

TECHNICAL NOTE

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A High Performance Liquid Chromatographic (HPLC) Study of Seven Common Explosive Materials

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ABSTRACT: High performance liquid chromatography (HPLC) can be used to analyze many types of forensic science evidence. Residue of explosives collected at the scene of an explosion is one of those types of evidence that is suited to HPLC analysis. HPLC will be used to separate nitroglycerine (NG), ethyleneglycoldinitrate (EGDN), cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), pentaerythritoltetranitrate (PETN), 2, 4, 6,-trinitrotoluene (TNT), and 2, 4, 6,-trinitrophenylmethylnitramine (tetryl). The minimum detectable limits for each of these explosives will be discussed considering variables such as extraction solvent and detector wavelength. Reports of analysis on standard solutions, spiked materials, and actual explosive debris will be included.

KEYWORDS: criminalistics, explosives, chromatographic analysis

Analysis of debris from the site of an explosion is one important responsibility of the forensic scientist. Although the scene investigation will often indicate the type explosive used, it is necessary for a forensic chemist to verify or identify the explosive material from its residue. Many techniques for examination of explosive residue have been proposed and evaluated by the forensic science community in recent years, but most investigators involved in this area employ an examination scheme consisting of screening techniques and identification techniques [1-7]. Recent literature has proposed the use of high performance liquid chromatography (HPLC) as an identification technique using various kinds of detectors ranging from ultraviolet to mass spectrometry [8-11]. In this investigation the intent was not solely to develop an identification technique, but also a practical screening technique for the most widely encountered explosive materials—nitroglycerine (NG), ethyleneglycoldinitrate (EGDN), cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), 2, 4, 6,-trinitrophenylmethylnitramine (tetryl), 2, 4, 6,-trinitrotoluene (TNT), and pentaerythritoltetranitrate (PETN).

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Reagents and Apparatus

Apparatus

The high performance liquid chromatograph was a Waters Associates Inc. Model 6000A solvent delivery system with a Model U6K injector, a Model 441 ultraviolet detector, and a Shimadzu Model C-R1A integrating recorder. The column was a Waters Associates, Inc. Radial Compression Module® (RCM) with reverse phase cartridge. The Syringe was a 25- μ L Hamilton Scientific.

Solvents and Reagents

The solvents were acetonitrile (HPLC) and methanol (HPLC). The manufacturer supplied samples of TNT, RDX, HMX, PETN, tetryl, and dynamite (age unknown). Additional supplies used included cinder block, nylon carpet, and soil.

Experimental Procedure

Standard solutions of 1000 ppm were prepared for each of the explosive materials (TNT, RDX, HMX, PETN, tetryl, and dynamite). The sample of dynamite used contained both NG and EGDN, but their concentrations were not known. The dynamite used was a straight 60% (60% by weight of NG and EGDN). Both acetonitrile and methanol were chosen as solvents because of the purported solubility of the explosives in them, and their low ultraviolet cutoff (190 and 205 nm). Injections of 10 μ L each were examined by reversed phase chromatography using the following parameters: mobile phase was 70% acetonitrile/30% water, flow rate was 1 mL/min, detector wavelength was 214 nm, and attenuation was 2.0 absorbance units full scale (AUFS).

Triplicate injections of each explosive material under the above conditions indicated an inadequacy for methanol to dissolve HMX and PETN satisfactorily. Because of this, methanol was discarded as a possible solvent.

Standard dilutions of 100, 10, and 1 ppm of each explosive were then prepared using acetonitrile as solvent. Duplicate 10- μ L injections of each explosive dilution were made using the above mentioned chromatographic conditions with changes in attenuation from 2.0 AUFS for the 1000-ppm solutions to 0.02 AUFS for the 1-ppm solutions. Additional dilutions of 0.5-ppm RDX, 0.5-ppm HMX, 0.1-ppm TNT, 0.01-ppm TNT, 0.1-ppm tetryl, and 0.05-ppm tetryl were made and examined with attenuation changes to 0.005 AUFS in some instances.

