AD-A008 399

DEVELOPMENT OF INDUSTRIAL HYGIENE SAMPLING AND ANALYTICAL METHODOLOGY FOR EVALUATION OF EXPOSURES TO TNT AND ASSOCIATED EXPLOSIVES

Bernard E. Saltzman, et al

Cincinnati University

Prepared for:

Army Medical Research and Development Command

January 1975

AD_____

DEVELOPMENT OF INDUSTRIAL HYGIENE SAMPLING AND ANALYTICAL METHODOLOGY FOR EVALUATION OF EXPOSURES TO TNT AND ASSOCIATED EXPLOSIVES

FINAL REPORT

Dr. Bernard E. Saltzman

Dr. William R. Burg

Dr. John E. Cuddeback

January 1975

Supported by

U.S. Army Medical Research and Development Command
Washington, D.C. 20314

Contract No. DADA17-73-C-3167
Department of Environmental Health
University of Cincinnati
Cincinnati, Ohio 45267

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
TNT Exposure						
TNT						
RDX Exposure						
RDX						
Industrial Hygiene Sampling						
Gas Chromatography						

AD A008 379

(Security classification of title, body of abstract and indexing annotation must be entered when the ove all report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Department of Environmental Health University of Cincinnati Cincinnati, Ohio 45267	Unclassified 2b. GROUP

3. REPORT TITLE

Development of Industrial Hygiene Sampling and Analytical Methodology for Evaluation of Exposures to TNT and RDX Explosives.

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final

5. AUTHOR(S) (First name, middle initial, last name)

Bernard E. Saltzman
William R. Burg
John E. Cuddeback

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
January 1, 1975	55	18

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
DADA17-73-C-3167 b. PROJECT NO.	Final 690
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	U. S. Army Medical Research and Development Command

13. ABSTRACT

A sampling and analytical method is described for the determination of personnel exposures to dust from TNT, RDX or their mixtures in the work place. Personal samples are collected at the breathing zone of the worker on 37 mm organic-free glass-fiber filters at a flow rate of 2 lpm for 10 minutes. The collected sample may be stored up to 10 days in a glass-stoppered vial before analysis. The TNT, RDX or their mixtures are removed from the filter paper by dissolution in ethyl acetate for injection into a portable gas chromatograph equipped with a flame ionization detector. The range is from 0.15 mg/m^3 to 150 mg/m^3 for TNT and 0.5 mg/m^3 to 150 mg/m^3 for RDX. The approximate precision is ±15%.

DD FORM 1 NOV 68 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

Unclassified
Security Classification

SUMMARY

The purpose of this work was the development of a sampling and analytical method suitable for determining personal exposures to TNT, RDX or their mixtures that could be completed in the field and required only a short sampling period. The exploratory work and a recommended procedure for sampling airborne TNT or RDX particulates on glass-fiber filters and analysis by gas chromatography have been described. Experimental results showed that organic-free glass-fiber filters collected and held airborne TNT or RDX particulates without significant losses. Sublimation of RDX at ambient conditions was found to be negligible. Storage of TNT samples in stoppered vials was adequate to avoid significant losses for up to 10 days. Losses of TNT during extended sampling periods were found to be only a minor fraction of the accepted TLV of 1.5 mg/m^3. The samples were conveniently analyzed by adding 2 ml of ethyl acetate to the vials and injecting 5 µl portions of the solutions into a portable gas chromatograph equipped with a flame ionization detector. A 6-foot glass column packed with 3% Dexsil 300 on Chromosorb effectively separated the solvent, TNT and RDX peaks. Quantitation was achieved by comparing the peak areas determined by triangulation with a calibration curve. Peak heights also were used with some loss in precision. Laboratory and field studies showed that a 10 minute sampling period at a flow rate of 2 lpm was adequate for the range 0.15 to 15 mg/m^3 (0.1 to 10 TLV) for TNT and 0.5 to 150 mg/m^3 (0.3 to 10 TLV) for RDX. The recommended procedure was convenient, rapid, and accurate to an overall precision of $\pm$ 15%.

FOREWARD

No copyrighted material or animal experimentations were used in this investigation.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

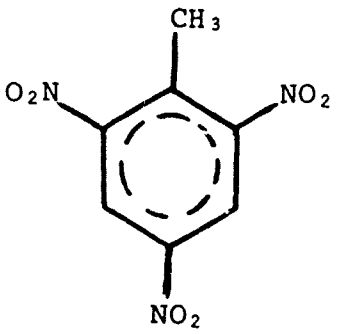
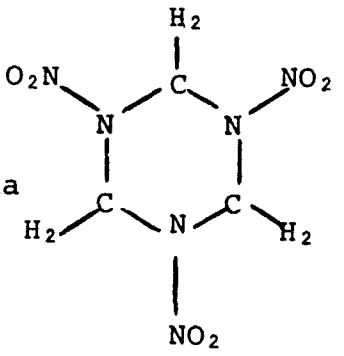
INTRODUCTION

The objective of this study was the development of a convenient and accurate industrial hygiene method for assessing the individual worker's exposure to airborne dust from TNT, RDX or their mixtures which was sufficiently sensitive to permit a short sampling period.

The term TNT used throughout this report refers to the compound 2,4,6-trinitrotoluene. Various other names are also used for this compound including α-TNT, trotyl, triton, tritol and tolite. RDX refers to the explosive cyclotrimethylene trinitramine, also called hexahydro-1,3,5-trinitro-5-triazine, cyclonite, hexogen and T4. The structures and selected properties for these compounds are shown in Table I.

TABLE I

STRUCTURES AND SELECTED PROPERTIES

TNT	Name	RDX
	Structural Formula	
227.1	Molecular Wt.	222.1
80.75°C	Melting Point	204.1°C
1.5 mg/m^3	Threshold Limit Value (ACGIH, 1974)	1.5 mg/m^3
Solubility (grams/100 g solvent at 25°C):		
∿80.0	Ethyl Acetate	∿4.0
88.0	Benzene	∿0.5
0.63	CS_2	Very low

Direct measurements of air levels (4,6,9,12) as well as biological methods using urinary excretion of metabolites (18) have been employed to determine exposures of workers to TNT or RDX. In accepted methods (3,12,15), TNT, RDX or composition B (a mixture of 60% RDX and 39% TNT) are absorbed from the air sample by an appropriate liquid in a midget impinger, and then determined by a colorimetric analysis. Use of a liquid absorbent for collecting personal samples requires appropriate glassware and careful handling, transportation and storage to avoid spillage, leakage or evaporation. Several colorimetric methods have been described (12,16,17) which involve treating the TNT solution with a base, or reducing and diazotizing it and adding a color forming reagent. These reactions are nonspecific and suffer from interferences. Although either TNT or RDX alone can be conveniently determined colorimetrically, a mixture such as composition B, requires a correction due to the overlapping of the absorption bands. Additional standard absorption curves and calculations are required.

It, therefore, appeared appropriate to develop more convenient collection methods and more specific analytical techniques based upon modern instrumentation. Certain requirements for the methodology were proposed in the original contract and developed in further discussions with the project officer, as follows:

1. The sample collection method must be suitable for use in an area where large quantities of explosives are being handled.

2. The sample collection device should be adaptable for use with the available personal pumps which have flow rates up to 2 lpm.

3. The sampling method should be capable of collecting TNT particulates at the usual workroom temperatures.

4. The analytical method should be sensitive enough to accurately determine TNT and RDX levels at 0.5 mg/m^3 with a sampling time of 10 to 30 minutes.

5. The analytical method should preferably employ an instrument useful for other pollutants, such as a gas chromatograph.

6. Both a field portable analytical method and a sampling method for analysis by shipment to a central laboratory were desired.

7. A gas chromatographic detector not containing radioactive material was preferred to avoid clearance complications.

Gas chromatography employing various detectors has been used to separate, identify and determine the levels of TNT in water (5), industrial environments (5), and ambient air around packages suspected of containing explosives (11). The levels in water ranged from high concentrations in the red water at production plants to very low levels in plant effluents after clean-up or with increasing downstream distance from the plant. The TNT was extracted into benzene or toluene for injection into a gas chromatograph. The determination of very low levels required the sub-nanogram sensitivity of an electron-capture detector (5) or that of 1 part in 10^{10} of a mass spectrometric detector (11) monitoring the m/e peak of 89. In the development of a "sniffer" for locating hidden explosives, ambient air levels near solid TNT were reported to be approximately 10^{-9} gm/100 ml depending upon the ventilation (11). For such low levels, a pre-concentration step was necessary. A platinum wire surprisingly collected and held the TNT and later, when heated, released it for analysis by a gas chromatograph equipped with a mass spectrometric detector.

The levels of suspended particulate TNT in the work place air are generally higher than those in ambient air or water samples. Methods for analyzing these levels included colorimetric determinations (6,12), gas chromatography (8), and a combination of thin layer and gas chromatography (10). Thin layer chromatography is relatively slow and requires operator skill. The gas chromatographic method has generally involved injecting a portion of the sample collected by passing the air through a midget impinger containing benzene or toluene. Navy personnel (5) determined worker exposure to TNT by a modification of the method used in water analysis. The particulate TNT was collected in a midget impinger containing water. Due to the low solubility of TNT in water, benzene or toluene then was used to concentrate and extract the TNT for injection into a gas chromatograph equipped with an electron capture detector. This method required collection in a liquid media, and sensitivity was limited by the considerable volume of solvent that was necessary. A temperature-programmed gas chromatograph equipped with a thermal conductivity detector was used to separate the isomers of TNT as well as the mono and di-nitrated reaction products; but the lowest detectable concentration of TNT with this detector using a 15 µl injection was a 0.2% in acetone solution (8). There are presently no commercially available portable gas chromatographs with temperature programming, and this feature was not regarded as essential.

For the range of concentrations expected for this project, the flame ionization detector appeared most suitable. The low sensitivity of the thermal conductivity detector required collecting a larger sample than desired. The mass spectrometric detector was not a portable unit, and its

high sensitivity required considerable dilution of the sample. The electron capture detector was also excessively sensitive, had a limited linear range, and might require involved clearances because of its radioactivity. The flame ionization detector had a convenient sensitivity and extended working range. Although benzene and toluene were suitable solvents for use with the electron capture detector, which has a low response to them, or with the mass spectrometric detector, which can respond to a characteristic m/e ratio, they were less suitable for the flame ionization detector, which responds strongly to them.

Because of the inconvenience of liquid sampling techniques, alternative methods of collecting airborne TNT were considered. An estimate of possible losses by volatilization was made from vapor pressure data for TNT. One report (11) listed the equilibrium vapor pressure of TNT at room temperature as 0.01 mg/m^3 without giving experimental details. Other data (6,13) gives the vapor pressure of solid TNT above 40°C as follows:

$$\log_{10} P \text{ (cm Hg)} = 14.34 - \frac{6180}{T(°K)}$$

Extrapolation to 25°C yields a value of 0.05 mg/m^3. This is only 3% of the Threshold Limit Value. Losses from sublimation appeared low enough not to preclude the feasibility of using filters to collect TNT dust.

The experimental development of a sampling and analysis method involving collection on a filter and analysis by gas chromatography is described in the following section.

EXPERIMENTAL

Purification and Storage of TNT and RDX.

Commercial TNT was purified by the following method for use in all experiments described in this report: 10 grams of TNT were added to 40 ml of ethanol and heated in a water bath to approximately 70°C. The solution was allowed to cool slowly to room temperature and then ice was added to the water bath for further cooling. After standing for approximately 30 minutes, the TNT was filtered through a sintered glass filter. The crystals were washed 4 times with successive 10 ml portions of cooled ethanol. They were then removed from the filter and dried overnight under vacuum. The dry, purified TNT was then placed in a glass stoppered vial and stored in the dark.

