



Cyclonite (RDX)

Method no. PV2135

Target Concentration: 1.5 mg/m³ (ACGIH TLV-TWA)

Procedure: Samples are collected by drawing known volumes of air through 37-mm glass fiber filters. Samples are extracted with acetonitrile and analyzed by high performance liquid chromatography (HPLC) using an ultraviolet (UV) detector.

Recommended air volume and sampling rate: 120 minutes at 1.0 L/min (120 L)

Detection limit of the overall procedure: 0.012 mg/m³ (based on the recommended air volume and the analytical detection limit)

Status of method: Partially validated method. This method has been partially evaluated and is presented for information and trial use only.

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George F. Lewis

Carcinogen and Pesticide Branch
OSHA Salt Lake Technical Center
Sandy UT-84070

1 General Discussion

1.1 Background

1.1.1 History of procedure

A set of samples collected on glass fiber filters in tandem with Tenax tubes requesting the analysis of RDX was received at the OSHA Lab.

This evaluation was undertaken to determine the effectiveness of a glass fiber filter as a sampling device for RDX. This study indicates a Tenax backup tube is not necessary.

1.1.1 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy).

Cyclonite is a highly explosive solid, more powerful than TNT that found extensive use during World War II. RDX is desensitized by mixing it with TNT to form cyclotols or by coating it with waxes, synthetic polymers, and elastomeric binders. RDX made in the U.S. is converted into either Composition B (60% RDX, 40% TNT, pt wax) or Composition A3 (RDX 91% wax 9%). (Ref. 5.1-5.2)

The following paragraph describing the toxicity of RDX is excerpted from the book Documentation of the Threshold Limit Values. (Ref. 5.2)

The clinical manifestations referable to the central nervous system of nausea, vomiting, convulsions, and unconsciousness seen in the workers paralleled those previously reported in animals by von Oettingen and Sunderman. Animals' studies show RDX not to be an acutely toxic substance. Human illness results from repeated exposures via the respiratory and gastrointestinal tracts and by skin absorption.

The following paragraph describing some effects and symptoms of RDX were taken from Industrial Hygiene and Toxicology. (Ref. 5.3)

Epileptiform seizures have occurred in workplace manufacturing trimethylenetrinitramine (T4) [RDX] in Italy. The convulsions occurred either without warning or after 1 or 2 days of insomnia, restlessness, and irritability. They were generalized tonic-clonic convulsions resembling in all clinical respects the seizures seen in epilepsy but occurring in individuals without a previous history of seizures. They were most frequent in persons doing the drying sieving and packing where the dust could be inhaled. The attacks disappeared when the workers were removed from contact with trimethylenetrinitramine. The seizures were followed by temporary post convulsive amnesia, malaise, fatigue, and asthenia but there was eventually complete recovery.

When cyclonite dust control was maintained below 1.5 mg/m³, relative good health has been reported. This TLV-TWA value was based on a suggestion by von Oettingen and co-workers. RDX has been given a TLV-TVA of 1.5 mg/m³ by the ACGIH. (Ref. 5.3)

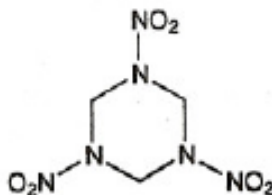
OSHA adopted this same value as its PEL in March 1989. Editorial Note: These March 1989 PELs were vacated on July 7, 1992 and ceased to be enforceable on March 23, 1993 (FR 58:35338-35351, 6/30/1993).

1.1.2 Potential workplace exposure

Widespread exposure to workers handling cyclonite occurred during World War II, and as late as 1962. No estimate of worker exposure to RDX since 1962 could be found. Potential exposure involves those individuals in manufacturing, formulation, and application of RDX.

