GAS CHROMATOGRAPHIC METHOD FOR THE ANALYSIS OF TNT AND RDX EXPLOSIVES CONTAMINATING WATER AND SOIL-CORE MATERIAL

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CONVERSION FACTORS

For use of those readers who may prefer to use metric units rather than English units, the conversion factors for the terms used in this report are listed below.

English	*Multiply by:*	*Metric*
gal (gallon)	3.785	l (litres)
in (inches)	$2.540 \times 10^{+1}$	mm (millimetres)
in^2 (square inches)	6.452×10^{2}	mm^2 (square millimetres)

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ABSTRACT

A gas chromatographic method for the analysis of both water and soil-core material for TNT and RDX is presented. The explosives may be determined to 0.01 microgram per litre in 1-litre water samples and 0.2 micrograms per kilogram in 50 grams of soil. Provision is made for removal of environmental interference by use of an alumina chromatographic column.

INTRODUCTION

The high explosive TNT (2,4,6-trinitrotoluene) was adopted as the primary, conventional bursting charge by the U.S. Army in 1904. RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), another important high explosive, is used extensively in mixtures with TNT as a semi-liquid fusable explosive and as a primary detonator. Because of the vast tonnage of TNT and RDX produced during and after World War II, there is increasing concern over the possible contamination of the environment by these compounds.

Inherent in the manufacture of explosives, and in other processes such as shell loading and demilling, is the use of large quantities of water. It has been estimated that a single plant can use as much as 500,000 gal (1.9 million litres) of water per day in the processing of explosives and in washing down equipment and buildings (Walsh and others, 1973). Walsh and others (1973) and Won and others (1974) stated if the volume of contaminated waste water exceeds the capability for disposal by incineration it is disposed of by discharging into streams or ponds. Munitions have also been disposed by dumping at sea (Hoffsommer and Rosen, 1972).

TNT is toxic to certain fish at concentrations of about 2 µg/ml (micrograms per millilitre) (Won and others, 1974) and is considered to be severely toxic to humans (Sax, 1957). Similarly, RDX is toxic to humans, but to a lesser degree (Sax, 1957). Hoffsommer and Rosen (1973) experimentally determined that, after more than 100 days in contact with sea water, TNT was not hydrolyzed to any measurable degree and RDX was only about 12 percent hydrolyzed. Both compounds, however, are known to hydrolyze when warmed with dilute alkali. In view of the recognized toxicity and refractory nature, discharge of TNT and RDX waste into streams or ponds (and potentially ground water) may constitute a pollution hazard.

Previous investigators (Hoffsommer and Rosen, 1972 and Hoffsommer and others, 1972) have developed techniques for the determination of explosives in sea water, ocean floor sediment and fauna. The following improved method affords an accurate determination of TNT and RDX in surface and ground water and in soil. The method is not hampered by the presence of many, naturally occurring, organic substances that may also be in the sample and is, therefore, useful in determining the extent and concentration of contaminants at very low levels.

METHOD

1. Summary of method

The explosives TNT and RDX are extracted from water or soil-core samples with volatile solvents. After drying and removing the bulk of the solvent the compounds are separated from extraneous material by column adsorption chromatography. TNT and RDX are determined by electron capture gas chromatography using two columns of different retention characteristics.

2. Application

This method is usable for the analysis of both water and soil-core material for TNT and RDX. These compounds may be determined to 0.01 µg/l (micrograms per litre) in 1-litre water samples and 0.2 µg/kg (micrograms per kilogram) in 50 g (grams) of core material.

3. Interference

Any compound or compounds having chemical and physical properties similar to TNT or RDX may cause interference. The procedure incorporates a column chromatographic technique for the purpose of removing extraneous material. To avoid contamination, only glass sample containers should be used. Teflon[1/] may be used for closure gaskets. No organic matter such as paints, plastics, oils, or drilling lubricants should be allowed to contact the sample.

[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. Apparatus

4.1 Chromatography columns: General utility glass columns, 10-mm (millimetre) ID (inside diameter) and 300-mm long having a sealed-in coarse porosity fritted disc. The columns are prepared by filling to a depth of 10-mm with granular-anhydrous sodium sulfate. An 80-mm layer of adsorbent is added, settled with vibration and topped with a 10-mm layer of sodium sulfate.

4.2 Compressed gases: Use gases recommended by the manufacturer of the particular instrument system being used. Select prepurified grade or better, furnished in size 1A high pressure cylinders (CAUTION: Never use oxygen regulators with other gases.)