RDX was obtained from the Naval Environmental Health Center that had been previously purified in a similar manner. It was stored under water in a glass vial kept in the dark and dried in a vacuum just before use.

Solutions of TNT or RDX or their mixtures were found to be stable for periods of at least a month. Evaporation of the solvent, especially CS_2, changes the concentration.

Selection of a Portable Gas Chromatograph.

An AID Model 511 Portable Gas Chromatograph equipped with both the flame ionization detector and the electron capture detector accessory was procured for this project from Analytical Instrument Development, Inc., Avondale, Pa., 19311. This was the only portable instrument commercially available of the quality required for serious analytical determinations. The major specifications as listed by the manufacturer were as follows:

TABLE II

MANUFACTURER'S SPECIFICATIONS FOR AID

MODEL 511 PORTABLE GAS CHROMATOGRAPH

FLAME IONIZATION DETECTOR: Single flame, isolated jet design. Line- or battery-operated. Sensitivity of at least 20 millicoulombs per gram carbon.

ELECTRON CAPTURE DETECTOR: 200 millicuries of H^3 suitable for operation up to 200°C ± 5°C.

COLUMN OVEN: Accepts up to 20 ft. x 1/8" metal columns and 12 ft. x 4 mm glass columns as standard.
Solid state proportional temperature controller settable to within 0.1°C.

INJECTION PORT: Temperature Range - Ambient to 250°C.

ELECTROMETER: Complete solid state device.
Sensitivity - 5×10^{-12} amps full scale on 2 millivolt recorder.
Noise: 1×10^{-13} amps peak to peak
Background Suppression - 7.5×10^{-7} amps
Time Constant - Less than 500 milliseconds on all ranges.

FLOW SYSTEM: Precision flow controller, column head-pressure gauge.
Secondary pressure regulator installed.
Individual gas controls for H_2 and air.

PHYSICAL CHARACTERISTICS:
Dimensions (Case): 15" x 18" x 10".
Weight: 38 lbs. (with power pack).
Electrical Requirements: voltage 115 A.C./28v.D.C.
Power - 35 watts maximum.

Experiments were conducted to determine the best column tubing material and packing, the optimal solvent for injection of samples, the optimal operating conditions, and the performances of the FID and EC detectors.

Selection of Column Tubing Material.

For a portable instrument, 1/8-inch o.d. stainless steel columns appeared to be a practical choice. Unfortunately, such columns yielded erratic results for this work. Responses to successive injections of TNT or RDX solutions increased until a constant response was obtained. This behavior was believed to be due to losses on the active sites on the metal column. After standing overnight, the decreased response was obtained again, which demonstrated the necessity of a "priming". Responses to TNT using a primed metal column are compared in Figure 1 to those using a glass column under the conditions of the final recommended procedure to be described below. Apparently half of the TNT was lost on the metal. Other tests were made with Teflon and Teflon-lined aluminum tubing. Both produced attenuation as well as broadening of the peaks.

Glass columns as expected were the material of choice. The glass column wall and the glass wool plugs were silanized with dimethyl dichlorosilane. Unfortunately, these columns are subject to breakage during installation and transportation. It is suggested that the instrument be hand carried on air flights. A suitably packed and preconditioned spare glass column should be available.

Selection of Column Packing.

A number of liquid phase coatings on 80-100 mesh Chromosorb WAW-DMCS were tested. Dexsil 300, Pentasil, FFAP, and SE 30 all gave satisfactory results. Retention times for TNT under the conditions of the recommended procedure were 4.3, 4.1, 3.8, and 3.6 minutes, respectively. Since the TNT peak came out on the tail of the solvent peak, the longer retention time of Dexsil 300 was desireable. A second advantage of this packing was the very low column bleed when the column was heated from ambient temperature to 180°C. The base line drift was 20% less than that observed for FFAP and SE 30. The column packing selected was 3% Dexsil 300 on 80-100 mesh Chromosorb WAW-DMCS.

Selection of Solvent for Sample Injections.

Desireable properties for a solvent for the samples included good solubility of TNT and RDX, and production of a GC peak with minimal tailing overlapping the sample peaks. Candidate solvents included acetone, benzene, carbon disulfide, ethyl acetate, ethyl ether, formic acid, methanol,

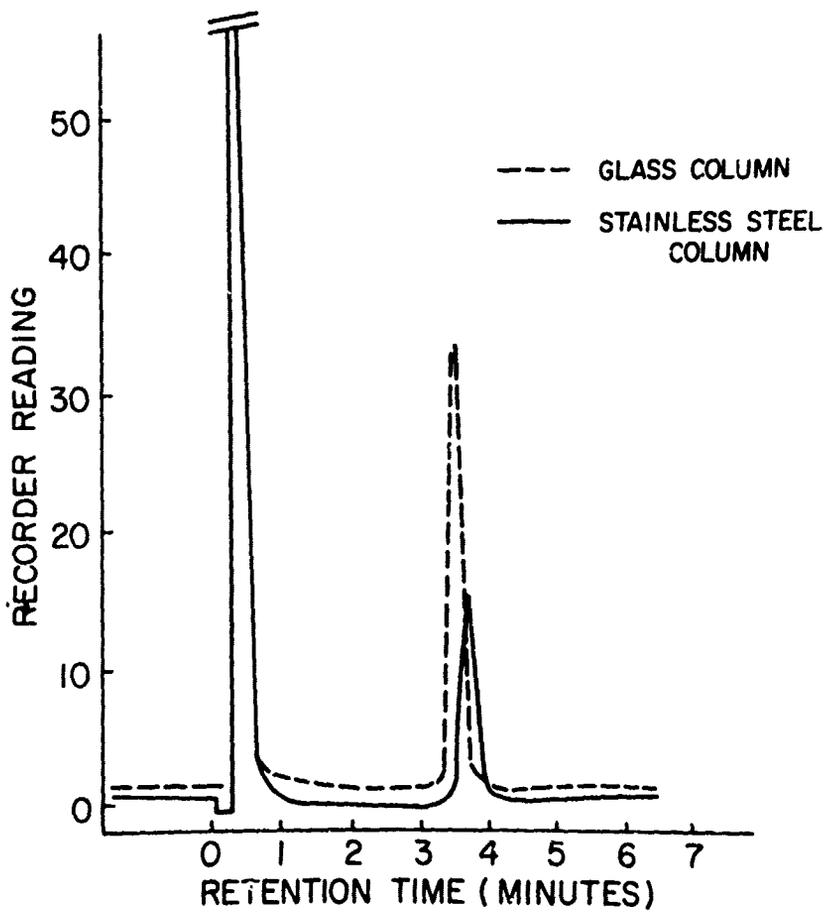


Figure 1. Comparison of Responses to TNT with Glass and Stainless Steel Columns Under Conditions of the Recommended Procedure.

methyl sulfonate and water. These solvents were injected into the gas chromatograph to determine the response peak patterns. In separate experiments, the solubility of TNT and RDX was determined. Although many showed good solvent power, they had unacceptable tailing. Both carbon disulfide and ethyl acetate were suitable solvents for TNT. The former was preferable because of its lower response with the FID detector and lesser overlapping with the TNT peak. Only ethyl acetate was an adequate solvent for RDX. If TNT and RDX are both present, ethyl acetate must be used. Behavior of these solvents under the conditions of the final recommended procedure are shown in Figure 2. Injections were 5 µl of CS_2 containing 7.5 µg/ml of TNT, and 5 µl of ethyl acetate containing this concentration of both TNT and RDX; attenuation was 1 x 4.

Injection Volume.

The best results were obtained using the solvent flush technique. 1 µl of solvent, 0.2 µl of air followed by 5 µl of sample was drawn into the syringe in this method. The entire sample was flushed out of the needle giving better accuracy and precision. If larger volumes are injected, the flame is occasionally extinguished. The amount of TNT and RDX from a 20 liter air sample dissolved in 2 ml of solvent is well within the linear range.

Optimum Column Temperature and Column Length.

The operating temperature for the column was selected as a compromise of performance for both TNT and RDX. At higher temperatures, separation of the TNT peak from the solvent peak decreased, but better shaped peaks were obtained for RDX. Below 170°C the vapor pressure of RDX appeared to be so low that the sample did not produce a peak, but rather an elevation of the base line. It was found that 180°C was suitable for a mixture of TNT and RDX. For TNT alone, a lower temperature is suitable. For RDX alone, a higher temperature slightly improves the peak shape. Retention times for TNT and RDX vs. temperatures are shown in Figure 3 and Table III for a 6-foot column. The RDX had a discontinuity just below 170°C.

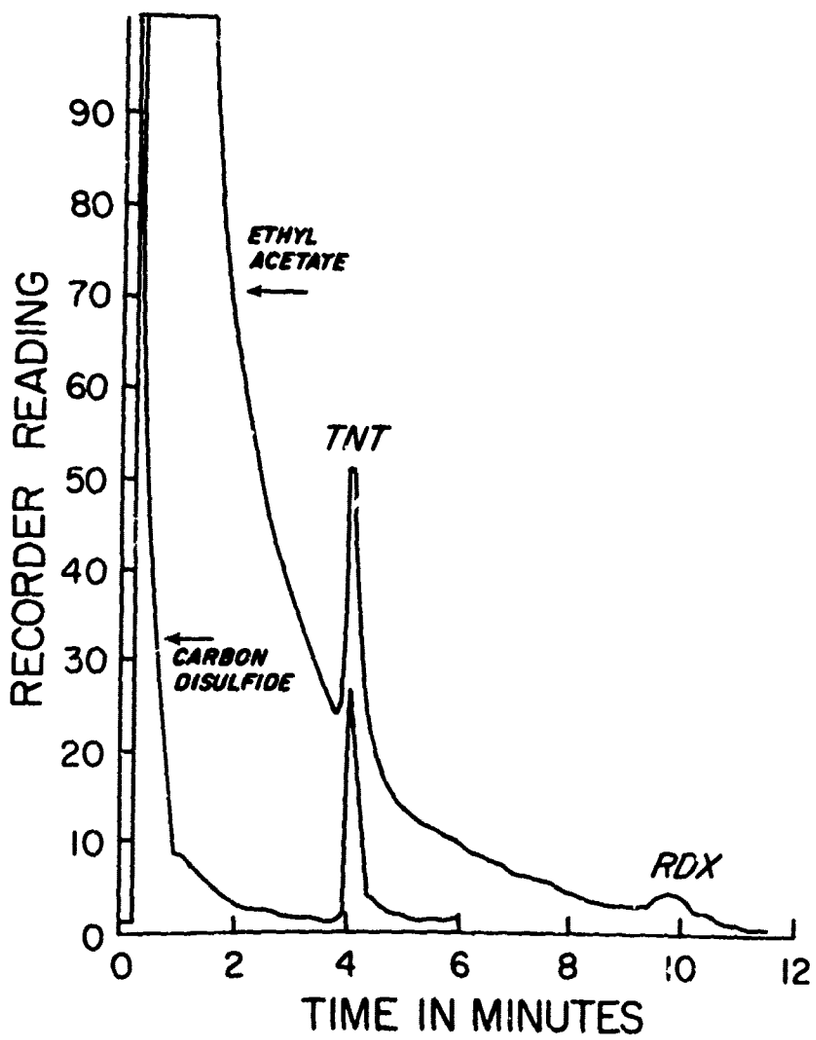


Figure 2. Responses of the FID Detector to Samples in Two Solvents Under Conditions of the Recommended Procedure.