1.1.3 Physical properties (Ref. 5.1-5.6)

Molecular weight:	222.15
Molecular formula:	C ₃ H ₆ N ₆ O ₆
CAS #:	121-82-4
IMIS #:	2224
Melting point:	205 to 206 °C
Vapor Pressure:	Log 10pa = 16.26 - 6785/K or Log paHg = 14.14 - 6785/K
Appearance:	white crystalline solid
Solubility:	One gram in 25 mL acetone; slightly soluble in acetonitrile, methanol, ether, ethyl acetate, glacial acetic acid; practically insoluble in water, carbon tetrachloride, carbon disulfide.
Synonyms:	RDX, Cyclonite, T4, Hexogen, Trimethylenetrinitramine, Cyclotrimethylenetrinitramine, 1,3,5-trinitrohexahydro-s-triazine
Chemical names:	Hexahydro-1,3,5-trinitro-1,3,5-triazine
UV spectrum:	See Figure 1.
Stability:	Stable (stored for 10 months at 85 °C without perceptible deterioration), Class A explosive (Detonation occurs by sudden shock, high temperature, or a combination of the two.)
Structural formula:	



1.2 Limit defining parameters

The detection limit of the analytical procedure is 4.823 ng per injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise.

2 Sampling Procedure

2.1 Apparatus

2.1.1 A personal sampling pump that can be calibrated to within $\pm 5\%$ of the recommended flow rate with the sampling device in line.

2.1.2 A 37-mm glass fiber filter mounted in a polystyrene cassette (with backup pad).

2.2 Reagents

No sampling reagents are required.

2.3 Sampling technique

- 2.3.1 Immediately before sampling, remove the plastic plugs from the filter cassette.
- 2.3.2 Attach the cassette to the sampling pump with flexible tubing so that air passes through the filter first. Place the cassette in the worker's breathing zone in such a manner that it does not impede work performance.
- 2.3.3 After sampling for the appropriate time, remove and seal cassette with plastic end caps.
- 2.3.4 Wrap each sample end-to-end with a Form OSHA-21 seal.
- 2.3.5 Submit at least one blank with each set of samples. Handle the blank the same as the other samples but do not draw air through it.
- 2.3.6 Submit any bulk samples in a separate container. Do not ship them with the air samples.

2.4 Extraction efficiencies

Nine glass fiber filters were each liquid spiked with a solution of RDX at a concentration of 4.859 mg/mL. Three filters were each liquid spiked with 18 μ L (0.5x PEL) of RDX standard. A second group of three filters was each liquid spiked with 38 μ L (1x PEL) of RDX standard. A third group of three filters were each liquid spiked with 76 μ L (2x PEL) of RDX standard. These filters were allowed to sit overnight on a desk at ambient temperature, then extracted with 3.0 mL of acetonitrile, and analyzed as in Sections 3.4 and 3.5.

Table 2.2
Glass Fiber Filter Extraction Study

filters	0.5x	1x	2x
F1	100.3	106.8	95.3
F1	100.4	97.3	101.1
F3	90.0	104.5	91.2
averages	96.9	102.9	95.9

2.5 Retention efficiency

Five glass fiber filters were each liquid spiked with 76 μ L (2x PEL) of a 4.859 mg/mL solution of RDX standard. One hundred twenty liters of humid air (approximately 70% relative humidity) was drawn through each of four filters. The fifth filter had 285 liters of humid air drawn through it and had a recovery of 101.9%. All five of these filters were then extracted and analyzed as in Sections 3.4 and 3.5.

Table 2.5
Retention Efficiency Study

filters	% recovery
RET1	107.0
RET2	99.5
RET3	98.3
RET4	89.7
average recovery	= 98.6%

2.6 Sample storage

Eighteen glass fiber filters were each liquid spiked with 38 µL (1x PEL) of a 4.859 mg/mL solution of RDX. One hundred twenty liters of humid air (approximately 70% relative humidity) were drawn through each filter. Half of the filters were stored in a drawer at ambient temperature, and the other half were stored in a refrigerator (2 °C). They were stored according to Table 2.6, extracted, and analyzed as in Sections 3.4 and 3.5.

Table 2.6
Storage Study

days	ambient	averages	refrigerator	averages
0	99.9%		103.2%	
	99.7%		108.9%	
	102.9%	100.8%	108.4%	106.8%
7	97.6%		100.8%	
	103.3%		94.9%	
	96.1%	99.0%	97.7%	97.8%
15	97.7%		95.5%	
	95.7%		98.4%	
	91.4%	94.9%	98.3%	97.4%

average recovery (ambient) = 98.2%
average recovery (refrigerated) = 100.7%

2.7 Recommended air volume and sampling rate.

2.7.1 The recommended air volume is 120 L.

2.7.2 The recommended flow rate is 1.0 L/min.

2.8 Interferences (sampling)

It is not known if any compounds will interfere with the collection of RDX. Suspected interferences should be reported to the laboratory with submitted samples. HMX (also an explosive) is a contaminant of and associated with RDX manufacturing and collection.