4.3 Concentrating apparatus: A Kuderna-Danish concentrator, 500-ml (millilitre) capacity with a 1-ball Snyder column and a 4.00-ml graduated receiver tube.

4.4 Gas chromatograph: A gas chromatograph having an electron-capture detector which, for an injection of 100 pg (picograms) of TNT gives 25-mv-s (millivolt-seconds) of response is adequate. A Varian-Aerograph Model 600-D, or equivalent may be used. (A radioisotope-byproduct-material license is required for electron-capture detectors employing radioactive sources.)

4.5 Gas chromatographic columns: Two gas chromatographic colums are fabricated from lengths of Pyrex glass tubing 1.5 m (metres) long x 1.8 mm ID. One column is packed with 80-100 mesh Supelcoport coated 3 percent by weight with Dexsil 300 GC and the other column is packed with 80-100 mesh Supelcoport coated 3 percent by weight with OV-17. Prepared and pretested column packing materials may be obtained from Supelco, Inc., Bellefonte, PA.

The columns are installed in the gas chromatograph and are conditioned, prior to use, as follows: (1) Purge the columns for 30 minutes with inert carrier gas. (2) Turn off the carrier gas flow and heat the columns to 250°C for 2 hours. (3) Reduce the temperature to 225°C and allow the temperature to equilibrate for 30 minutes. (4) Turn on carrier gas flow to about 30 ml/min (millilitres per minute) and continue heating the columns at 225°C for 12 hours. The columns should not be connected to the detectors during conditioning.

After conditioning, the columns are ready for use. Performance and retention-time characteristics must be determined for each column by use of standards.

4.6 Erlenmeyer flasks: 250-ml and 500-ml plain-top erlenmeyer flask and 500-ml erlenmeyer flask having ground-glass stoppers and having spring clips for securing the stoppers.

4.7 Integrating equipment: A compensating polar planimeter readable to the nearest 0.01 in^2 (0.25 mm^2) is acceptable. Other instruments or methods of integration demonstrating equal or greater accuracy may be used.

4.8 Microbalance: A Cahn Gram Electrobalance or equivalent.

4.9 Microlitre capillary pipets: Volumetric micropipets in 1,5,10 and 25-µl (microlitre) sizes, glass disposable type are satisfactory.

4.10 Microlitre syringes: A microsyringe having a capacity of 10 µl and an accuracy of ± 0.1 µl.

4.11 Oven: A thermostated convection current oven capable of maintaining 150°C.

4.12 Recorder: A 1-mv (millivolt) full scale response, 1-second pen speed, strip chart recorder. Such a recorder having a fixed or selectable chart speed of 0.5 in (13 mm) per minute is acceptable.

4.13 Sandbath: A thermostated-fluidized sandbath, Tecam or equivalent.

4.14 Shaker: A mechanical wrist action shaker having a 12-container capacity.

4.15 Separatory funnels, Squibb form, 1- or 2-litre capacity. No lubricant is used on the stopcocks.

4.16 Volumetric glassware, Class A volumetric flask in 5, 10 and 25-ml sizes. The stoppers should fit well because volatile organic solvents are used for dilutions. Volumetric ware such as supplied by Kontes Glass Co., or equivalent is acceptable.

5. Reagents

5.1 Acetone, pesticide-analysis quality, Nanograde, distilled in glass, or equivalent.

5.2 Alumina, neutral aluminum oxide, activity grade I, Woelm. Weigh 45.0 g activated alumina into a dry 250-ml glass-stoppered erlenmeyer flask and quickly add 5.0 g distilled water. Stopper the flask and mix the contents thoroughly by tumbling until all lumps are gone. Allow at least 2 hours before use. Keep tightly stoppered and store in a desiccator.

5.3 Benzene, pesticide-analysis quality, Nanograde, distilled in glass, or equivalent. Benzene is the required solvent for the preparation of standard solutions. It is relatively nonvolatile and the solutions can be stored for long periods in a safety refrigerator. Most importantly, if other solvents are used, reduced response in the electron-capture system may result.

5.4 n-Hexane, pesticide-analysis quality, Nanograde, distilled in glass or equivalent.

5.5 Sodium sulfate, anhydrous, granular. Prepare by heating at 300°C overnight and store in a tightly covered glass jar having a Teflon lined screw top closure.

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

5.7 Water, distilled, obtain 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 water is constantly irradiated with ultraviolet light during storage. A gravity delivery system is used, and no plastic material other than Teflon is allowed to contact the distilled water.

