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## **Extraction and Analysis of Explosives Following US EPA Method 8095**

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# Abstract

The standard environmental test method for nitroaromatic, nitramine, and nitroester analysis has been US EPA method 8330<sup>1</sup>. This method uses HPLC separation and detection by ultra-violet absorption. Analysts have been interested in a GC method that overcomes the disadvantages of the HPLC method, including high solvent usage, multiple co-elutions, and long run times.

US EPA method 8095<sup>2</sup> has been written as a GC/ECD alternative to method 8330. This GC/ECD method was developed at the U.S. Army Cold Regions Research and Engineering Laboratory<sup>3</sup>. Method 8095 includes all of the method 8330 target compounds plus 3,5-dinitroaniline, nitroglycerine, and PETN.

Restek has designed two new stationary phases, Rtx<sup>®</sup>-TNT and Rtx<sup>®</sup>-TNT 2 columns, specifically for method 8095. The TNT columns provide better resolution and higher thermal stability than any of the columns currently recommended in Method 8095. The Rtx<sup>®</sup>-TNT, primary column and Rtx<sup>®</sup>-TNT 2, confirmational column, operate under identical GC oven temperature programs, allowing simultaneous dual-column confirmational analysis of all 16 nitroaromatic compounds.

# Explosives Analysis by Gas Chromatography Using Method 8095

- GC more common than HPLC in environmental laboratories
- Selective detection using ECD
- Direct flash injection of ACN extract
- Simultaneous dual-column analysis

# Explosives Target Compound List

## Method 8095

1. nitrobenzene
2. 2-nitrotoluene
3. 3-nitrotoluene
4. 4-nitrotoluene
5. nitroglycerine
6. 1,3-dinitrobenzene
7. 2,6-dinitrotoluene
8. 2,4-dinitrotoluene
9. 1,3,5-trinitrobenzene
10. trinitrotoluene
11. PETN
12. RDX
13. 4-amino-2,6-dinitrotoluene
14. 3,5-dinitroaniline
15. 2-amino-4,6-dinitrotoluene
16. tetryl
17. HMX

# Sample Extraction and Preparation

## Water Samples

- A main difference in sample preparation for GC is that the samples are not diluted 1:1 with reagent water prior to being injected, as is the case for HPLC samples
- Method 8095 requires solid phase extraction (SPE) disks or cartridges to extract analytes of interest from water samples, such as described in EPA 3535A<sup>2</sup>. The extraction is performed using SDB/RPS-type disks or RDX type cartridges. Please note that method 8095 does not use the acetonitrile/salting out extraction procedure as described in method 8330.
- The use of SPE for explosives extraction requires extra drying time after the sample is loaded. Most explosive compounds have low water solubility, so the extra drying time helps their recovery into the acetonitrile elution solvent, and reduces the water content in the injected sample. Safety considerations prevent explosive extracts from further concentration by Kuderna-Danish concentrators. The extra drying time, when using SPE, leads to drier extracts which reduce the need for recalibration and maintenance when using water-sensitive electron capture detectors.

# Sample Extraction and Preparation

## Soil Samples

- In Method 8095, analytes of interest are extracted from soil and sediment samples using the same acetonitrile extraction with ultra-sonication procedure as described in Method 8330. Samples are air-dried at room temperature or cooler to a constant weight. Then the samples are screened with a colorimetric test, such as EPA Method 8515, to determine if they contain too much explosive residue to be safely ground with a mortar and pestle. If the sample contains less than 1% explosive residue, generally it is considered safe to be ground with a mortar and pestle. Two grams of the finely ground soil are extracted using 10 milliliters of acetonitrile in a cooled ultra-sonication bath for 18 hours. The acetonitrile extracts are then dried and filtered before analysis.
- A main difference in sample preparation for GC is that the samples are not diluted 1:1 with reagent water prior to being injected, as is the case for HPLC samples

# Injection Modes

## Cool On-column Injection

- While few laboratories routinely use cool on-column injection ports because of the perception of high maintenance, it has several advantages over direct injection for the analysis of explosives. These advantages include complete sample transfer into the column via a highly inert pathway and reduced peak width.
- For those with more questions about on-column injection ports, Jack Cochran, LECO Corporation, will be presenting a talk on on-column injection ports and explosives analysis.