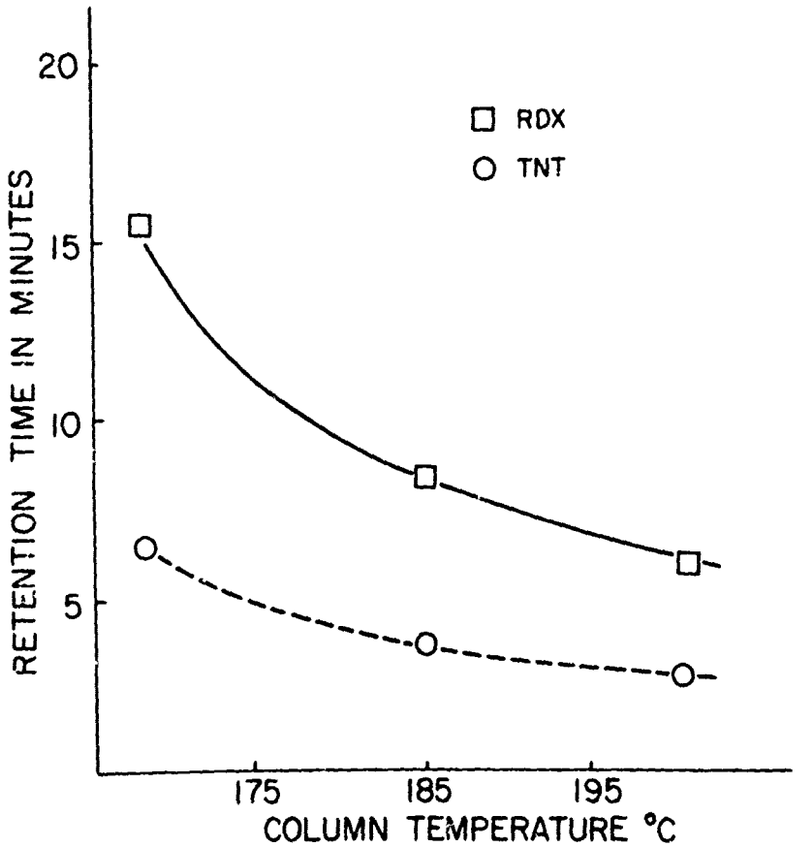


Figure 3. Effect of Column Temperature on Retention Times of TNT and RDX.

TABLE III

RETENTION TIMES OF TNT AND RDX AT VARIOUS TEMPERATURES UNDER CONDITIONS OF RECOMMENDED PROCEDURE

Instrument Setting	°C	Carrier Pressure P.S.I.	Retention Time, Minutes			Corrected Retention Time, Minutes	
			Air	TNT	RDX	TNT	RDX
905	170	24.4	0.28	6.28	15.24	6.00	14.96
955	185	25.5	0.28	3.73	8.43	3.45	8.15
975	200	26.1	0.27	2.59	5.68	2.32	5.41

The AID portable gas chromatograph can utilize glass columns up to 12 feet in length. A 12-foot glass column exhibited double the retention time for TNT compared to a 6-foot column. However, the solvent peak tailing also increased by approximately the same factor so there was no improvement in the solvent and TNT separation. To avoid increased analysis time and the additional cost and fragility of the longer columns, a 6-foot column was recommended.

Evaluation of the Flame Ionization Detector.

The AID portable gas chromatograph was ordered with both the flame ionization detector and the accessory electron capture detector which could be installed alternatively, in order to fully explore their capabilities and limitations. A preliminary estimate of the required sensitivity range was made on the basis of collecting a 10 minute sample using an MSA Model G personal sampler pump operating at 2 liters per minute and assuming a concentration of TNT or RDX of 1.5 mg/m^3, (1,2) the Threshold Limit Value. This would collect 30 micrograms of sample. If this were dissolved in 2 ml. of solvent, it would produce a concentration of 15 µg/ml, and a convenient 5 microliter injection into the gas chromatograph would contain 75 nanograms of the test component.

The response of the flame ionization detector was relatively insensitive to variations in hydrogen flow rates between 25 to 35 ml/min. and burner air flows between 95 and 125 ml/min. The optimum conditions were found to be 30 ml/min. for hydrogen, 110 ml/min. for air, and 25 ml/min.

for the nitrogen carrier gas. These were close to the manufacturer's recommendations. Tests made by injection of pure cyclohexane, under the conditions of the final procedure to be described later showed results in Figure 4. The small flame apparently became saturated with the large injections, and a non-linear response was observed. This was most marked on the curve for the peak heights, which reached a plateau. The peak areas, however, did not reach a plateau, although they increased non-linearly. The shapes of the peaks for larger samples showed a constant height but spreading of the peak bases. Thus it appeared that the upper limit of this portable model of detector was smaller than that of a laboratory chromatograph.

The manufacturer's response specifications for the FID detector were verified by determining the response to a 0.5% solution of toluene in carbon disulfide, within the linear range for toluene. This solution was injected into the instrument fitted with a 6-foot Dexsil column maintained at 84°C. The toluene and carbon disulfide peaks were widely separated under these operating conditions so that solvent tailing interference was avoided. The responses were linear throughout the range of quantities used and consistent with different attenuations. Results of these tests are presented in Figure 5. The ordinate in this plot is the product of the disc integrator counts and the attenuation factor. A full scale reading of 100 divisions on the recorder (which had a 2 millivolt span) produced 100 counts (1 sweep) per second on the integrator. The slope of the line in Figure 5 was 8.30×10^5 counts/µl CS_2 solution. The specification for the AID electrometer was 5×10^{-12} amp for full scale deflection on a 2 mv recorder, the density of toluene was taken as 0.85 mg/µl, and its concentration was 0.5%. The detector sensitivity was calculated in terms of millicoulombs/gram of toluene as follows:

$$S = \frac{8.30\times10^{5}\ \frac{\text{counts}}{\mu\text{l}} \times \frac{2\ \text{mv.sec.}}{100\ \text{counts}} \times \frac{5\times10^{-12}\ \text{amp.}}{2\ \text{mv.}} \times \frac{10^{3}\ \text{m coul.}}{\text{coul.}}}{1\ \mu\text{l}\,CS_2 \times \frac{5\times10^{-3}\ \mu\text{l toluene}}{\mu\text{l}\ CS_2} \times 0.85\ \frac{\text{mg}}{\mu\text{l}} \times 10^{-3}\ \frac{\text{gm.}}{\text{mg}}}$$

S (Sensitivity) = 9.8 millicoulomb/gram.

This value was only half of the manufacturer's sensitivity specification of 20 millicoulombs/gram, which was apparently optimistic, but was similar to values reported for other instruments in a discussion of these methods and definitions (14).

The detectability was calculated by dividing the product

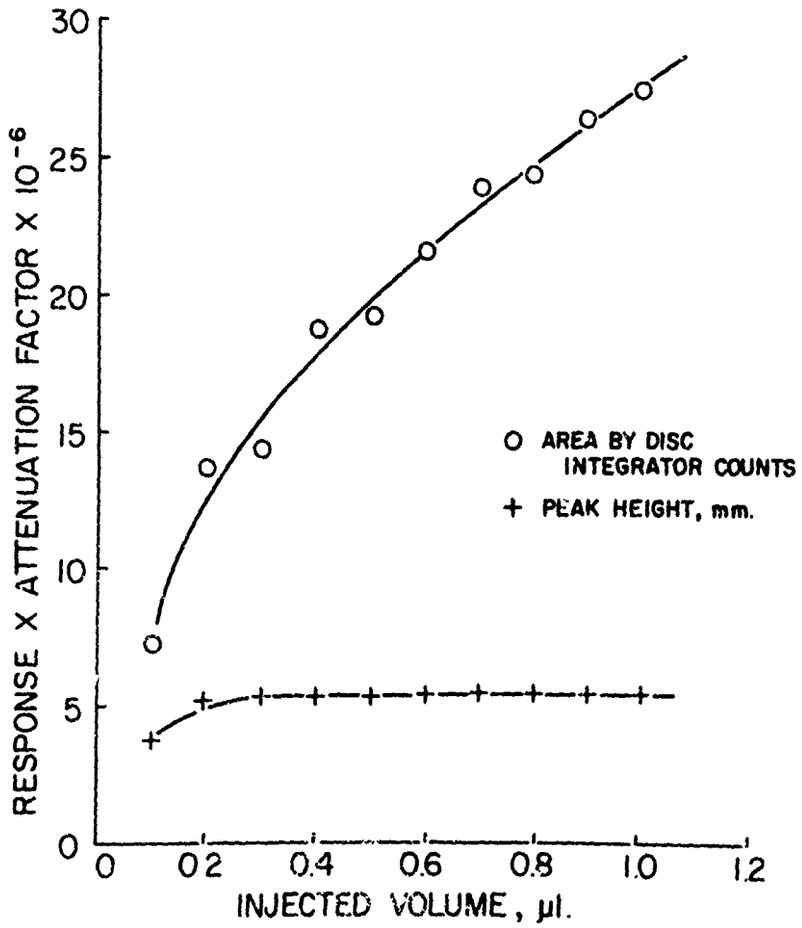


Figure 4. FID Detector Response to Bulk Quantities of Cyclohexane.

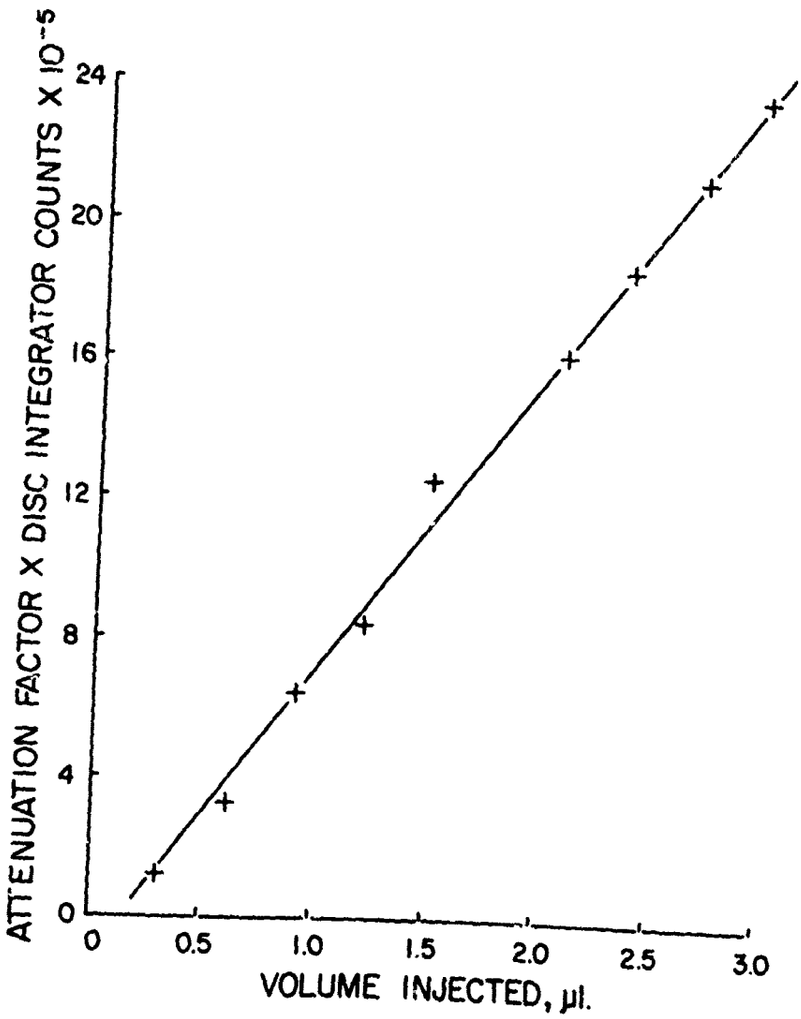


Figure 5. Response of FID Detector to 0.5% Toluene in CS_2.

of 2 times the noise level by the sensitivity. The AID instrument has a rapidly fluctuating random noise of about 1 division superimposed on a signal with a period of 15 minutes and a peak to peak amplitude of 24 divisions. This slow oscillation of the base line, like long-term drift, was disregarded because it did not interfere with the analysis. The detectability for toluene was:

$$D = \frac{2N}{S} = \frac{0.02 \times 5 \times 10^{-12} \text{ amp}}{0.009\text{8 coulombs/gram}}$$

or

$$D = 1.02 \times 10^{-11} \text{ gram/sec.}$$

This value may be compared with a typical value of 2×10^{-12} g/sec. (14).