6. Procedure

6.1 Standardization: Each chromatographic system must be calibrated to reference standards at the operating conditions to be used for analysis.

6.1.1 *Picogram standards:* Weigh 1.00 mg (milligram) of analytical reference grade compound on the microbalance and transfer into a 10.00-ml volumetric flask. Dilute to volume with benzene and mix thoroughly. Prepare a series of picogram standards from this solution. (Example: Take 1.0 µl of the above solution and dilute to 10.00 ml with benzene. The concentration of compound in the resulting solution is 10×10^{-12} g/µl (gram per microlitre) or 10 pg/µl (picograms per microlitre).

6.1.2 *Calibration:* A 5.0-µl volume of each of the appropriate standard solutions is injected into the gas chromatograph. The concentration of compound in the series of standard solutions should be such to calibrate the full range of linear detector response. The injection should be made so that the solution enters the injection port in a single volume and in a reproducible manner. The volume injected should be measured by reading the syringe before and after injection. Calibration should be performed on both the Dexsil 300 and OV-17 columns. Calibration curves are prepared from peak-area response plotted against the amount of compound injected.

6.2 Procedure for water samples. Samples (1-litre) should be collected according to the recommended practice for the collection of samples for organic analysis (Goerlitz and Brown, 1972). Special care must be taken to avoid contamination, see section 3, Interferences. The sample must be cooled in ice or refrigerated immediately after sampling. Shipment should be made by the most expeditious means so there are no delays in transit and so the sample reaches the laboratory during working hours. No preservative is used. Unless analyzed without delay, the sample should be protected from light and stored in a refrigerator but not frozen. A reagent blank should accompany the analysis.

6.2.1 Determine the weight of the water sample to three significant figures and pour the water into a 1- or 2-litre separatory funnel.

6.2.2 Add 50 ml of benzene to the sample in the separatory funnel. Stopper and shake the separatory funnel vigorously for 1 full minute, venting the pressure often. Allow the contents to separate for at least 10 minutes and draw off the aqueous layer into the original container. Collect the benzene layer in a 250-ml erlenmeyer flask containing about 1.0 g anhydrous sodium sulfate.

6.2.3 Repeat the extraction of the water sample three more times in the same manner using 50 ml of benzene each time. Combine all extracts in the 250-ml erlenmeyer flask containing the first extract and drying agent. Cover the flask containing the extract with foil and set aside for at least 30 minutes.

6.2.4 Filter the extract through glass wool into a 500-ml Kuderna-Danish apparatus. Add a sand-size boiling stone and remove most of the benzene by heating in a fluidized sand bath at 100-125°C. (CAUTION: the evaporation of benzene must be conducted in a well ventilated fume hood.) When the ball in the Snyder column just stops bouncing, remove the apparatus from the heat and allow to cool. Further reduce the volume of solvent to between 0.4 - 0.5 ml by directing a stream of dry nitrogen on the surface of the liquid while gently warming with a heat lamp.

6.2.5 Proceed to column chromatographic separation and purification, step 6.4 below.

6.3 Procedure for soil samples. Soil samples should be collected according to the recommended practice for samples for organic analysis (Goerlitz and Brown, 1972). Special care should be taken to avoid contamination, see section 3, Interferences. Collect 150 g of solids, if possible, for soil analysis. Any particle size separations should be performed without delay and the soil not allowed to desiccate. No preservatives are used. Samples should be shipped promptly to the analytical laboratory. Unless analyzed without delay the samples should be protected from light and stored in a refrigerator. Do not freeze the sample. A reagent blank should accompany the analysis.

6.3.1 Thoroughly mix the sample and then weigh 50.0 g into a 500-ml glass-stoppered erlenmeyer flask. Also at this time, weigh an additional 10.00 g of the sample into a tared 50-ml beaker to be heated at 130°C overnight, in an oven, for moisture determination.

6.3.2 Measure 40 ml of acetone into the erlenmeyer flask containing the sample and clamp the stopper in place. Mix the contents of the flask for 20 minutes, on a wrist-action shaker, to thoroughly disperse the solids in the acetone. Set the resulting slurry aside for at least 12 hours.

6.3.3 After allowing to stand for 12 hours or more, add 80 ml of hexane to the contents of the extraction flask, clamp the stopper in place, and shake for 10 minutes. Decant the extract into a 500-ml erlenmeyer flask containing 1 g of anhydrous sodium sulfate.