Tuesday Morning, Room 261, 8:30 AM, (428)

**New Tools for the Analysis of Explosives: An On-column Injection Liner for a PTV Inlet, Two TNT GC Columns, and a Gas Chromatograph/Time-of-Flight Mass Spectrometer.**

# Injection Modes

## Direct Flash Injections

- Most laboratories will analyze explosive samples by direct injection. Many direct injection parameters need to be optimized for successful analysis of these compounds. The injection port temperature must be determined carefully to provide good response for the thermally labile compounds, such as nitroglycerine and PETN, and sufficient vaporization for the high boiling compounds, such as HMX. For most analyses, an injection port temperature between 250 – 275 °C is best.
- Restek offers a unique Siltek deactivated sleeve to meet the needs of explosive analysis by direct injection. The internal diameter of the sleeve was reduced from the typical 4mm ID to a new 1mm ID. This reduction of dead volume in the injection port reduces peak broadening. Initial results with Siltek indicate improved reproducibility and better inertness to explosive residues than standard deactivations. Most sample residue can be solvent rinsed off of Siltek, allowing the sleeve to be reused without the need for re-deactivation.



# Carrier Gas Flow

- Explosive analysis by GC works best when using very high carrier gas flows. While low-boiling compounds (e.g., nitrotoluenes) could be analyzed well at normal carrier gas flow rates, the high boiling compounds (e.g., HMX) are best analyzed with carrier gas flow rates five to seven times the normal linear velocity.
- Most laboratories will find a column head pressure of 2 to 3 psi is optimum for this analysis. This should provide a linear velocity of 100 to 140 cm/second, or a flow of 12 – 17 ml/min..

# Oven Temperature Programming and Solvent Focusing

- While Method 8095 recommends an initial oven temperature of 100 °C, Restek discovered improved solvent focusing and decreased peak widths by using an initial oven temperature of 80 °C with acetonitrile injections. This improvement was seen with both cool on-column and direct injections.

# Columns Recommended in Method 8095

- EPA 8095 lists the DB<sup>®</sup>-1 (100 % dimethylpolysiloxane) and the HP<sup>®</sup>-5 (5% diphenyl 95% dimethylpolysiloxane) as possible primary columns.
- The DB<sup>®</sup>-1 completely co-elutes RDX and PETN.
- The HP<sup>®</sup>-5 resolves RDX and PETN but usually co-elutes 4-amino-2,6-dinitrotoluene and 3,5-dinitroaniline.
- The Rtx<sup>®</sup>-TNT is much better than the DB-1 since RDX/PETN is a critical separation.
  
- EPA 8095 list the Rtx<sup>®</sup>-200 (trifluoropropyl methyl polysiloxane) and the Rtx<sup>®</sup>-225 ( 50% cyanopropyl methyl 50% phenyl methyl polysiloxane) as the possible confirmational columns.
- The Rtx<sup>®</sup>-200 is significantly more retentive than any of the primary columns. HMX is usually not detected. RDX and 2-amino-4,6-dinitrotoluene co-elute. Nitroglycerin and 2,6-dinitrotoluene co-elute.
- The Rtx<sup>®</sup>-225 has poor thermal stability. The column is only stable to 260 °C. This column is also too retentive. ECD bleed levels are also an issue with cyano containing polymers.
- The Rtx<sup>®</sup>-TNT2 is better than any of the confirmational columns since all compounds can be detected with the the Rtx<sup>®</sup>-TNT in a simultaneous dual-column run.

# Gas Chromatography Column Design Criteria for the Rtx<sup>®</sup>-TNT and Rtx<sup>®</sup>-TNT2

- Short Column, Wide-bore, Standard  $d_f$
- Analysis Time < 20 min
- Low Bleed with ECD
- Critical Resolution
- Column Inertness
- Dual Column Analysis Capability



# Stationary Phase Optimization

- Window Diagramming
- Computer Simulation of Retention Time
- Computer Prediction of Optimized Stationary Phase Composition and Column Dimensions