Similar tests were made for TNT and RDX under conditions of the final recommended procedure, yielding the data shown in Figure 6 and 7, respectively, and the calculated values listed in Table IV. RDX had a lower detectable limit because the peak was lower and broader and, therefore, more difficult to distinquish from background noise.

TABLE IV

PERFORMANCE OF THE FID DETECTOR

Compound	Injection Volume µl	Sensitivity, m coul/gram	Limit of Detection, grams/sec.	Linear Range, mg
Toluene	5	9.8	1.02×10^{-11}	∿.1
TNT	5	.35	2.8×10^{-10}	>.75
RDX	5	.065	1.5×10^{-9}	>.75

It should be noted that both sensitivity and detectability depend upon the operating conditions as well as the compound and that a peak of the size defined by detectability is hardly quantitative. These values were used to determine the lowest range for the recommended procedure that we believe can be routinely achieved in the field.

Results for three methods of quantitating peaks are shown in Figures 6 and 7: area by the disc integrator, area by triangulation and peak height. Any of these methods are satisfactory. Although the disc integrator is very convenient it is not available on portable battery-operated

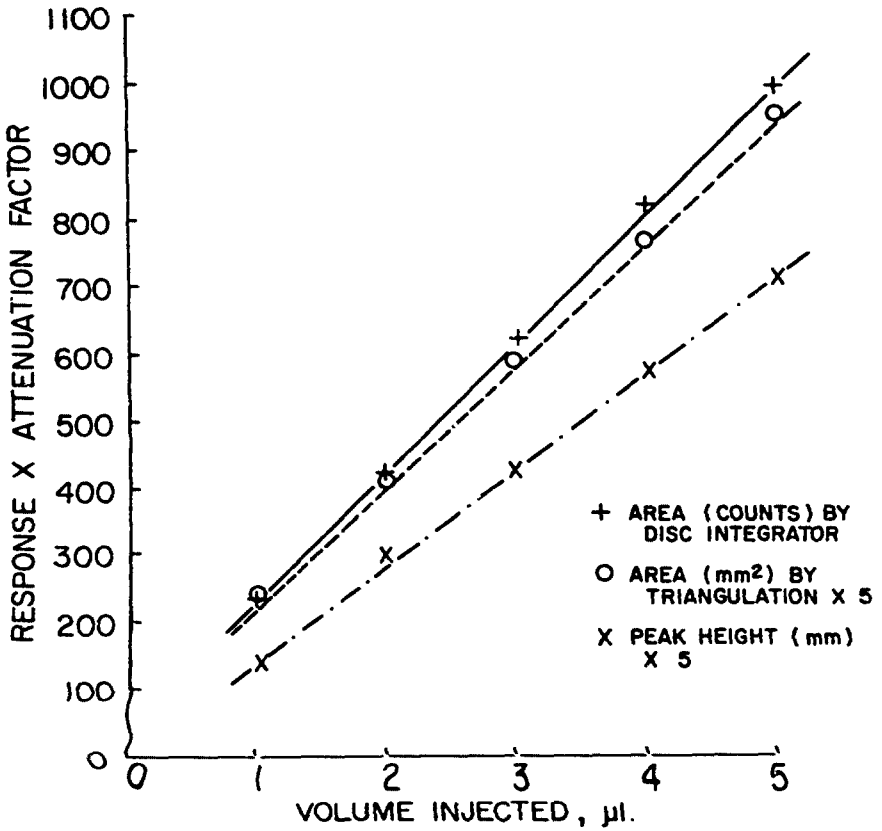


Figure 6. Response of the FID Detector to TNT in Ethyl Acetate (30 µg/ml).

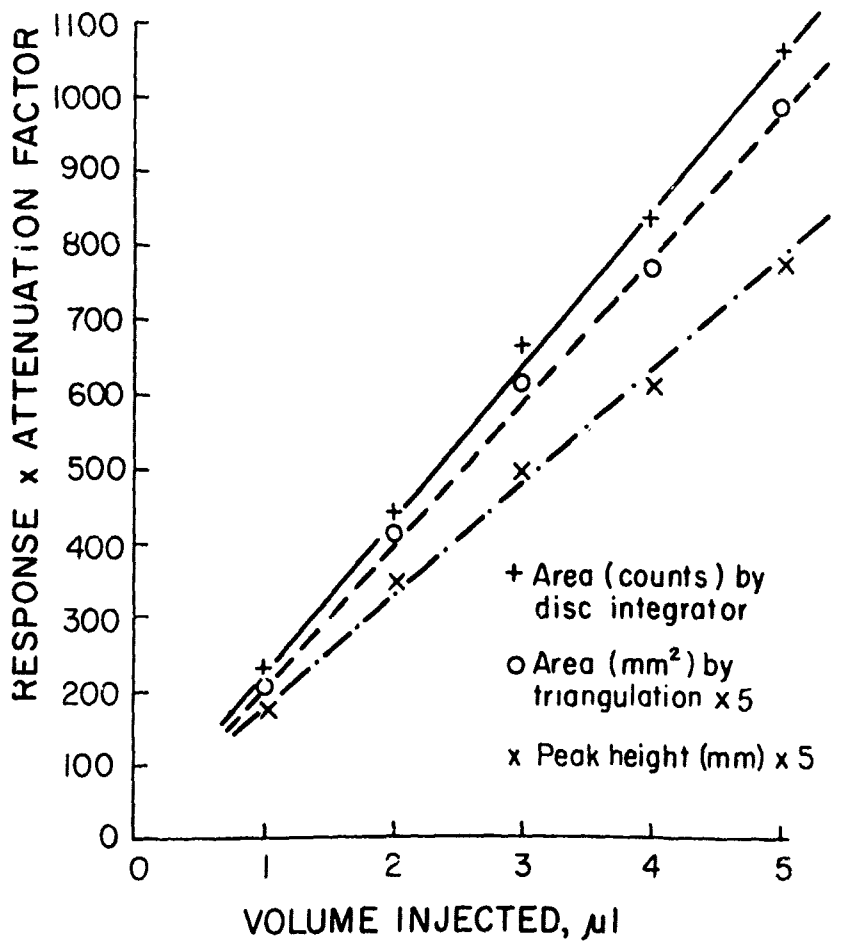


Figure 7. Response of the FID Detector to RDX in Ethyl Acetate (150 µg/ml).

recorders. The method of triangulation is almost as precise and is recommended for field use. Area was determined by multiplying the peak heights by the width at half-height. The alternate method in which a triangle is drawn by the intersections of the base with lines drawn as tangents to the peak was not used in this study.

Evaluation of the Electron Capture Detector.

The electron capture detector was briefly examined to determine its capabilities. Results for TNT under conditions of the final recommended procedure are shown in Figure 8. The ordinate in this plot is peak height X attenuation factor. The linear range of response was limited, making it inconvenient to use. The slope in the linear region was 3.2×10^{13} divisions/gram. Using 16 divisions as the detectable signal, the calculated limit of detection was 5.1×10^{-13} grams. The high sensitivity would require large dilutions of TNT samples. The EC detector was even less desirable for use with RDX because of condensation of this less volatile material inside its working volume, which substantially reduced its standing current and sensitivity. The AID instrument has only a single control for selecting the column oven temperature and the independent injection port and detector heaters are slaved to operate 5 degrees higher. This problem was not noted for TNT. However, RDX lowered the standing current for up to six hours after injections at the optimal column temperature of 180°C. Further studies on temperature effects are needed before a complete evaluation of the suitability of the EC detector for the analysis of RDX can be made. However, because of the cumbersome plant clearances that would be required for bringing in an instrument containing a radioactive component, together with the disadvantages cited above, no further work was deemed to be justified.

Selection of the Sampling Filter.

Blank filters of various commercially available types were placed in separate portions of carbon disulfide, and ethyl acetate, allowed to stand for thirty minutes and 5 µl of each solvent were injected into the gas chromatograph. The cellulose acetate membrane filters were soluble in ethyl acetate and, therefore, produced a solution that was not suitable for injection. Whatman 31 and Whatman 42 paper filters contained unidentified soluble substances which interfered with the TNT and RDX peaks. Flash-fired organic-free glass-fiber filters were found to give satisfactory blanks. These filters did not have any soluble components and could be handled without fragmentation.

Effects of Filter-Holders.

Glass-fiber filters were placed in commercial filter holders

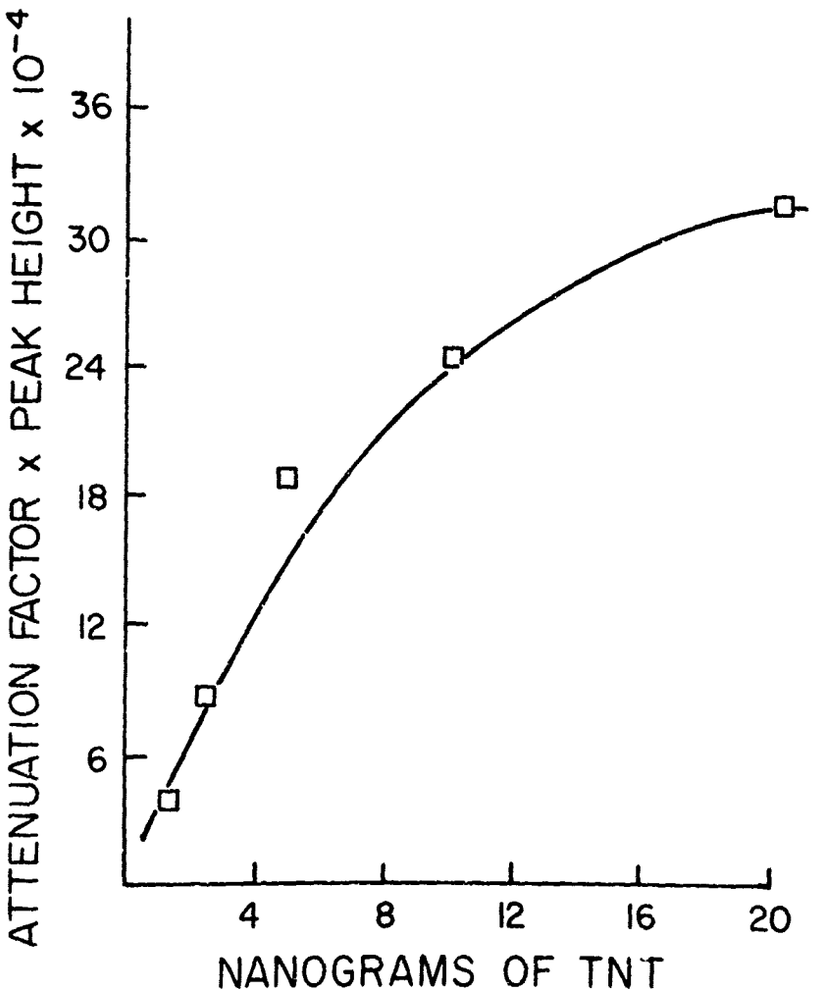


Figure 8. Response of Electron Capture Detector to TNT.

constructed of different materials to determine whether the filter could absorb any possible interferents from the holders. Tenite filter holders which are commonly supplied by the Millipore Company have a noticeable odor when new. The filters slowly absorbed substances from the holder which resulted in a number of interfering peaks in the GC analysis. This effect was not observed with polypropylene filter holders and thus the filters may be placed in them at any convenient time. In the event that only Tenite filter holders are available, results indicated that they may be used if the filter is placed in the holder immediately before use.