Samples of fiber backed clean nylon carpet, untreated concrete block, and soil (mixture of humus and clay) were next placed in 250-mL beakers. Twenty-seven such samples were prepared—three sets of nine. To one beaker of each type material was added 1 mL of each of three concentrations (1000, 100, and 10 ppm) of dynamite, thus yielding nine spiked samples. This procedure was repeated with a mixture of TNT and tetryl and a mixture of RDX, HMX, and PETN. After several hours of air drying at room temperature, approximately 40 mL of acetonitrile was added to each beaker and the samples were allowed to stand overnight. This time frame was to allow for complete extraction. The samples were then filtered, evaporated to dryness, and redissolved in from 1 to 2 mL of acetonitrile. Note that during evaporation NG and EGDN might be lost in part or in total. If either of these explosives are suspected the evaporation should be done without heat. The effect of cover glasses was not noted and blank beakers were not used because percent recovery was not to be determined. Each of these 27 samples was then examined by the HPLC technique to determine the detectability of explosive residue at each of the three levels—1000, 100, and 10 ppm. Injection size remained 10.0 μ L with attenuation varying from 2.0 AUFS for 1000-ppm samples to 0.02 AUFS for the 10-ppm samples.

Results

The chromatographic conditions were found to separate the seven explosive materials in less than 7 min. Reproducibility was found to be $\pm 0.06 k'$ using nine injections of each explosive at concentrations ranging from 1000 to 1 ppm (Table 1). The value k' is defined as the peak retention time divided by the void volume retention time. Note that retention times did shift because of slight changes in pressure in the Radial Compression Module, but this shift also affected the solvent peak. This situation can be dealt with by using standard explosive injections to standardize a sequence of examinations.

The limits of detectability for this technique compare quite favorably with thin-layer chromatography (TLC) as seen in Table 2. Figures 1 and 2 illustrate the resulting chromatograms of 0.1-ppm TNT and 0.5-ppm RDX, respectively. It is evident that even at these levels the HPLC system described performs favorably and the chromatograms are easily interpreted.

In applying a more practical approach, it was found that 10 ng (1 mL of 10-ppm solution) of each explosive tested could be recovered from three different materials (nylon carpet, soil, and block) and detected with this technique. Figure 3 illustrates this capability by detection of RDX, HMX, and PETN from block. Although this chromatogram does not show a peak for PETN, by changing the attenuation to 0.05 AUFS the PETN peak becomes evident. The effect of the various materials on resultant chromatograms varied slightly. Materials containing a wide range of organics, either natural (soil) or manufactured (nylon carpet), tended to exhibit somewhat high backgrounds and thus increased the difficulty in reaching a conclusion when low levels of the explosives were present. It was, however, still possible to detect each of the explosives at the 10-ng level.

TABLE 1—The k' values \pm a deviation from the mean for nine injections of each explosive.

Explosive	k'
HMX	1.88 \pm 0.05
RDX	2.09 \pm 0.04
EGDN	2.31 \pm 0.04
Tetryl	2.47 \pm 0.05
NG	2.64 \pm 0.05
TNT	2.85 \pm 0.04
PETN	2.90 \pm 0.06

TABLE 2—Limits of detectability for seven explosives using TLC [5] and HPLC.

Explosive	TLC, μ g	HPLC, μ g
NG	NA ^a	0.01 ^b
EGDN	0.5	0.01 ^b
HMX	0.25	0.005
RDX	0.25	0.005
Tetryl	0.25	0.0005
TNT	0.20	0.0001
PETN	0.40	0.01

^a TLC limits not available.

^b NG and EGDN were detectable in a 1-ppm solution of dynamite that contained both compounds.

