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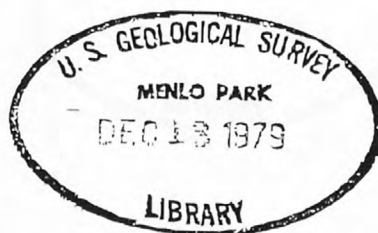
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GEOLOGICAL SURVEY

DIRECT ANALYSIS OF RDX AND TNT IN WATER BY
HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY



OPEN-FILE REPORT 79-916

This report is preliminary and has not been edited or reviewed for conformity
with Geological Survey standards and nomenclature

Menlo Park, California

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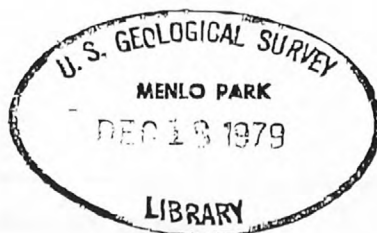
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By D. F. Goerlitz

U. S. GEOLOGICAL SURVEY

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Menlo Park, California
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UNITED STATES DEPARTMENT OF THE INTERIOR

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GEOLOGICAL SURVEY

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OPEN-FILE REPORT

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CONTENTS

	Page
Abstract-----	1
Introduction-----	2
Method-----	3
Summary of method-----	3
Application-----	3
Interference-----	3
Apparatus-----	3
Reagents-----	4
Procedure-----	4
Calculation-----	5
Report-----	6
Precision-----	6
References Cited-----	7

Conversion Factors

For those readers who may prefer metric rather than inch-pound units, the conversion factors for terms used in this report are listed below.

Inch-pound	Multiply by:	Metric
gal (gallons)	3.785	L (liters)
in (inches)	25.40	mm (millimeters)
in ² (square inches)	645.2 x 10 ²	mm ² (square millimeters)
lb/in ² (pounds/square inch)	6.897	kPa (kilopascal)

DIRECT ANALYSIS OF RDX AND TNT IN WATER BY
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By D. F. Goerlitz

ABSTRACT

A method for the determination of RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and TNT (2,4,6-trinitrotoluene) directly in water is given. The high-performance liquid chromatographic technique permits detection down to 0.1 microgram per liter in filtered water. No ancillary extraction or concentrating procedures are used.

INTRODUCTION

The Geological Survey has investigated at least two occurrences of suspected ground-water contamination by explosives (Tracy and Dion, 1976; Van Denburgh and Squires, 1976). The high explosive TNT (2,4,6-trinitrotoluene) was adopted as the primary, conventional bursting charge by the U.S. Army in 1904. Heavy production and use of both TNT and RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) during and after World War II have resulted in many waste-disposal problems, not only at manufacturing plants but also at sites of filling, emptying and cleaning bombs and shell casings. Until recently, it has been common practice to dispose of waste fluids from these operations into unlined ponds. Consequently, contamination of ground water by seepage or percolation of waste water has occurred.

Previous investigators (Hoffsommer and Rosen, 1972; Goerlitz and Law, 1975) used gas chromatography for the determination of TNT and RDX in water. Both compounds are thermally unstable, especially in the presence of metal. This property requires the use of so-called all-glass chromatographic systems (from injection port to detector). To avoid problems associated with the thermal instability and low volatility of these and similar compounds, Daoli and Juhasz (1974) demonstrated the application of high-speed liquid chromatography for analysis of propellants and explosives. Also, Vouros et al. (1977) took advantage of non-destructive HPLC (high-performance liquid chromatography) for forensic analysis to isolate microgram quantities of explosive compounds. Both of the above methods were performed by normal-phase HPLC, and although this technique is non-destructive it is less sensitive than gas chromatography. Normal-phase HPLC, as well as gas chromatography, requires isolation by solvent extraction of the compounds from water.