All filter holders were found to irreversibly absorb TNT. It was necessary to remove and store the filter in a glass vial.

RECOMMENDED PROCEDURE FOR SAMPLING AND ANALYSIS OF TNT, RDX OR COMPOSITION B IN AIR

Analyte:	TNT, RDX, or their mixtures Composition B is 60% RDX and 39% TNT
Matrix:	Air
Range:	0.15 mg/m^3 to 150 mg/m^3 for TNT 0.5 mg/m^3 to 150 mg/m^3 for RDX
Precision:	± 15%

1. Principle

   1.1 The airborne dust of TNT, RDX or mixtures of both is collected on organic-free glass-fiber filters at a flow rate of 1 to 2 lpm.

   1.2 The collected sample may be stored in a glass-stoppered vial for future analysis or analyzed in the field by solution in an organic solvent and injection into a portable gas chromatograph equipped with a flame ionization detector.

2. Range and Sensitivity

   2.1 The portable gas chromatograph (Analytical Instrument Development, Inc., Model 511) when operated according to these instructions has a lower limit of 3 µg of TNT or 10 µg of RDX per sample. This limit is based on dissolving it in 2 ml. of solvent and injecting 5 µl. The use of metal columns will substantially decrease the sensitivity.

   2.2 For a 20 liter air sample, the lower limits of the method are 0.15 mg/m^3 for TNT and 0.5 mg/m^3 for RDX. Increased sampling times and flows can substantially extend the sensitivity. The upper limit of the range is determined only by filter blockage or loss of sample from the filter media. Samples may always be brought into the linear dynamic range of the gas chromatograph by a dilution procedure.

3. Interferences

3.1 Any compound, which may be present in the sample and which has the same retention time as TNT or RDX at the gas chromatograph analytical conditions described in this method, can be considered an interference. Some plastic filter holders have been found to produce an interfering substance which is taken up by the filter upon prolonged exposure. Proper use of filters and holders eliminates this problem.

4. Precision and Accuracy

4.1 The precision of the analytical method, which includes preparation of standards, solution of the sample and gas chromatographic analysis, was $\pm$ 8% (based on a limited number of laboratory tests and measurement of GC peak area.

4.2 The precision of the entire method including the sampling operation was $\pm$15%.

4.3 No collaborative tests have been performed on this method.

5. Advantages and Disadvantages of This Method

5.1 The sampling method uses a small portable filter rather than liquids. Sampling time may be as brief as 5 to 10 minutes or may be extended. Samples may be analyzed immediately or stored for weeks. The gas chromatographic determination is more specific than colorimetric procedures.

5.2 The major errors of the method are due to the limits of precision of the personal sampling pumps. The requirement for prompt removal of the filter from the filter holder and for transferring it to a glass vial is a disadvantage.

6. Apparatus

6.1 Personal sampling pump approved for explosive atmospheres and capable of maintaining a 2 lpm flow rate.

6.2 Organic-free 37 mm glass fiber filters (Gelman type A) and plastic filter holder.

6.3 Gas chromatograph equipped with a glass column 6 ft. x 1/8 inch OD packed with 80/100 mesh, 3% Dexsil 300 on Chromosorb WAW-DCMS, and a flame ionization detector.

6.4 Recorder suitable for GC output.

6.5 Syringes, 10 µl.

6.6 Small glass stoppered or Teflon sealed vials or tubes.

6.7 Pipettes and volumetric flasks for standard solution preparation.

7. Reagents

7.1 Carbon disulfide, spectroquality

7.2 Recrystallized dry TNT

7.3 Ethyl acetate spectroquality

7.4 Recrystallized dry RDX

7.5 Nitrogen, compressed air and hydrogen for gas chromatograph

8. Procedures

8.1 Cleaning of Equipment: Equipment should be washed with detergent and rinsed with tap water and distilled water.

8.2 Calibration of Personal Pump: Calibrate flow with a representative glass-fiber filter in the line. A one-liter soap bubble meter is convenient.

8.3 Collection and Storage of Samples:

8.3.1 Assemble the filter unit by mounting the filter disc in the holder not more than 30 minutes before use.

8.3.2 Secure the filter unit (open or closed face) to the worker's lapel with the filter entrance pointing down.

8.3.3 Connect the exit end of the filter to the pump, and begin sample collection. The flow rate, times, atmospheric pressure and temperature should be recorded. Twenty liters should be taken for most sampling areas, however, the sample volume may be more or less depending on conditions.

8.3.4 The filter should be removed from the filter holder within one hour and placed in a glass

stoppered vial. The sample may be stored for up to 10 days before analysis. The sample should not be stored at elevated temperatures, or in the filter holders.

8.4 Analysis of Samples:

8.4.1 Add exactly two ml of the solvent directly to the filter contained in the glass stoppered vial. For TNT, carbon disulfide is the preferred solvent. For samples containing RDX, ethyl acetate must be used as the solvent.

8.4.2 The sample vials should be kept capped and 20 minutes allowed for complete solution before analysis.

8.4.3 Typical operating conditions for the AID portable gas chromatograph are: 25 ml/min nitrogen carrier gas; 30 ml/min hydrogen gas flow to detector; 110 ml/min air flow to detector; 185°C injector temperature; 185°C detector temperature and 180°C isothermal column temperature.

8.4.4 For sample injection, the solvent flush technique is employed. One microliter of pure solvent is drawn into the syringe, the needle removed from the solvent, and 0.2 microliters of air drawn in. Then the needle is inserted into the sample and 5 microliters of sample are drawn into the syringe. The contents of the syringe are then injected in the usual manner into the injection port.

8.4.5 The peak areas are determined by triangulation or integrator. When ethyl acetate is used as a solvent, TNT appears on the tail of the solvent peak. Measurements are made from the base line. Peak heights also may be used.

8.4.6 Treat a blank filter through which no air has been drawn in the same manner as the sample filters. This blank is carried through the entire analytical procedure, and the results subtracted from those for samples. The blank from impurities present in the solvent or desorbed from the filter should normally be zero.

9. Calibration and Standards:

TNT and RDX standards are stable for at least a month if tightly stoppered and stored in the dark. Should solvent evaporation occur during storage, new standards should be prepared.

9.1 Standards may be prepared from the purified and dried crystals. It is convenient to express concentrations in terms of µg/2 ml of solvent since the filter samples will be dissolved in 2 ml of solvent:

> 10.0 mg of the pure dry explosive is dissolved in 10 ml of the appropriate solvent (ethyl acetate for RDX and TNT or carbon disulfide for TNT alone). One ml of this stock solution is diluted to 10 ml to give a 200 µg/2 ml solution which is equivalent to approximately 7 times the TLV for a 20 liter sample. Further 10-fold dilutions may be made as above to produce 20 µg/2 ml and 2 µg/2 ml solutions.

9.2 The series of standards should be prepared and analyzed under the same GC conditions and during the same time as the unknown samples. Standards are run exactly as described for samples using a 5 µl injection volume. Curves are prepared by plotting peak areas or heights versus concentrations of standards.

10. Calculations:

10.1 Determine the total micrograms of explosive in the sample from the calibration plot. Calculations are simplified because the same volume of samples and standards are injected and because the standard curve is based on µg/2 ml.

10.2 Deduct the µg for the blank filter from the µg for the sample, to give the corrected µg.

10.3 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$V_c = V_s \times \frac{P}{760} \times \frac{298}{t+273}$$

V_c = corrected volume, in liters

V_s = volume of air in liters as measured

t = temperature during sampling, in degrees Centigrade

P = barometric pressure during sampling, in mm Hg.

10.4 Calculate concentration for each sample as follows:

$$mg/m^3 = \frac{\text{corrected } \mu g}{V_c, \text{ liters}}$$

If Composition B is known to be present, it may be calculated on the basis of its being 60% RDX and 39% TNT.

LABORATORY VALIDATION STUDIES OF RECOMMENDED PROCEDURE

Losses on Prolonged Sampling

The collection efficiency for particulates by glass-fiber filters was known to be high, especially for the relatively coarse dusts found in munitions plants, as will be described later. However, an investigation was made of possible losses on prolonged sampling, to determine if aeration could decompose or volatilize the collected explosives during periods of low dust concentrations. This work was done by passage of pure air over TNT, the more volatile of the two materials. Initial experiments on the recovery of TNT from filters indicated increasing losses with time. In order to determine whether this loss was due to sublimation, air was pulled through a tube containing TNT crystals and an impinger filled with toluene in series. Although there were weight losses from the crystalline TNT, no TNT could be found in the impinger contents. A similar experiment using a cold trap at dry ice temperature also failed to collect a detectable amount of TNT. In a subsequent experiment, TNT on a filter was placed on a plate in a covered glass Petri dish without touching the sides and after standing for three days, the filter was removed and the walls of the dish were rinsed and analyzed for TNT. It was found that sublimation had occurred and TNT was deposited on the walls during this substantial interval.

To accurately determine the losses of TNT from the filters, the following experiment was conducted. To each of five 37 mm glass-fiber filters, 10.0 µg of TNT was deposited by placing on it 0.1 ml of a 100.0 ppm solution of TNT in CS_2 and allowing the solvent to evaporate. After 20 minutes each of four of the filters was placed into a filter holder and room air was pulled through it at 2.0 lpm. At 2 hour intervals one of the remaining filters was removed from its holder, CS_2 added to dissolve the TNT and 5 µl of the solution injected into the gas chromatograph. The weight losses and times are shown in Figure 9. Calculation from the slope of the line and the air flow rate shows that the concentration of TNT in the exiting air corresponded to 0.007 mg/m^3, a small fraction of the TLV of 1.5 mg/m^3. This experiment gives losses for the worst case of a very fine crystalline deposit of TNT.

