the river water (Table II, sample 7), but the other trace organics were different from those previously observed. This may be attributed to variation of the nature of organic pollutants in the river water over the time between its use in the munitions process and the later sampling.



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With a few exceptions, notably 3, the trace organics identified are commercially available. The genesis of 3 is obscure and particularly intriguing in view of its infrequent citation in the chemical literature. It was first reported in 1971 as the end product of a synthesis requiring six steps from commercially available compounds[19], but was recently identified as one of many trace organics in two highly polluted rivers in Japan[20] and in volatile constituents of certain fungi[21].

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