Reverse-phase HPLC permits the analysis of aqueous samples using a water-miscible solvent as the eluting or mobile phase. Walsh and others (1973) used the reverse-phase technique for analysis of explosives in munition wastes. TNT and by-products were sorbed from manufacturing waste water on a column of styrenedivinyl benzene resin, and then eluted with acetone. TNT in the range of 1 to 100 ppm (parts per million) was readily determined in the aqueous concentrate. Poyet and others (1976) applied reverse phase HPLC to the analysis of very polar explosives stabilizers and normal phase HPLC to the analysis of RDX.

The following method permits accurate determination of RDX and TNT in water at submicrogram-per-liter levels, directly, without preconcentration or solvent extraction. This improved technique employs reverse-phase HPLC with gradient elution and requires minimal sample preparation.

METHOD

1. Summary of method

The explosives RDX and TNT are determined directly in filtered water samples. The filtrate is analyzed by reverse-phase HPLC using a water-acetonitrile linear gradient elution program for the mobile phase.

2. Application

This method is useful for the determination of both RDX and TNT in filtered water samples down to a detection limit of 0.1 µg/L (micrograms per liter).

3. Interference

Any compounds having chemical and physical characteristics similar to RDX or TNT may cause interference. Care must be taken in order to avoid adding contaminants during sampling and transport of samples. Only glass sample containers should be used; teflon may be used as closure gaskets. No organic matter such as paints, plastic, oils or well-drilling lubricants should be allowed to contact the sample. All apparatus must be meticulously clean and reagents must be purified, or of HPLC quality, especially the acetonitrile and water-mobile phases.

4. Apparatus

4.1 Centrifuge: Bench-top, accomodating 15-mL centrifuge tubes and a variable speed to 3000 revs/min (revolutions per minute).

4.2 Chromatograph: A high-performance liquid chromatograph capable of operating to a pressure of 4000 lb/in² (pounds per square inch) or greater, having a calibrated sample-injection loop of 2.0 mL or greater, a linear solvent gradient elution program capability, and an ultraviolet detector set at 254 nm (nanometer) wavelength. A Waters Associates^{1/} ALC/GPC 204 liquid chromatograph equipped with the dual channel detector, the model 6000A solvent delivery system, and the model 660 solvent flow programmer was used.

4.3 High-performance liquid chromatographic column: A stainless-steel column, 3.9 mm inside diameter by 300 mm long, packed with reverse-phase material having a particle size of 10 micrometers. A Waters Associates µBondapak C18, part number 27324, was used.

4.4 Filtration apparatus: All-glass filter apparatus for vacuum filtering, using 47-mm diameter membrane filters, and having a funnel volume of 300 mL and a flask volume of 1 L; a Millipore part, number XX 15 047 00, was used. A Swinny-syringe filtration apparatus consisting of a 10-mL glass syringe and a 25-mm diameter filter holder having standard Luer fittings; a Millipore part, number XX 30 025 00, was used.

^{1/} The use of brand names in this report is for identification purposes only and does not imply endorsement by the U. S. Geological Survey.

4.5 Filter membranes: A membrane filter inert to acetonitrile, having a pore diameter of 0.45 μm (micrometer) or less, for vacuum filtration. Sela's Flotronics silver membrane filter number FM-47.45 was used. For water filtration a methanol-water leached membrane of 0.45 μm or less. A Nucleopore Corp. 0.4 μm , number 111107, was used. For syringe filtration, a Nucleopore Corp. 0.1 μm number 110605 was used. Leaching of membranes is performed in the filtration apparatus just prior to use.

4.6 Integrating equipment: A compensating polar planimeter readable to the nearest 0.1 mm^2 or 0.01 square inches is acceptable. Other means of integration demonstrating equal or greater accuracy may be used. A Spectra-Physics System 1 with calculation accessory was used.

4.7 Microbalance: A Cahn Gram Electrobalance or equivalent.

4.8 Recorder: A strip chart recorder having a chart speed of 13 mm per min, a pen speed of 1 sec, and a span of 10.0 millivolts.

4.9 Syringes: A syringe having a capacity of 10.0 mL and a needle size compatible with the liquid chromatograph injection port.