Another experiment was conducted to determine the losses of particulate TNT of a larger size more closely resembling that of field sampling. The particulates were generated diluted, dried and collected on filters using the apparatus shown schematically in Figure 10. Purified air at 4.5 lpm was pumped through the Pen-A-Sol generator and room air entered the dilution chamber tangentially for make-up to the total flow of 14.2 lpm drawn through the apparatus by a

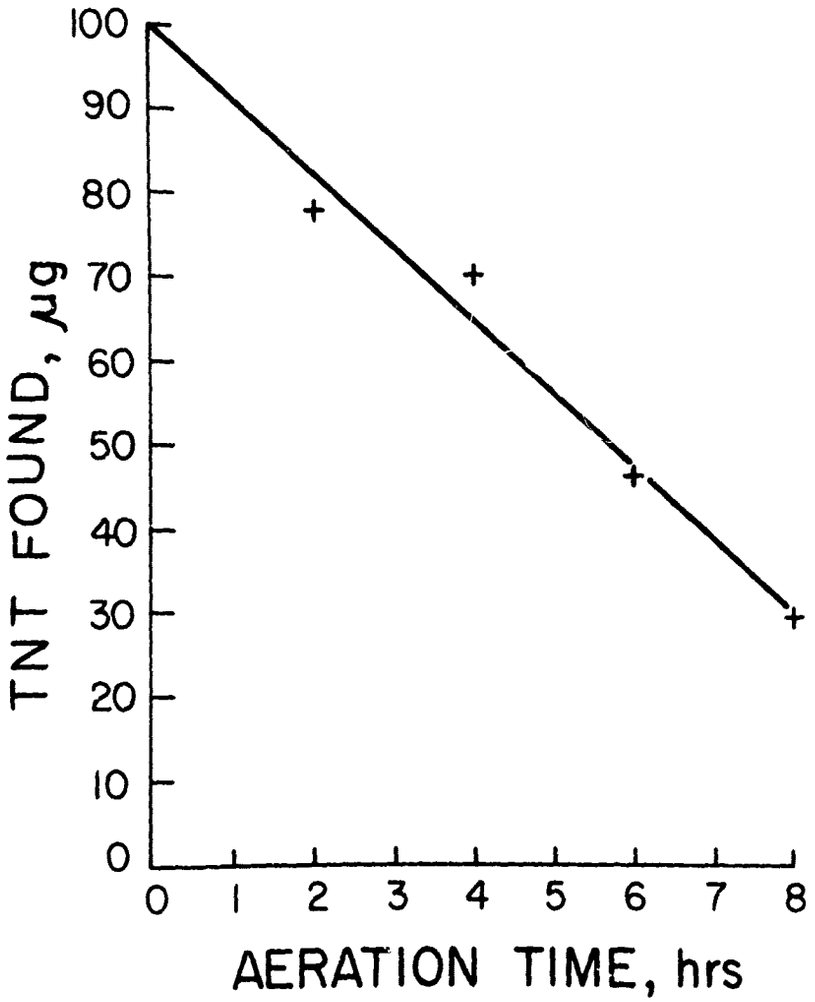


Figure 9. Losses of TNT from 37 mm Glass Fiber Filter Upon Prolonged Aeration at 2 lpm.

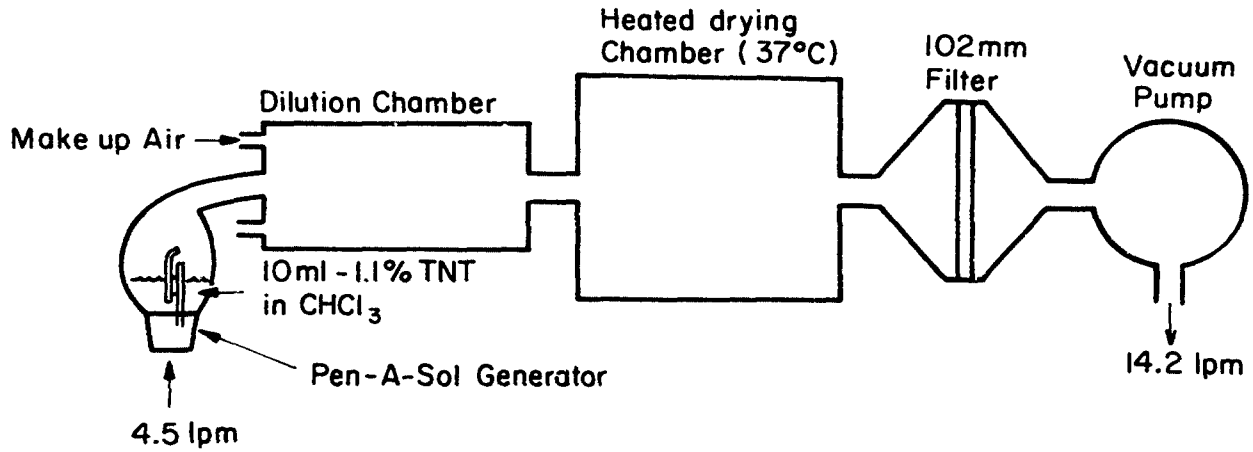


Figure 10. Schematic Daigram of TNT Particle Generator

vacuum pump. There was only enough TNT solution to run approximately 40 sec. The procedure was to start the vacuum pump then the air flow through the generator. The TNT particulate was collected on a 102 mm glass-fiber filter of material similar to that used in the recommended 37 mm sampling filters. Four 37 mm circles were cut with a die, and each piece was placed in a 37 mm filter holder. Air was then pulled through them at 1 lpm. The filters were removed and analyzed after 1, 2 and 4 hour intervals. The remainder of the 102 mm filter was analyzed and used to calculate the initial amount on each of the cut circles. The results are shown in Table V.

TABLE V

LOSSES OF PARTICULATE TNT ON 37 MM GLASS FIBER FILTERS UPON PROLONGED AERATION AT 1 LPM

Run No.	Initial TNT, µg	Losses of TNT, µg		
		1 Hr.	2 Hr.	4 Hr.
1	768	7	29 64	7
2	719	-18[a]	29 32	72
3	724	-29[a]	66	32 101
4	726	72	64	77 89
5	771	73	152	88 128

[a] Apparent gain

Each TNT analysis was done by replicate injections into the gas chromatograph, with good agreement. The scatter may, therefore, represent non-uniformity of the deposit on the large 102 mm filter. The average initial amount of TNT on the 37 mm filters was 742 µg, which was much greater than the 3 µg needed for analysis. If the 4-hour losses are averaged, the loss rate is about 2% per hour, which is not serious. Only a 10 minute sample is ordinarily needed. An Anderson sampler was inserted in place of the filter in the TNT aerosol apparatus shown in Figure 10 in order to determine the particle size distribution. Glass-fiber filters

were cut to fit each stage of this sampler and subsequently analyzed to determine the masses of TNT. The results of four runs were a mass median diameter of 0.88 μ and a geometric standard deviation of 1.54.

Losses on Sample Storage

Preliminary studies indicated a decrease in the recovery of TNT collected on glass-fiber filters with storage time. Although this may not be an important problem if an immediate field analysis is made, that may not always be possible. Experiments were conducted to determine the magnitude and cause of these losses and how they could be minimized. In the Petri dish experiment described in the previous section it was shown that although TNT sublimed onto the glass walls, it could be recovered by rinsing them.

In another more quantitative experiment, to one-half sections of glass-fiber filters, 1 ml of 12.0 μg/ml solutions of TNT and RDX were added in 50 μl portions. The filters were allowed to dry in the room air for one hour. Then one set of filter sections was stored in the open in a dark cabinet, a second set was placed in Tenite filter holders and a third set was placed in glass stoppered vials. At selected times the filters were analyzed for TNT. The samples stored in the open or in filter holders were transferred to glass stoppered vials and 1 ml of ethyl acetate added. To the samples stored in glass vials, one ml of ethyl acetate was added in a manner to wash down the walls. The results for TNT are shown in Table VI and Figure 11. No losses of RDX occurred after filters were stored for 24 hours in air, or after 6 days in a similar experiment with 6 replicate filters.

It is clear that unacceptable TNT losses occurred from the filters left in the open or stored in filter holders, but not from those in the vials. These losses of TNT during long storage periods were believed to result from sublimation or irreversible absorption but not from decomposition of the TNT. The analyses of the filters stored in the dark did not show the presence of any additional peaks which might result from decomposition products. TNT is relatively stable in light although colorless fresh crystals change to a yellowish color on standing. If the analysis is conducted within 10 days in the manner specified in the recommended procedure, storage losses should be minor.

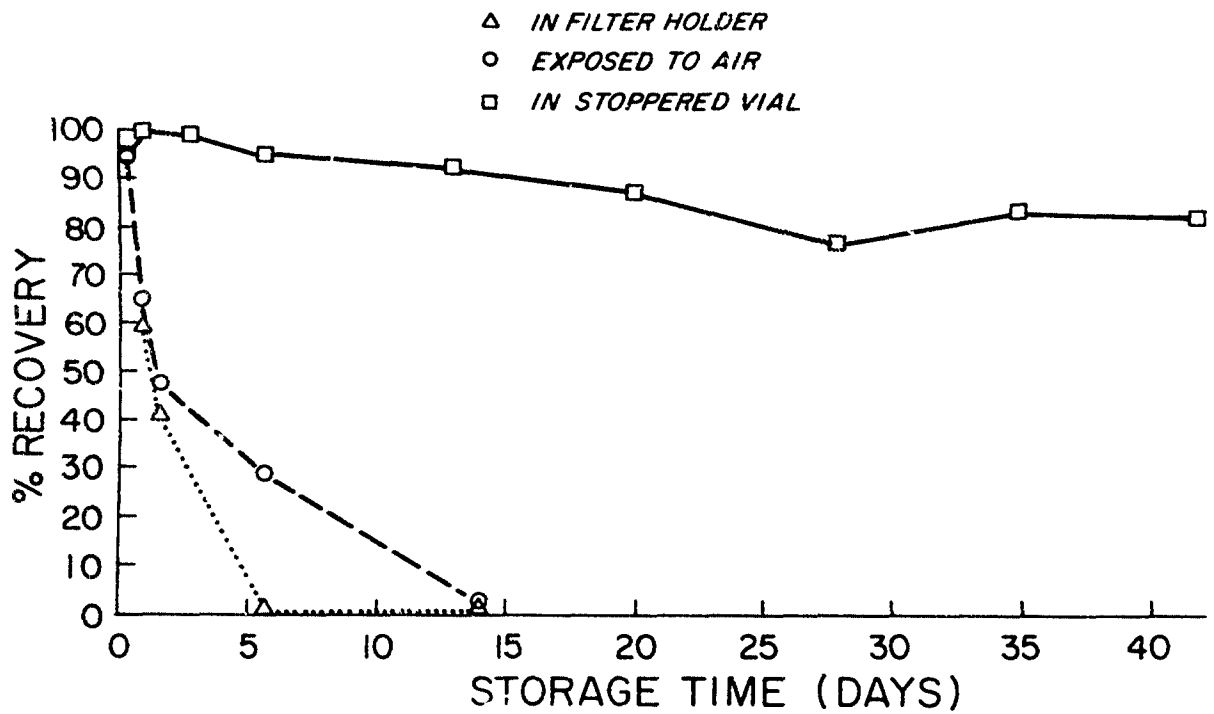


Figure 11. Losses of TNT on Filters Upon Storage.

TABLE VI

LOSSES OF TNT ON GLASS FIBER FILTERS

STORED IN VARIOUS WAYS

In Glass Stoppered Vials		In Tenite Filter Holders		Open in Dark Cabinet	
Storage Time, days	% Recovery	Storage Time, days	% Recovery	Storage Time, days	% Recovery
0.04	94.3	0	95.4	0.04	95.4
0.04	96.5	0	94.6	0.04	94.6
0.75	100.2	0.72	59.1	0.75	65.1
1.75	98.5	1.46	41.0	1.50	47.2
5.75	94.9	5.62	1.0	5.67	28.8
13	92.2			14	2.0
20	87.2				
28	76.6				
35	83.0				
42	82.2				

Accuracy of the Recommended Method.

The percentage error of the entire procedure is the sum of the percentage errors introduced in the individual steps which make up the procedure. If the flow rate of the personal sampling pump is carefully calibrated with a primary standard and periodically checked, the error may be attributed to the reading of the rotameter. The recovery experiments previously described indicated that the accuracy is affected by storage time. This error may be minimized by analyzing the collected samples within a few hours of collection or by applying a correction based on the results shown in Figure 11.