6.3.4 Add 20 ml of acetone to the extraction flask, clamp the stopper in place and shake for 20 minutes. Add 80 ml n-hexane to the extraction flask, clamp the stopper in place, and shake for 10 minutes. Decant the extract into the 500-ml erlenmeyer flask containing the solvent from the first extraction.

6.3.5 Extract the soil a third time as in the second extraction collecting the extract in the 500-ml erlenmeyer flask. Cover the flask, containing the soil extract, with foil and set aside for at least 30 minutes.

6.3.6 Filter the extract through glass wool into a 500-ml Kuderna-Danish apparatus. Add a sand size boiling stone and remove most of the solvent by heating in a fluidized sand bath at 100-125°C. (CAUTION: the evaporation of the mixed acetone-hexane solvents must be conducted in a well ventilated fume hood.) When the ball in the Snyder column just stops bouncing, remove the apparatus from the heat and allow to cool. Further reduce the volume of solvent to between 0.4 - 0.5 ml by directing a stream of dry nitrogen on the surface of the liquid while gently warming with a heat lamp.

6.4 Column chromatographic separation and purification, for samples containing extraneous interfering co-extractives and when separation of TNT and RDX is necessary.

6.4.1 Using a dropping pipet, quantitatively transfer the contents of the Kuderna-Danish receiver to the top of an alumina chromatographic column as prepared in step 4.1.

6.4.2 Elute the extract from the alumina column using benzene. Collect 40 ml of eluate. (TNT and RDX separate completely on the described alumina chromatographic column. TNT passes through the column with the first 5 ml of the eluant. RDX starts eluting after 20 ml of solvent have passed through the column, and is completely eluted after the passage of 35-40 ml of eluant.)

6.4.3 Reduce the volume of the column eluate to 1.0 ml by directing a stream of dry nitrogen on the surface of the liquid while gently warming with a heat lamp.

Note - The compounds TNT and RDX elute from the alumina chromatographic column in a predictable manner and this may be used to augment subsequent gas chromatographic analysis.

6.5 Gas chromatographic analysis. Extracts of soil and water are analyzed by electron-capture gas chromatography. Two chromatographic columns, described in section 4.5, Apparatus, having different retention characteristics, are utilized. The extracts are analyzed in the same manner as the standards and under the same, previously optimized, operating conditions. Each gas chromatographic system, namely each column, must be calibrated to benzene solutions of authentic reference standards at the operating conditions to be used. As an aid to evaluating column performance the operating conditions and retention values shown in table 1 may be used.

Table 1. *Gas chromatographic retention values for TNT and RDX*

Columns ..... 1.5 m long x 1.8 mm ID

Carrier gas flow ..... 30 ml/min nitrogen

Column temperature ..... 185°C

Injection port temperature ..... 210°C

Electron-capture detector

Compound	Retention time (seconds)	
	3 percent Dexsil 300	3 percent OV-17
TNT	177	217
RDX	439	641

6.5.1 The extract is first analyzed by electron-capture gas chromatography using a 3 percent OV-17 column. Concentration or dilution of the solution may be required to permit quantitative analysis. Proceed with the analysis by injecting 5.0 µl of the extract into the chromatograph, recording the volume of the extract and the volume injected to two significant figures. Do not make any subsequent injections into the chromatograph until the last compound has eluted and the baseline returned to normal.

6.5.2 Run a calibration-retention-time standard and a reagent blank as an analysis check. Should the chromatogram of the extract reveal a peak that corresponds to either TNT or RDX, a check standard of approximately the same concentration should be analyzed. Reanalyze the extract by electron-capture gas chromatography utilizing a 3 percent Dexsil 300 column.

6.5.3 Determine the amount of TNT or RDX in the injection from the calibration curve.

7. Calculations

Each gas chromatographic system must be calibrated with standards. The response of the gas chromatographic detector is usually the display of an analog signal on a strip-chart recorder. The signal is recorded as a differential curve or peak. The area inscribed beneath the peak is proportional to the amount of material passing through the gas chromatographic detector. The time elapsed from the introduction of the sample to the differential curve maximum is designated as the retention time for a particular component. The retention time for a compound on a specified column is nearly unique and is used for qualitative analysis. The response of the chromatograph must be standardized at optimum conditions and enough determinations made so that the data may be treated by the method of least squares. During analysis, the standard curve must be checked by running at least two standards at different concentrations so corrections can be made for day to day fluctuations.

