



# Standard Test Method for Analysis of Nitroaromatic and Nitramine Explosive in Soil by High Performance Liquid Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 5143; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method describes a procedure for the laboratory determination of the concentration of nitroaromatic and nitramine explosives in soil. The explosives involved in this test method are as follows: HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), TNT (2,4,6-trinitrotoluene), TNB (1,3,5 trinitrobenzene), DNB (1,3 dinitrobenzene), tetryl (methyl-2,4,6-trinitrophenylnitramine), and 2,4-DNT (2,4-dinitrotoluene).

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *This standard does not purport to address the safety concerns associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

C 670 Practice for Preparing Precision Statements for Test Methods for Construction Materials<sup>2</sup>

D 653 Terminology Relating to Soil, Rock, and Contained Fluids<sup>3</sup>

E 11 Specification for Wire Cloth Sieves for Testing Purposes<sup>4</sup>

E 682 Practice for Liquid Chromatography Terms and Relationships<sup>5</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 Refer to Terms and Symbols D 653 for the definitions of standard terms relating to soil and rock.

### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *HPLC*—high power liquid chromatography.

## 4. Significance and Use

4.1 This test method can be used to make reliable and reproducible measurements in soil in the range from the detection level to the percent levels of each of seven explosive compounds.

4.2 This test method does not attempt to quantify the reactivity or mobility of the explosive content, only the concentration of these compounds in the soil.

4.3 This test method can be used to determine the extent of contamination resulting from the use, misuse, or spillage of explosive compounds. It is useful to determine the effectiveness of clean-up actions at disposal sites, and to determine the environmental impact at explosives disposal, manufacturing, or storage sites.

## 5. Apparatus

5.1 *Liquid Chromatograph*, conforming to the description and requirements of Practice E 682 and equipped with two 25 cm by 4.6 mm reversed-phase HPLC columns (one LC-18, one LC-CN); a fixed 254 nm UV detector; an integrator and a 100  $\mu$ L sample loop injector.

5.2 Solvent Delivery Module, should be reliable enough for isocratic analysis with flow range capability from 0.1 to 3.0 mL/min.

5.3 *Volumetric Pipets*.

5.4 *Scintillation Vials*.

5.5 *Plastic B-D Syringe*, fitted with a disposable 0.5  $\mu$ m filter assembly.

5.6 *Vortex Mixer*.

5.7 *Amber Injector Vials*.

5.8 *Mortar and Pestle*.

5.9 *Rubber Tipped Pestle*.

<sup>1</sup> This method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.06 on Physico-Chemical Properties of Soils and Rocks.

Current edition approved Nov. 30, 1990. Published January 1990.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 04.02.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 04.08.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 14.01.

## 6. Reagents

6.1 Unless otherwise stated, it is intended that all reagents conform to the specification of the committee on Analytical Reagents of the American Chemical Society.<sup>6</sup>

6.2 *HPLC Grade Methanol.*

6.3 *HPLC Grade Acetonitrile.*

6.4 *ASTM Type I Water.*

6.5 Reference Standards of the following:

6.5.1 HMX,

6.5.2 RDX,

6.5.3 TNT,

6.5.4 DNB (1,3-dinitrobenzene),

6.5.5 TNB (1,3,5-trinitrobenzene),

6.5.6 Tetryl, and

6.5.7 2,4-DNT and 2,6-DNT.

## 7. Procedure

### 7.1 Sample Preparation:

7.1.1 Air dry the soil to a constant mass out of direct sunlight at normal ambient humidity and 20 to 25°C (room temperature).

7.1.2 Disaggregate the soil using a rubber tipped pestle and mortar, and sieve the soil through a No. 10 sieve to remove the coarser stones and pebbles. Discard only those particles that are not passable through the No. 10 sieve.

7.1.3 Grind the soil using a pestle and mortar.

7.1.4 Sieve the soil through a 30 mesh sieve. Ensure that all of the particles are ground to pass through the sieve openings and are collected prior to continuing.

7.1.5 Thoroughly mix the collected soil fraction and draw a 2.00 gm sample for each test replicate.

7.1.6 Thoroughly clean the sieves, pestles, and mortars with laboratory soap and water followed by an isopropanol rinse between samples.

### 7.2 Extraction of Soil:

7.2.1 Weigh out exactly 2.00 g of soil into a 11.1 mL (6 dram) screw top glass vial equipped with a TFE-fluorocarbon-lined cap.

7.2.2 With a volumetric pipette, introduce 10.0 mL of acetonitrile to the soil, and screw on the closures tightly.

7.2.3 Place the vials on a vortex mixer for 1 min followed by placing the sample in an ultrasonic bath for 18 h.

7.2.4 The ultrasonic bath should be maintained near ambient temperature to minimize loss of tetryl due to thermal degradation. Remove the samples from the bath and allow them to stand for a minimum of 15 min to allow the larger particles to settle.

7.2.5 With a volumetric pipet, remove a 5.00 mL aliquot of the suspension and mix it with a 5.00 mL of 5 g/L aqueous CaCl<sub>2</sub> in a glass scintillation vial. Shake the vials and allow to stand for 15 min.

7.2.6 Filter about 5 mL of the clarified sample into a clean scintillation vial by forcing the supernatant through a 0.5 µm filter using a 3 mL disposable syringe. The first millilitre is discarded and the remainder saved for analysis. Place the filtered sample in an amber injection vial for analysis.