Because the gas chromatographic analysis of TNT or RDX is a comparative method, the calibration standards must be accurate. If the reference solution is prepared by weighing TNT or RDX, they should be carefully purified and dried, and

the standard solutions should be freshly prepared. The calibration curves previously given in Figures 6 and 7 show responses to injections of different volumes at a fixed concentration. To check the validity of the method, other calibration curves were prepared by injecting a fixed volume (5 µl) of ethyl acetate solution of different concentrations. Consistent results were obtained as shown in Figures 12 and 13 and Table VII. These are typical calibration curves for use in the procedure. The precision of the procedure was calculated from results of replicate injections of the samples and calibration solutions. The relative standard deviation was 3% for TNT and 4% for RDX, based on measurements of peak areas in mm^2.

TABLE VII

CALIBRATION DATA FOR TNT AND RDX

IN ETHYL ACETATE (5 µl INJECTIONS)

Conc. µg/ml	Attenuation	Peak Response X Attenuation		Integrator Counts
		Height, mm	Area, mm^2	
		TNT SOLUTIONS		
1.5	1 x 1	43.6	65.4	a
1.5	1 x 2	48.0	67.2	a
3.0	1 x 1	95.0	123.5	a
3.0	1 x 2	93.0	125.6	a
3.0	1 x 4	93.2	130.4	a
7.5	1 x 2	228.2	308.0	a
7.5	1 x 4	237.6	320.8	1760
7.5	1 x 8	217.6	293.6	1760
15	1 x 4	464.0	603.2	3320
15	1 x 8	496.8	645.6	3840
15	1 x 16	496.0	644.8	3440
30	1 x 8	1033.6	1344.0	7840
30	1 x 16	1060.8	1379.2	8160
60	1 x 16	2182.4	2836.8	15360
90	1 x 32	3275.6	3910.4	22080
120	1 x 32	5760.0	7200.0	38720

TABLE VII (continued)

Conc. µg/ml	Attenuation	Peak Response X Attenuation Height, mm	Area, mm^2	Integrator Counts
		RDX SOLUTIONS		
3.0	1 x 2	6.0	9.0	a
7.5	1 x 4	16.8	46.4	a
7.5	1 x 8	15.2	50.4	a
15.0	1 x 4	28.8	88.0	a
15.0	1 x 8	36.8	88.0	a
15.0	1 x 16	41.6	99.2	a
30.0	1 x 8	80.8	226.4	a
	1 x 16	81.6	228.8	a
	1 x 16	171.2	480.0	2560
	1 x 16	257.6	721.6	4080
90.0	1 x 32	246.4	690.2	4320
120.0	1 x 32	432.0	1209.6	6560

[a] Not in accurate range.

FIELD STUDIES

Field trips were made to two production plants for the purposes of: 1) Measuring the particle size in the work area, 2) Testing the recommended method in the field, 3) Comparing the levels measured by the impinger method and the recommended procedure, and 4) Modifying the procedure if necessary for improvements.

Army Munitions Plant at Newport, Indiana.

The first plant visit was conducted on January 17, 1974 at the Newport, Indiana installation. Briefly, production of TNT consisted of the following steps: 1) nitration of toluene, 2) purification by the Sellite process, 3) pumping the purified liquid TNT to the packaging area, where it was cooled and flaked prior to being dropped into paper sacks for shipment. It is during the packaging process, primarily a manual method, that significant worker exposures

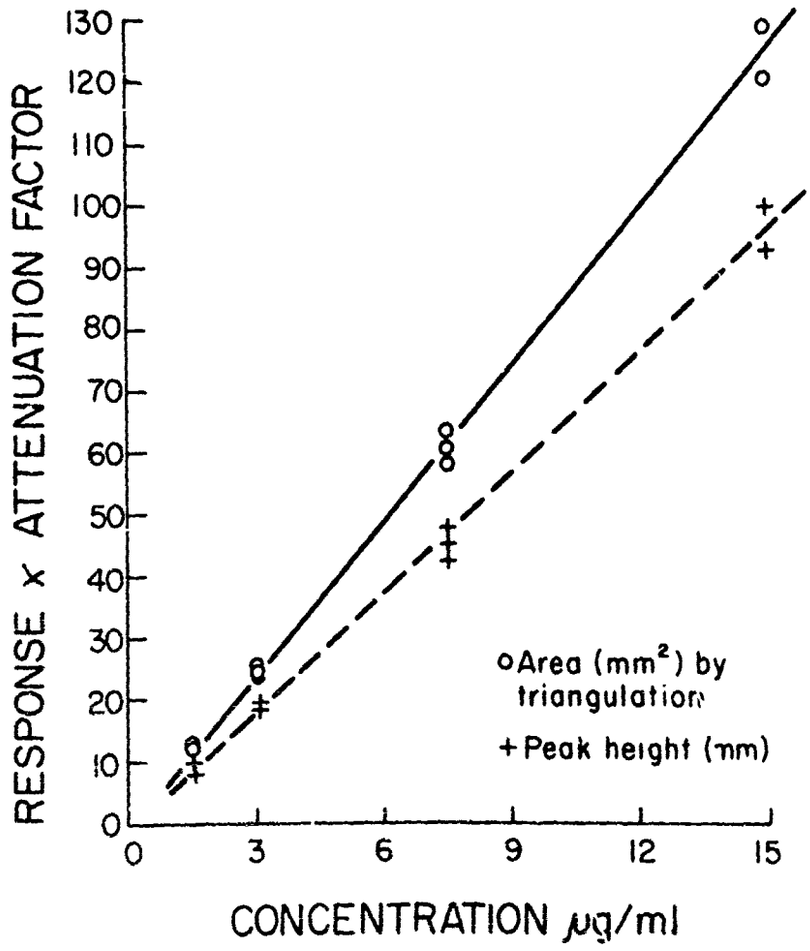


Figure 12. Responses to 5 µl Injections of TNT in Ethyl Acetate Solutions.

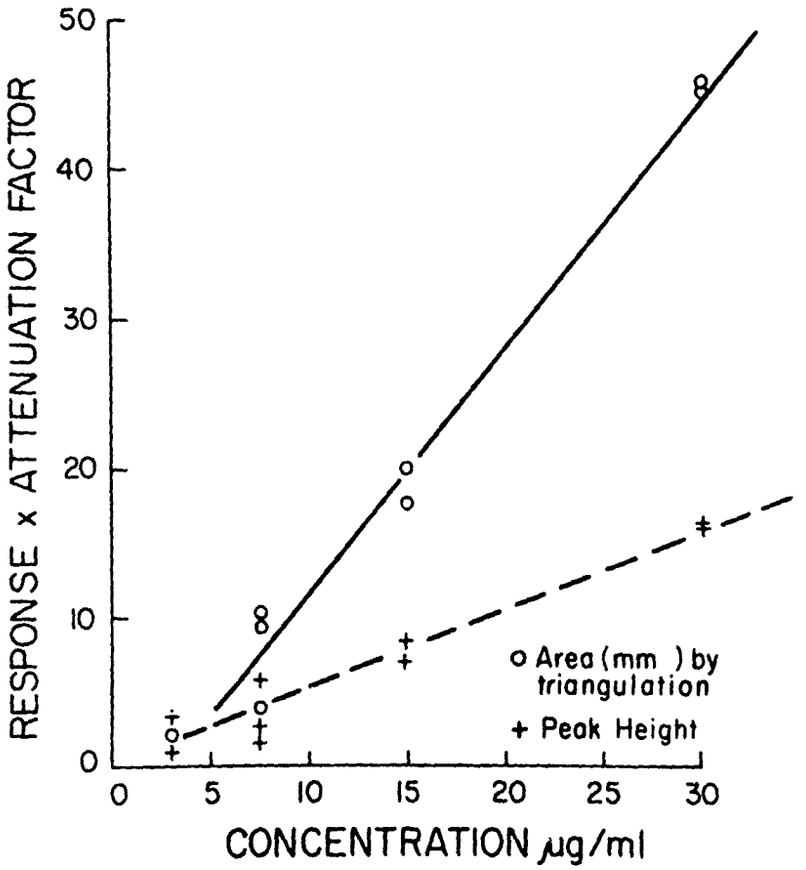


Figure 13. Responses to 5 µl Injections of RDX in Ethyl Acetate Solutions.

can occur, even though they appeared to be using good work practices. The wide size range of TNT dust particles forcibly expelled by air displacement when the sack was being filled may have reached the breathing zone or settled on the skin of workers. A significant portion of these particles was not captured in the local exhaust systems. Additional significant amounts of TNT dust also were expelled when the paper bag was creased and folded before sealing the cardboard shipping containers. Similar exposures may be expected when the bags are emptied and when they are collapsed for disposal.

A 7-stage Anderson sampler was used to establish the size distribution of the TNT particles to which the workers were exposed. To avoid any spark hazard, a hand-operated vacuum pump was used, which had been previously calibrated with a dry gas meter. A flow rate of 21 lpm required 36 crank revolutions per minute. During two 10 minute sampling periods, uniform flow rates were maintained by counting the strokes while observing a stop-watch (363 and 351 strokes for samples 1 and 2, respectively). An organic-free glass-fiber filter cut to 7.5 cm diameter was fitted on the top of each stage to collect the particle fractions. Small particles passing through the sampler were collected on a 47 mm glass-fiber filter installed downstream. The sampler was taken to a TNT-free area and each filter was removed, folded and inserted in an individual 10 ml glass stoppered vial, for subsequent laboratory analysis for TNT by the recommended procedure.

Sample No. 1 was collected at the bag filling operation near the edge of the exhaust hood where they were not captured, and, therefore, contributed to the worker's exposure. The average airborne level, calculated by dividing the sum of the weights of TNT found on each filter by the volume of air, was 0.9 mg/m^3. The size distribution is shown in Table VIII and Figure 14. Sample No. 2 was taken at the sack closing operation. The sampling head was inverted 5 feet above the floor and 2 feet away from the bag, which was representative of the sacker's exposure. His exposure may have been somewhat lower because the ventilation tended to carry the particles away from him. The level found was 8.5 mg/m^3 which is 5.6 times above the standard. The size distribution is shown in Table VIII and Figure 15. Most of this material was above the respirable size range.

A sample of the final product, Military Grade TNT, was analyzed in the laboratory with a temperature programmed gas chromatograph and found to be of high purity. No additional peak due to isomers or mono- or di-nitration products could be found. It was, therefore, assumed that determination of the α-TNT was an appropriate measure of

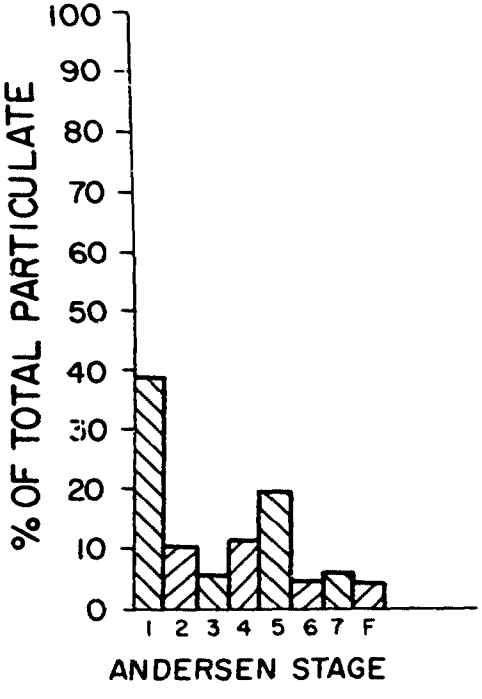


Figure 14. Size Distribution of TNT Dust at Sack Filling Operation.