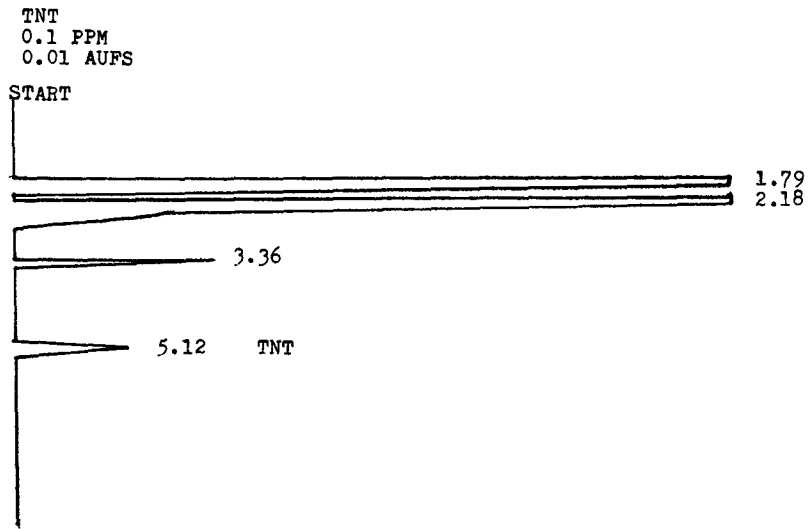


FIG. 1—Ten-microlitre injection of TNT standard solution (0.1 ppm).

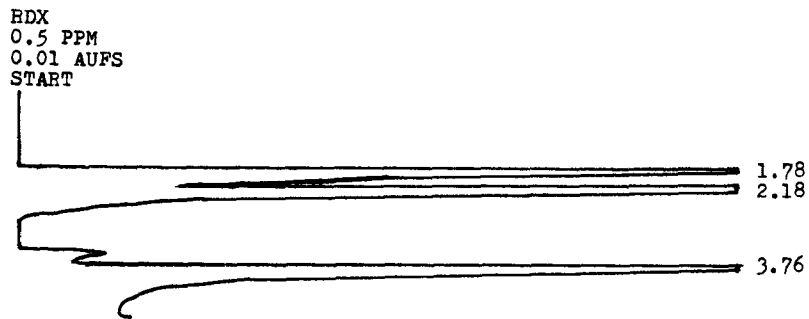


FIG. 2—Ten-microlitre injection of RDX standard solution (0.5 ppm).

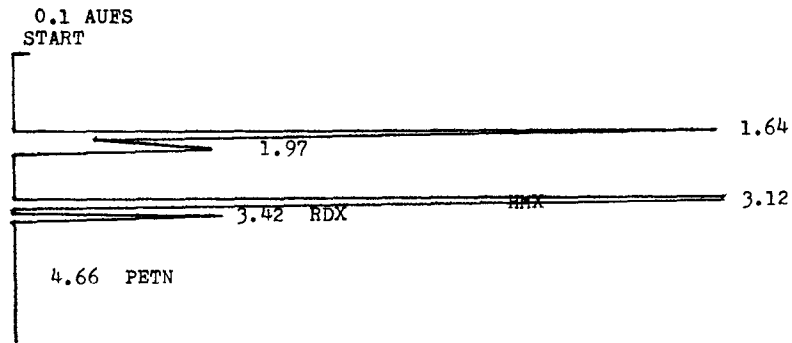


FIG. 3—Ten-microlitre injection of cinder block extract; block had been spiked with 10 ng of RDX, HMX, and PETN.

Summary

The HPLC conditions above can be used both as a screening technique and as an aid to identification. EGDN, NG, TNT, RDX, HMX, PETN, and tetryl can be separated in less than 7 min and detected at levels less than present TLC techniques. It should be pointed out that a low level of NG in the presence of TNT or tetryl or both is masked. This can be dealt with by changing the wavelength to 229 nm and noting either a larger peak (TNT or tetryl) or a smaller one (NG). Extraction of explosives from various materials does not diminish the usefulness of this technique. It does however, set limits beyond which the substrate effect is important. In this work 10 ng of each explosive was detectable, thus illustrating the level of usefulness for routine use of this technique. This technique has been applied to several cases involving explosive debris. Although the substrate effect has prevented conclusive results in some samples, other samples have reacted favorably.

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