5. Reagents

5.1 Acetonitrile, high-performance liquid chromatography quality.

5.2 Methanol, high-performance liquid chromatography quality.

5.3 RDX and TNT standards: Reference or analytical grade chemicals can be obtained from chemical specialty suppliers or from military sources.

5.4 Water, distilled, obtained from a high-purity tin-lined still. The feed water is passed through an activated carbon filter. The distillate is collected in a tin-silver storage tank, and the stored water is irradiated with ultraviolet light. A gravity delivery system is used and no plastic material other than Teflon contacts the distilled water. For HPLC, the water is filtered through a 0.45 μm membrane filter. J. T. Baker Chemical Co. catalog number 3-4218 HPLC grade water can be used.

6. Procedure

6.1 Calibration: Calibrate each chromatographic system using RDX and TNT reference standards at concentrations ten times greater than the lower detection limit and under operating conditions to be used for analysis. A 2.0-mL injection of a solution containing 1.0 $\mu\text{g/L}$ of either RDX or TNT should give a full-scale response on the recorder at a detector setting of 0.005 absorbance units full-scale at 254 nm wavelength and a solvent flow rate of 2.0 mL/min. RDX elutes in 310 seconds and TNT elutes in 600 seconds on a linear gradient from 100 percent water to 100 percent acetonitrile in 10 min.

6.2 Sampling: Collect samples according to recommended practice for organic analysis (for example, Goerlitz and Brown, 1972, p. 2-3). Special care is required to avoid contamination; see Section 3, Interference. The sample is cooled in ice or refrigerated immediately after sampling. Shipment to the laboratory is by the most expeditious means to limit delays before analysis. No sample preservation other than chilling is used and samples are analyzed immediately upon receipt.

6.3 Analysis: Transfer 15 mL of sample into a centrifuge tube.

6.3.1 Centrifuge sample at 2000 revs/min for 5 min.

6.3.2 Prepare the Swinny-syringe filtration unit and clean the filter by passing through it 5 mL of methanol followed by 5 mL of reagent water.

6.3.3 Filter the supernatant (discarding the first 3 mL) directly into the 2.0-mL sample loop of the liquid chromatograph until full. The calibrated loop is designed to permit excess sample to exit the tube to insure filling it.

6.3.4 Inject the sample and allow the water mobile phase to flush the sample loop for a total of 90 seconds. Close the sample loop to permit the mobile phase to by-pass the loop.

6.3.5 Start the solvent program on a linear gradient from 100 percent water to 100 percent acetonitrile in 10 min. The start of the solvent program is also the starting time for the chromatographic analysis. Avoid any delays between sample injection and the start of the gradient elution.

6.3.6 Calibration reference standards, except for centrifugation, are filtered and analyzed in the same manner as the samples.

7. Calculation

Each chromatographic system must be calibrated with standards. The response, or absorbance, of the detector is an analog display on the strip-chart recorder, and the area under the curve is proportional to the amount of material passing through. The time elapsed from the start of the solvent elution program to the differential curve maximum is designated as the retention time for a particular component.

7.1 Qualitative analysis: Direct comparison of the retention time of the sample component with that of an authentic standard in the method used for qualitative identification.

7.2 Quantitative analysis: Measurement of the chromatogram-peak area by use of a planimeter or any other method of equal or greater accuracy is acceptable. If a planimeter is used, the average of at least two measurements is taken.

8. Sample calculation: The concentration of RDX and TNT found in the water can be calculated using the following equation:

$$\text{Concentration of component } (\mu\text{g/L}) = \frac{A}{m} \cdot \frac{1000}{V_i}$$

where A = area of component response,

m = slope (calibration factor), in unit area per μg , and

V_i = ml of sample injected.

9. Report

Determination of RDX and TNT is reported as follows: At concentration less than 1.0 $\mu\text{g/L}$, report to the nearest tenth; at concentration of 1.0 $\mu\text{g/L}$ or greater, report to two significant figures.

10. Precision

Tests of the method using well water fortified with RDX and TNT, each at 10 $\mu\text{g/L}$ concentration, gave 97 ± 8 percent recovery.

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