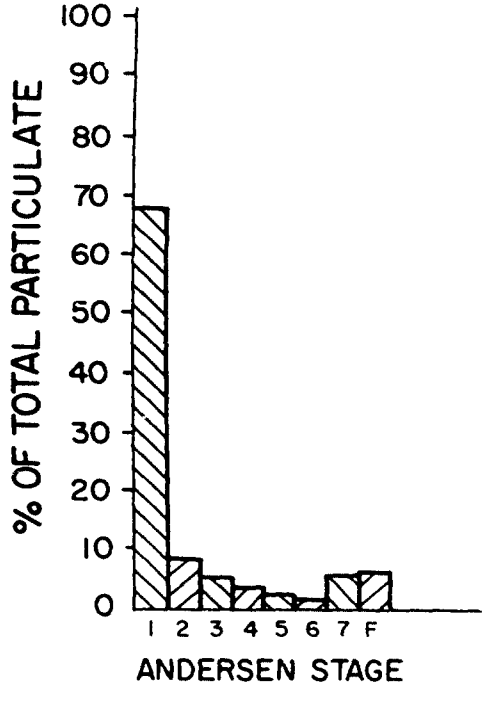


Figure 15. Size Distribution of TNT Dust at Sack Closing Operation.

potential exposures.

TABLE VIII

SIZE DISTRIBUTIONS OF TNT DUST AT SACKING OPERATIONS

Anderson Stage No.	Size, μm ($SECD_{50}$)	Sack Filling TNT, μg	Sack Filling Weight %	Sack Closing TNT, μg	Sack Closing Weight %
1	7.4	72.8	39.0	1180.0	67.5
2	5.4	19.8	10.5	147.5	8.5
3	2.95	10.0	5.5	88.5	5.0
4	1.53	21.8	12.5	68.5	4.0
5	0.93	36.0	19.0	43.0	2.5
6	0.54	7.5	4.0	28.0	1.5
7	0.24	11.0	6.0	94.5	5.0
Filter	<0.24	7.5	4.0	102.5	6.0

Nineteen samples were collected to determine the concentrations of TNT in air. In the sacking room they were collected at Line No. 2 on the side opposite from the operators, and downwind from them. Visible particles of TNT were being discharged, and these levels probably were substantially higher than operator exposures. In four sets simultaneous samples were collected with impingers containing toluene for comparisons. All samples were collected at 2 lpm, for 10 minutes unless listed otherwise. Because of lack of time, the samples were brought back to the laboratory rather than being analyzed in the field. Results are given in Table IX. Samples of each set (first letter in sample number) were collected simultaneously and close together, although large particles could have entered one more than another by chance. The glass-fiber filters effectively collected and held the TNT, since there were no detectable amounts of TNT found in any of the in series downstream impingers. Comparison of the levels of TNT collected in parallel indicated that the filters have equal or higher values than the impingers. The samples on open face-filters were significantly higher than those on

the closed-face filters. The faces of these filters were approximately vertical, and they apparently collected a greater fraction of the larger TNT particles. These were larger than the respirable size range, but significant as a skin hazard, which is the basis of the TLV for TNT. It seems likely that in hot weather, sweat could hold the particles on the skin and cause a high exposure.

TABLE IX

TNT IN AIR SAMPLES COLLECTED AT ARMY MUNITIONS PLANT, NEWPORT, INDIANA

January 17, 1974

Sampling Location	Sample No.	Sampling Device[a]	TNT mg/m^3
Sack filling shaker,	A-1	CF	1.29
3 ft. above floor	A-2	CF	0.72
		Imp.D.	0.00
3 ft. above floor	A-3	Imp.	0.70
Sack closing	B-1	OF	47.7
Sack closing	B-2	OF	13.3
		Imp.D.	0.0
Sack closing	B-3	Imp.	7.2
Lapel, W.R.B.	C-1	CF	0.72
Breathing zone of bag folding operator	D-1	CF	1.74
Sack filling shaker	E-1	CF	2.41
6 ft. above floor	E-2	CF	0.98
Lapel, W.R.B.	F-1	CF	1.97
Middle of remelt room	G-1	CF	0.77[b,c]
Middle of remelt room	G-2	CF	0.95[b]
Nitration room	H-1	CF	3.74
5 ft. from 1st reactor		Imp.D.	0.00
Nitration room above separator unit	J-1	CF	1.14
Nitration room above separator unit	J-2	Imp.	0.05
Blank	Bl.		0.00

[a] CF = closed-face filter, OF = open-face filter, Imp. = impinger, Imp.D. = impinger in line downstream from filter.

[b] 15 min. sample; all others 10 min.

[c] Filter previously in holder for 3 days.

Holston Ammunition Plant, Kingsport, Tennessee.

The second plant visit was to the Holston Ammunition Plant, Kingsport, Tennessee on August 5, 1974 to demonstrate the recommended sampling and analytical procedures to the Army Medical Research and Development Command personnel. Samples were collected at 2 lpm for 10 minutes from various areas of the plant on glass-fiber filters by Army personnel. They were not analyzed at Holston because the glass column inside the gas chromatograph was broken during transportation. A spare metal column proved to be of only marginal value because during the calibrations it absorbed more TNT and RDX than was expected from previous laboratory studies. Standards were injected several times before the response approached the expected value. This rapid decay with time of the response prompted the decision to delay sample analysis until a new glass column could be installed. The samples were placed in glass stoppered vials for transportation and storage. The analyses were conducted in the recommended manner, four days later. The results, which were previously reported to the U. S. Army Environmental Hygiene Agency, are shown in Table X.

TABLE X

AIR SAMPLES COLLECTED AT HOLSTON

AMMUNITION PLANT, KINGSPORT, TENNESSEE

August 5, 1974

Description	Analysis Number	Milligrams/m^3 TNT	RDX
#1 TNT Dumping	74A-3285	0.75	<0.5
#7-7 Bldg. M-7	74A-3286	0.36	<0.5
#7-2 Bldg. M-7	74A-3287	32.0	13.5
#2 TNT Dumping	74A-3288	0.4	<0.5
#4 TNT Dumping	74A-3289	0.2	<0.5
#3 TNT Dumping	74A-3290	0.9	<0.5
#7-4 Bldg. M-7	74A-3291	0.2	<0.5
#7-8 Bldg. M-7	74A-3292	0.3	<0.5
#8 TNT Dumping	74A-3293	0.2	<0.5
#5 TNT Dumping	74A-3294	0.3	<0.5
#7-3 Bldg. M-7	74A-3295	0.1	<0.5
#6 TNT Dumping	74A-3296	0.3	<0.5
#7-6 Bldg. M-7	74A-3297	7.3	6.7
#7-5 Bldg. M-7	74A-3298	6.9	6.4
#7 TNT Dumping	74A-3299	0.5	<0.5
#7-1 Bldg. M-7	74A-3300	61.0	60.0

The portable gas chromatograph was self-contained and could be moved from one location to another, although it was heavy and awkward to handle. The instrument performed satisfactorily except for breakage of the glass column. The column did not slip from the fittings, but broke from shock during handling. It is recommended that a spare be carried in a suitable container. It must be installed carefully as it is easily broken then as well. Because the electrical parts were not explosion proof and the detector had an open flame, the instrument was operated at a convenient site which was isolated from the production quantities of TNT.

The instrument required approximately 3.5 hours to heat from room to operating temperature (180°C). It is essential that this column temperature be attained if RDX is analyzed to avoid peak spreading. Standards injected 15 minutes apart will have the same retention times when the temperature has equilibrated. The preparation of standards in the field can be accomplished conveniently if appropriate portions of TNT or RDX are previously weighed and placed in stoppered volumetric flasks. The standards can be prepared at the site by adding the necessary amounts of solvent.

LITERATURE CITED

1. American Conference of Governmental Industrial Hygienists. "Documentation of the Threshold Limit Values for Substances in Workroom Air", 3rd ed., P. O. Box 1937, Cincinnati, Ohio, 1971.

2. American Conference of Governmental Industrial Hygienists. "Threshold Limit Values for Chemical Substances in Workroom Air Adopted by the ACGIH for 1974."

3. American Industrial Hygiene Association. AIHA Hygienic Guide Series, 66 South Miller Road, Akron, Ohio 44313.

4. Cone, T. E., Jr.: "Determination of TNT (2,4,6-trinitrotoluene) in Air". U. S. Naval Med. Bull. 41:219 (1943).

5. Crawl, James, Unpublished communication, Naval Industrial Environmental Health Center, Cincinnati, Ohio, 1974.

6. Cumming, W. M., and W. G. D. Wright: "Determination of Airborne Trinitrotoluene, Tetryl and Dinitrotoluene." Brit. J. Ind. Med. 2:83 (1945).

7. Edward, G.: "The Vapour Pressure of 2,4,6-trinitrotoluene." Trans., Faraday Soc., 46:423-7 (1950).

8. Gehring, D. G., and J. E. Shirk: "Separation and Determination of Trinitrotoluene Isomers by Gas Chromatography." 1315 (1967).

9. Goldman, F. H., and D. E. Rushing: "Diethylaminoethanol as a Reagent for the Detection and Colorimetric Determination of Small Amounts of Trinitrotoluene in Air." J. Ind. Hyg. Toxicol. 25:164 (1943).

10. Hoffsommer, John C.: "Quantitative Analysis of Nitro Compounds in the Micro-to-picogram Range by a Combination of Thin-Layer and Vapor Phase Chromatograph with Nickel-63 Electron Capture Detector." J. Chromatog. 51:243-51 (1970).

11. Karasek, F. W.: "Detection of TNT in Air, Research and Development, p 33, May, 1974.

12. Kay, K.: "Determination of TNT (2,3,6-trinitrotoluene) in the Air." Can. J. Research 19:86 (1941).

13. Lindner, Victor: "Kirk-Othmer Encyclopedia of Chemical Technology," 2nd Ed., John Wiley and Sons, Vol. 8, p 611, 1966.

14. McNair, H. M. and E. J. Bonelli, "Basic Gas Chromatography" 5th Ed., Varian Aerograph p 118, 1969.

15. Pinto, S. S. and J. P. Fahy: "A New Colorimetric Method for the Determination of TNT (2,4,6-trinitrotoluene) in Air." J. Ind. Hyg. Toxicol. 24:24 (1942).

16. Ruchhoft, C. C., M. LeBosquet, Jr., and W. G. Meckler: "TNT Wastes from Shell-Loading Plant." Ind. Eng. Chem., Anal. Ed. 37:939 (1948).

17. Ruchhoft, C. C. and W. G. Meckler: "Colored TNT Derivatives and Alpha-TNT in Colored Aqueous Alpha-TNT Solutions." Ind. Eng. Chem., Anal. Ed. 17:430 (1945).

18. Von Oettingen, W. F., et al.: "Experimental Studies on the Toxicity and Potential Dangers of Trinitrotoluene." Public Health Service, Washington, D. C. (1944).

PUBLICATIONS AND PERSONNEL SUPPORTED

The work was presented by Dr. Burg as Paper No. 110 on May 16, 1974 at the meeting of The American Industrial Hygiene Association in Miami, Florida, and the following abstract was published in the program schedule:

ABSTRACT

110. The Analysis of TNT Dust in Air by Gas Chromatography

BERNARD E. SALTZMAN, JOHN E. CUDDEBACK and

WILLIAM R. BURG, University of Cincinnati, Cincinnati, Ohio.

A method for the sampling of TNT dust in the work place and the analysis of the sample by a gas chromatograph is described. Sampling, stability of samples and sample handling are discussed. The subsequent analysis of the samples may be performed in the field with a portable gas chromatograph or at a central laboratory. Operating conditions, column materials and detectors for the gas chromatograph which allow the separation and quantitation of the important TNT isomers and related explosives are presented. The relative suitability of the electron capture and flame ionization detectors is examined for the analysis of TLV levels of TNT.

The following personnel were supported in part by this contract:

Bernard E. Saltzman
John E. Cuddeback
William R. Burg
Leo Ertl