2.9 Safe precautions (sampling)

2.9.1 Attach the sampling equipment in such a manner that it will not interfere with work performance or employee safety.

2.9.2 Follow all safety practices that apply to the work area being sampled.

3 Analytical Procedure

3.1 Apparatus

3.1.1 An HPLC equipped with a UV detector and a manual or automatic injector. A Waters 600 pump, Waters 712 autosampler, and Waters 490E UV detector were used in this evaluation.

3.1.2 An HPLC column capable of separating RDX from any interference. A (25-cm x 4.6-mm i.d.) Econosphere CN (5-µm) column was used in this evaluation.

3.1.3 An electronic integrator or other suitable means of measuring detector response. A Hewlett-Packard 3357 data system was used in this evaluation.

3.1.4 Vials, 4-mL glass including septa lined with polytetrafluoroethylene (PTFE).

3.1.5 Volumetric flasks, pipettes, and syringes.

3.2 Reagents

3.2.1 Acetonitrile, Tetrahydrofuran, HPLC grade.

3.2.2 Water, HPLC grade. A Millipore Milli-Q system was used to prepare the water in this evaluation.

3.2.3 RDX. A 91% pure standard with 9% MIL-C4408 desensitizer was used in this evaluation.

3.3 Standard preparation

Prepare stock standard solutions by adding tetrahydrofuran to preweighed amounts of RDX in volumetric flasks. Prepare working range standards by diluting stock solutions with acetonitrile. Store stock and dilute standards in a freezer.

3.4 Sample preparation

3.4.1 Transfer glass fiber filter from the cassette to a 4-mL vial.

3.4.2 Add 3.0 mL of acetonitrile to each vial.

3.4.3 Seal the vials with PTFE-lined septa and shake them for half an hour on a mechanical shaker.

3.5 Analysis

3.5.1 Liquid chromatographic conditions

Column:	25 cm x 4.6 mm i.d. stainless steel column packed with 5- μ m Econosphere CN
Mobile Phase:	42% acetonitrile / 58% water
Flow rate:	1 mL/min
UV detector:	230 nm
Retention time:	3.96 min
Injection volume:	10 μ L

3.5.2 Chromatogram (See Figure 2)

3.6 Interferences (analytical)

3.6.1 Any compound having a retention time similar to that of the analyte is a potential interference. Generally, chromatographic conditions can be altered to separate interferences from the analyte. HMX is a possible interference with RDX and must be separated from it.

3.6.2 Retention time on a single column is not proof of chemical identity. Analysis by an alternate HPLC column, detection at another wavelength (for comparison of

absorbance response ratios) and confirmation by mass spectrometry are additional means of identification.

3.7 Calculations

- 3.7.1 Construct a calibration curve by plotting detector response versus standard concentration.
- 3.7.2 Determine the concentration of RDX in each sample from the calibration curve. If RDX is found in the blank, make blank corrections.
- 3.7.3 Determine the air concentration by the following formula.

$$\text{mg} / \text{m}^3 = \frac{(\mu\text{g} / \text{mL}) \times (\text{extraction vol, mL})}{(\text{air vol, L}) \times (\text{extraction efficiency, decimal})}$$

3.8 Safety precautions (analytical)

- 3.8.1 Avoid exposure to all standards.
- 3.8.2 Avoid exposure to all solvents.
- 3.8.3 Wear safety glasses at all times.

4 Recommendations for Further Study

- 4.1 A better desorption solvent than acetonitrile might be found.
- 4.2 This method should be fully validated for the following group of polynitro explosives: HMX, RDX, TETRYL, TNT, 2,4-DNT, and 2,6-DNT. It has been shown that all of the above analytes can be separated from each other by HPLC.