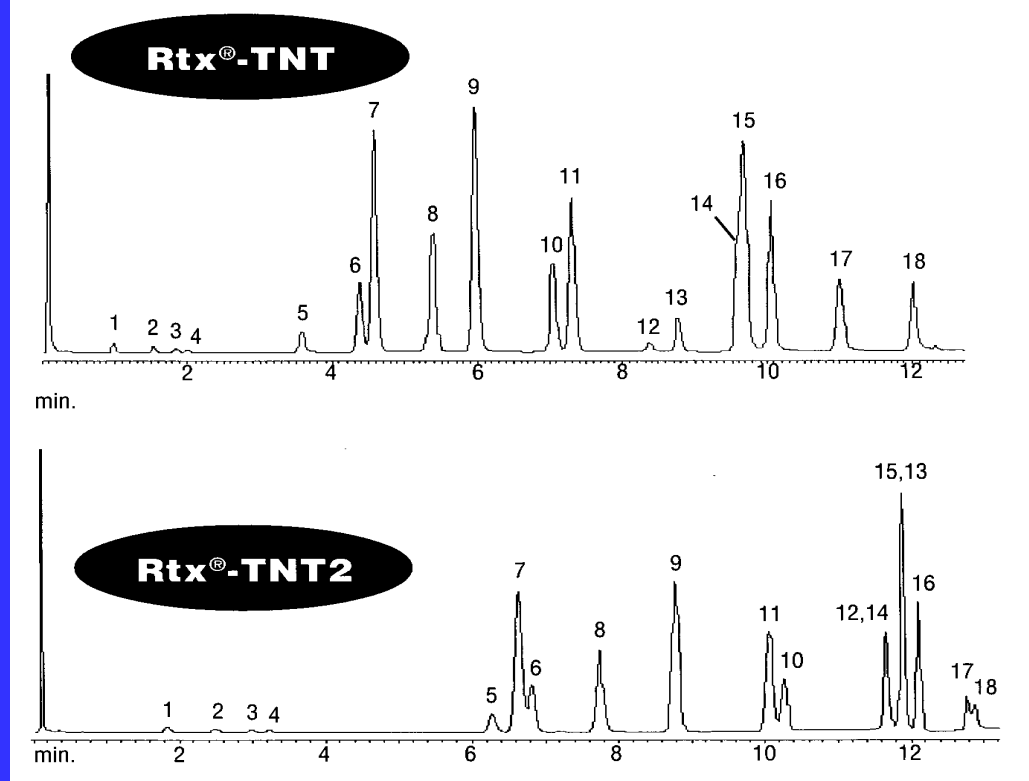


# 6 m x 0.53 mm Restek Rtx-TNT Columns

## Direct Injection

- 1 Nitrobenzene
- 2 2-Nitrotoluene
- 3 3-Nitrotoluene
- 4 4-Nitrotoluene
- 5 Nitrolycerin
- 6 1,3-Dinitrobenzene
- 7 2,6-Dinitrotoluene
- 8 2,4-Dinitrotoluene
- 9 3,4-Dinitrotoluene
- 10 1,3,5-Trinitrobenzene
- 11 TNT
- 12 PETN
- 13 RDX
- 14 4-Amino-2,6-dinitrotoluene
- 15 3,5-Dinitroaniline
- 16 2-Amino-4,6-dinitrotoluene
- 17 Tetryl
- 18 HMX

*Rtx<sup>®</sup>-TNT and Rtx<sup>®</sup>-TNT2 columns provide the best resolution of nitroaromatic explosive compounds in under 13 minutes.*



6m, 0.53mm ID, 1.50µm Rtx<sup>®</sup> -TNT (cat. #12998)

6m, 0.53mm ID, 1.50µm Rtx<sup>®</sup> -TNT2 (cat. #12999).

Direct injection using a 1mm Siltek<sup>™</sup> Uniliner<sup>®</sup> (cat. #21052-214.1).

On-column conc.: 200-1000pg for each compound. 8095 Calibration Mix A (cat.# 31607), 8095 Calibration Mix B (cat.# 31608), and 3,4-dinitrotoluene (cat.#31452).

Oven temp.: 80°C (hold 1 min.) to 180°C @ 10°C/min. to 300°C @ 30°C/min. (hold 3 min.);

Inj. temp.: 250°C; Det.: ECD @ 330°C with anode purge;

Dead time: 4.4 sec.; Head pressure:

He @ 3psi (20.7 KPa);

Flow rate: He @ 17mL/min. @ 80°C.

# Analytical Reference Materials

- Obtaining pure, neat compounds for the preparation of calibration standards can be very difficult. Some of these compounds are not available commercially at a high enough purity for accurate analytical results. These materials can contain desensitizing agents, such as beeswax, water, plasticizers, or other manufacturing by-products. Many commercially available explosives are shipped wet and must be dried carefully before solution preparation.
- To ensure the highest quality explosive standards, Restek chemists carefully purified or synthesized all of the compounds listed in Method 8095. All compounds used to prepare these standards have 98% purity or higher. Multiple analytical techniques, including GC, HPLC, GC/MS, FTIR, and DSC, are used to verify raw material purity.



# Conclusions

- Using GC/ECD for explosives analysis as per Method 8095 is now an excellent alternative to HPLC analysis. Careful consideration of sample extraction, preparation, and analytical techniques will ensure successful analysis of the explosives. Restek has optimized the column stationary phases and dimensions, injection technique, and analytical reference materials to help achieve the best resolution of nitroaromatic compounds in the fastest analysis time.

# References

- 1. US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846 Update III, Office of Solid Waste, Washington, DC, 1997.
- 2. US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846, Proposed Draft Update IVB, Office of Solid Waste, Washington, DC, 1999.
- 3. M. E. Walsh, T. Ranney. “Determination of Nitroaromatic, Nitramine, and Nitrate Ester Explosives in Water Using Solid-Phase Extraction and Gas Chromatography-Electron Capture Detection: Comparison with High-Performance Liquid Chromatography.” *Journal of Chromatographic Science*, Vol. 36, pp. 406–416, August 1998.