7.1 Qualitative analysis: Direct comparison of the retention time of a sample component and a reference standard on both OV-17 and Dexsil 300 columns is the method used for qualitative identification.

7.1 Quantitative analysis: Measurement of gas chromatogram peak areas by use of a planimeter or by any method of equal or greater accuracy is acceptable. If a planimeter is used the average of at least two measurements is taken as the peak area.

7.2.1 Using log-log graph paper, plot area of response, in square inches against picograms of compound injected. If six or more values fall in the linear response region of the detector, the equation of the line may be found by the method of least squares, as follows:

$$m = \frac{n \cdot \Sigma(xy) - \Sigma x \cdot \Sigma y}{n \cdot \Sigma x^2 - (\Sigma x)^2} \qquad \text{(eq. 1)}$$

and

$$b = \frac{\Sigma x^2 \cdot \Sigma y - \Sigma x \cdot \Sigma(xy)}{n \cdot \Sigma x^2 - (\Sigma x)^2} \qquad \text{(eq. 2)}$$

where

x = injection amounts, in picograms,
y = area response values, in square inches,
b = y intercept,
m = slope, and
n = number of points selected.

For the equation of the straight line,

$$y = mx + b \qquad \text{(eq. 3)}$$

the value for b, the y intercept, is an indication of whether any experimental bias exists.

Two or more daily response check standards are used to correct the slope of the standard curve, as follows:

$$C = \frac{Ac}{As} \qquad \text{(eq. 4)}$$

where

C = correction factor,
Ac = area of check standard obtained from the standard curve,
and As = area obtained from chromatogram of the check standard.

7.2.2 *Calculations for samples:* The concentration of TNT or RDX in water or soil samples may be calculated using the following equation:

Concentration of compound (µg/l)

$$= \frac{AC-b}{m} \times \frac{Vext}{Vinj} \times \frac{1}{V_s} \times 10^{-6} \qquad \text{(eq. 5)}$$

where

A = area of component, in square inches
C = correction factor from eq. 4
b = y intercept from eq. 3, in square inches
m = slope from eq. 3, in square inches per picogram
Vext = volume of extract, in millilitres
Vinj = volume injected in millilitres, and
Vs = volume of sample, in litres

Equation 5 may be used to calculate the concentration of TNT or RDX in soil by substituting the calculated weight of dry sample in kilograms for the sample volume (Vs) with the resulting concentration expressed as micrograms per kilogram.

Recovery test performed on distilled water samples fortified with TNT and RDX at the 0.5 - 1.0 µg/l level gave the following results: mean recovery for TNT was 95 ± 15 percent; mean recovery for RDX was 85 ± 10 percent. The recovery of TNT and RDX from soil is mainly dependent on two factors: (1) the ability of the solvent to remove the compound from the soil, and (2) the amount of solvent reclaimed at each extraction step. Comparative studies of single and exhaustive extractions of soil samples contaminated with TNT and RDX in situ showed that the extraction technique described removed 93-99 percent of the compounds. However, only about 55 percent of the TNT and RDX was removed from the soil in the first extraction, unless the soil was allowed to remain in contact with acetone for 12 hours or more. It is imperative that sufficient solvent be reclaimed at each extraction step to avoid low results. Recovery of 93 - 99 percent of the desorbed TNT and RDX may be expected if at least 75 percent of the solvent is recovered at each extraction step. Recovery test of the entire soil analysis procedure gave the following results: mean recovery for TNT was 85 ± 15 percent and mean recovery for RDX was 93 ± 10 percent.

8. Report

TNT or RDX found in water samples are reported as follows: at concentrations of less than 0.1 µg/l the concentration is reported to the second decimal. Report less than 0.005 µg/l as 0.00 µg/l. At concentrations of 1.0 µg/l and greater, report to two significant figures. TNT and RDX found in soil samples are reported as follows: less than 1.0 µg/kg is reported to one decimal; 1.0 µg/kg and above to two significant figures. For concentrations of 1.0 µg/l or greater in water and of 10 µg/kg or greater in sediment, specific detection must be employed. Identities of compounds in concentrations of 2.0 µg/l or greater in water and of 20 µg/kg or greater in sediment must be confirmed by mass spectrometry.

9. Precision

Precision of the determinative step of the gas chromatographic technique is variable for multicomponent analysis. The response of one component may be considerably greater or less than that of another. Peaks of compounds having longer retention times are affected more by instrumental noise and drift. Under ideal conditions a precision of ± 3 percent may be attained upon repetitive injections of a single component standard solution.

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