### 7.3 Liquid Chromatographic Analysis:

7.3.1 Accomplish the liquid chromatograph separations isocratically by the use of a 5 µm, reversed-phase LC-18 and LC-CN cartridge column, with a 50/50 methanol/water mobile phase, at a flow of 1.5 mL/min. The LC-CN cartridge column is used for confirmation of the analytical results.

7.3.2 Make quantifications at the 254 nm wavelength.

7.3.3 Base quantitation on response factors established by replicate analysis of a single high range standard. Dilute standards, controls, and blanks 1:1 with aqueous CaCl<sub>2</sub> prior to analysis.

7.3.4 The elution time for the total assay is less than 15 min.

## 8. Calculation

8.1 Experience indicates that a linear calibration curve with zero intercept is appropriate for each compound. Therefore, calibration is accomplished by repeated analysis of a high range standard. The mean response (*R*) for each compound obtained in the peak height mode is calculated for each analyte. The response factors (*RF*) are then obtained by dividing each *R* by the known solution concentration (*C*) for that compound in units of µg/L.

$$RF = R/C \quad (1)$$

8.2 The concentrations of analytes in the extracts are obtained by dividing the response of each analyte (*R<sub>a</sub>*) by the appropriate response factor (*RF<sub>a</sub>*).

$$C_a = R_a/RF_a \quad (2)$$

8.3 The concentration in soil (*X<sub>a</sub>*), on µg/g basis, is then obtained by multiplying the solution concentration by the total volume of extract (0.010 L) and dividing by the actual mass of dried soil used (*M*).

$$X_a = (C_a \times 0.010)/M \quad (3)$$

## 9. Report

9.1 For each soil tested, report the following information:

9.1.1 The sample identification,

9.1.2 The specific analyte,

9.1.3 The detection limit, and

9.1.4 The concentration of explosive found in µg/g of dry soil.

## 10. Precision and Bias

### 10.1 Precision:

10.1.1 *Within-Laboratory Precision*—The within-laboratory standard deviations (also called repeatability) for the seven analytes were obtained by means of a collaborative test. The test results were obtained from seven laboratories conducting analysis of eight soils in duplicate. Four of the test soils were field contaminated soils and four were spiked soils. The within-laboratory standard deviation was obtained from the

<sup>6</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

agreement of duplicates (see Footnote 7).<sup>7</sup> Within-laboratory precision estimates are presented in Table 1. Therefore, the results of two properly conducted tests by the same operator with the same equipment on duplicate samples should not be considered suspect unless they differ by more than the values presented in the within lab, 2ds column of Table 1 (See

Footnote 7).<sup>7</sup> The data in Table 1 satisfy the 1s and 2ds requirements outlined in Practice C 670.

10.1.2 *Between-Laboratory Precision*—The between-laboratory precision (also called reproducibility) was obtained from the results of a seven-laboratory collaborative test. The between-laboratory precision estimates (see Table 1) were obtained by the method described in Footnote 8.<sup>8</sup> Therefore, the results of two properly conducted tests by different operators with the different equipment on duplicate samples should not be considered suspect unless they differ by more than the values presented in the between lab, 2ds column of Table 1.

10.2 *Bias*—The procedure in this test method for measuring the explosive content of soils has no bias because the value of the explosive residue content is only defined in terms of the test method. However, to aid the user of this standard in determining bias relative to other methods, the percent recovery was obtained from regression analysis of the four spiked soils analyzed in duplicate in the collaborative test described above. Results are presented in Table 1.

## 11. Keywords

11.1 Army; explosives; liquid chromatography; military; soil.

<sup>8</sup> Youden, W. J. and Steiner, E. H. Statistical Manual of the AOAC, 1978.

<sup>7</sup> U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory Report 87-7, Development of an Analytical Method for Explosive Residues in Soil, June 1987.

**TABLE 1 Performance Data for Method for Determination of Nitroaromatics and Nitramines Residues in Soil**

Analyte	Retention Time, Min	Detection Limits, <sup>A</sup> µg/g	Bias (Recovery) <sup>B</sup> , %	Precision <sup>C</sup> , µg/g	
				Within-Lab	Between-Lab
				1s (2ds)	1s (2ds)
HMX	2.4	1.27	95.4	3.7 (10.5)	5.7 (16.1)
RDX	3.7	0.74	96.8	2.3 (6.5)	4.3 (12.2)
TNB	5.1	0.29	92.0	4.4 (12.4)	6.8 (19.2)
DNB	6.2	0.11	93.0	4.0 (11.3)	6.9 (19.5)
Tetryl	6.9	0.12	74.7	17.9 (50.6)	30.7 (86.8)
TNT	8.4	0.08	96.8	3.5 (9.9)	4.7 (13.3)
2,4-DNT	10.1	0.03	96.0	3.4 (9.6)	4.4 (12.4)

<sup>A</sup> Obtained using EPA MDL procedure at the 99 % confidence level.

<sup>B</sup> Obtained from the slope of the regression line versus known concentrations collaborative tests.

<sup>C</sup> Obtained from collaborative test results.

## References

- (1) 0.2 U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory Report 88-8, Development of an analytical method for the determination of explosive residues in soil, Part II; Additional development and ruggedness testing. July, 1988.
- (2) 0.3 U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory Report 89-9, Development of an analytical method for the determination of explosive residues in soil, Part III; Collaborative test results and final performance evaluation. 1989.
- (3) 0.4 U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory Report 85-15, TNT, RDX, and HMX explosives in soils and sediments, analysis techniques and drying losses. October 1985.
- (4) 0.5 U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory Report 85-22, Comparison of extraction techniques and solvents for explosive residues in soil. November, 1985.

*ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.*

*This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).*