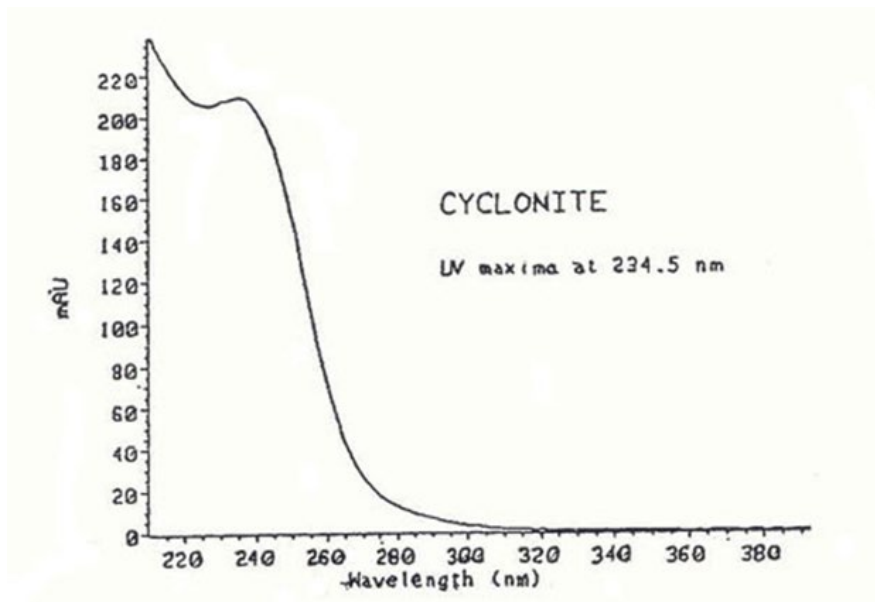


Figure 1. UV Spectrum of RDX in Acetonitrile

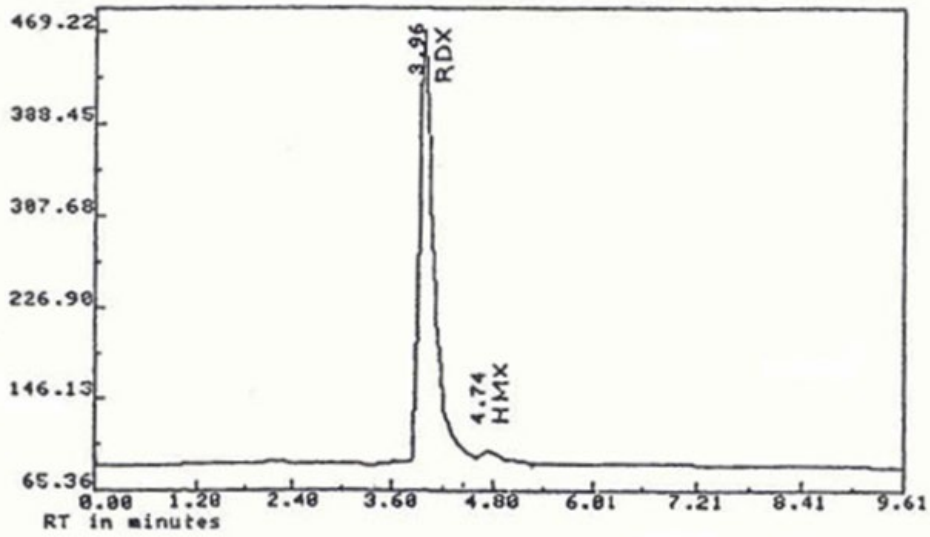


Figure 2. Chromatogram of Cyclonite (RDX)

5 References

- 5.1 "Kirk-Othmer Encyclopedia of Chemical Technology", 3rd ed.; Grayson, K.; John Wiley and Sons: New York, NY, 1980; vol. 9, pp 581-584.
- 5.2 "Documentation of the Threshold Limit Values and Biological Exposure Indices," 5th ed.; American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1986; P 221.
- 5.3 "Documentation of the Threshold Limit Values", 3rd ed.; American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1981 P 221.
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- 5.5 "Merck Index", 10th ed.; Vindholz, M., Ed.; Merck and Co.: Rahway, NJ, 1983; P 393.