



ENVIRO-CLEAN[®] DVB Cartridges

EPA Method 529 Revision 1.0

Part Number: ECDVB156

September 01, 2010

The unique styrene divinylbenzene cartridge **ECDVB156** is designed to provide a high level of performance in solid-phase extraction for the analysis of **explosives and related compounds** in finished drinking water.

EPA Method 529* Summary

Determination Of Explosives And Related Compounds In Drinking Water By Solid Phase Extraction And Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS)

Scope and Application

This method provides procedures for the determination of explosives and related compounds in finished drinking water. The method may also be used for the analysis of untreated source waters and other types of water samples, but it has not been evaluated for these uses. The method is used for a variety of explosives that are efficiently partitioned from the water sample onto a solid phase extraction (SPE) sorbent, and are sufficiently volatile and thermally stable for gas chromatography.

Method Summary

Analytes and surrogates are readily extracted when a 1 L water sample is drawn through a solid-phase extraction cartridge containing a unique styrene divinylbenzene sorbent. The organic compounds are eluted from the solid-phase with a small quantity of ethyl acetate. The solvent is concentrated and an internal standard (IS) added. The sample components are identified after injection on a fused silica capillary column of a GC/MS equipped with a large volume injection injector or cold on-column injector. The mass spectrometer must be capable of electron ionization energy of 70 eV to produce positive ions, scan from 45 to 250 amu in 0.7 seconds or less.

Interferences

- Major contaminant sources are reagents
- Interfering contamination generally occurs when a sample of low concentration is analyzed immediately following a sample of high concentration
- A blank sample should be inserted between suspect samples of low and high concentration to minimize potential carryover

Sample Collection, Preservation and Storage

- When collecting from tap water, open tap and flush for about 2 minutes
- Collect 1 L. Sample does not need to be free of headspace
- Do not rinse preservatives from bottle during collection
- All samples must be dechlorinated and preserved from microbes at collection time
- Use copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) at 0.5 g/L of water. Alternatively, the following may be used: 0.3 g of tris(hydroxymethyl)aminomethane and 4.7 g of tris(hydroxymethyl)aminomethane hydrochloride may also be used for each liter of sample water
- All samples should be iced during shipment and must not exceed 10°C during the first 48 hours, then held at 6°C or below until extraction
- Samples must be extracted within 14 days of collection
- Extracted samples may be stored for 30 days in amber vials at 0°C or less

Safety

- The toxicity or carcinogenicity of many of the chemicals used in this method has not been determined and each chemical should be treated as a potential health hazard. Exposure to these chemicals should be minimized

Procedure

(solid-phase cartridge extraction, manual vacuum manifold or automated system)

1) Cartridge Conditioning

- a) Place a cartridge(s) in a suitable vacuum manifold
- b) Mark the level of liquid on the sample bottle for accurate volume determination and verify that the sample pH is between 5 and 7 and free of chlorine
- c) Add an aliquot of the surrogate fortification solution for a final concentration of 1-5 µg/L and mix (Note 1)
- d) Rinse the cartridge with 3 x 5 mL aliquots of ethyl acetate
- e) Let the cartridge drain completely dry between each addition
- f) Rinse the cartridge with 3 x 5 mL aliquots of methanol

Do not let the cartridge go dry after this step otherwise repeat methanol step)

- g) Rinse the cartridge with 2 x 10 mL aliquots of reagent water. Leave a visible layer of water in the cartridge

Proper conditioning of the cartridge is essential for good precision and accuracy

2) Sample Extraction

- a) Adjust the vacuum setting so that the flow rate is 10-15 mL/minute
- b) Add the water sample to the cartridge and draw completely through
- c) After sample extraction draw air through the cartridge for **10 minutes at full vacuum** but not longer than 15 minutes

3) Cartridge Elution

- a) Insert a clean collection tube in the manifold
- b) Rinse the inside of the sample bottle with 5 mL ethyl acetate and add to cartridge
- d) Add another 5 mL aliquot of ethyl acetate to the cartridge and draw through to collection at low vacuum
- e) Pass the eluate through a **UCT ECSS15M6** drying tube or use a bed of anhydrous sodium sulfate
- f) Wash the drying tube using 4 mL of ethyl acetate
- g) Concentrate the eluate under a gentle stream of nitrogen in a warm water bath to 0.9 mL
- h) Add internal standards and bring final volume to 1.0 mL for analysis

Sample Analysis by GC/MS

a) Injection volume 1-2 μ L

Retention Times and Suggested Quantitation and Confirmation Ions for Explosive Analytes

| Analyte | Retention Time (min) | Quantitation Ion (m/z) | Confirmation Ion (m/z) |
|--------------------------------------|----------------------|------------------------|------------------------|
| Nitrobenzene (NB) | 7.72 | 51 or 77 | 51,77,123 |
| 2-nitrotoluene (2NT) | 9.40 | 65 | 91,120 |
| 3-nitrotoluene (3NT) | 10.18 | 91 | 65,137 |
| 4-nitrotoluene (4NT) | 10.57 | 65 or 91 | 65,137 |
| 1,3-dinitrobenzene (DNB) | 15.13 | 50 or 75 | 65,91,137 |
| 2,6-dinitrobenzene (2,6DNB) | 16.60 | 165 | 50,75,76 |
| 2,4-dinitrotoluene (2,2DNT) | 19.35 | 165 | 63,78 |
| 1,3,5-trinitrobenzene (TNB) | 19.43 | 75 or 213 | 74,75,213 |
| RDX | 21.97 | 210 | 63,89 |
| 4-amino-2,6-dinitrotoluene (4AmDNT) | 22.81 | 46 | 78,104 |
| 3,5-dinitroaniline (DNA) | 23.00 | 180 | 63,64,183 |
| 2-amino-4,7-dinitrotoluene (2AmDNT) | 23.47 | 183 or 64 | 52,78,180 |
| Tetryl | 24.77 | 180 or 78 | 51,77,194 |
| 3,4-dinitrotoluene (IS) | 17.42 | 194 or 77 | 63,78,182 |
| Nitrobenzene- d_5 (SUR) | 7.66 | 82 | 54,128 |
| 1,3,5-trimethyl-2-nitrobenzene (SUR) | 12.33 | 148 or 91 | 91,93,148 |
| 1,2,4-trimethyl-5-nitrobenzene (SUR) | 14.72 | 148 or 91 | 77,91,148 |

Injector Programs

Note: Deactivated post liners should be used

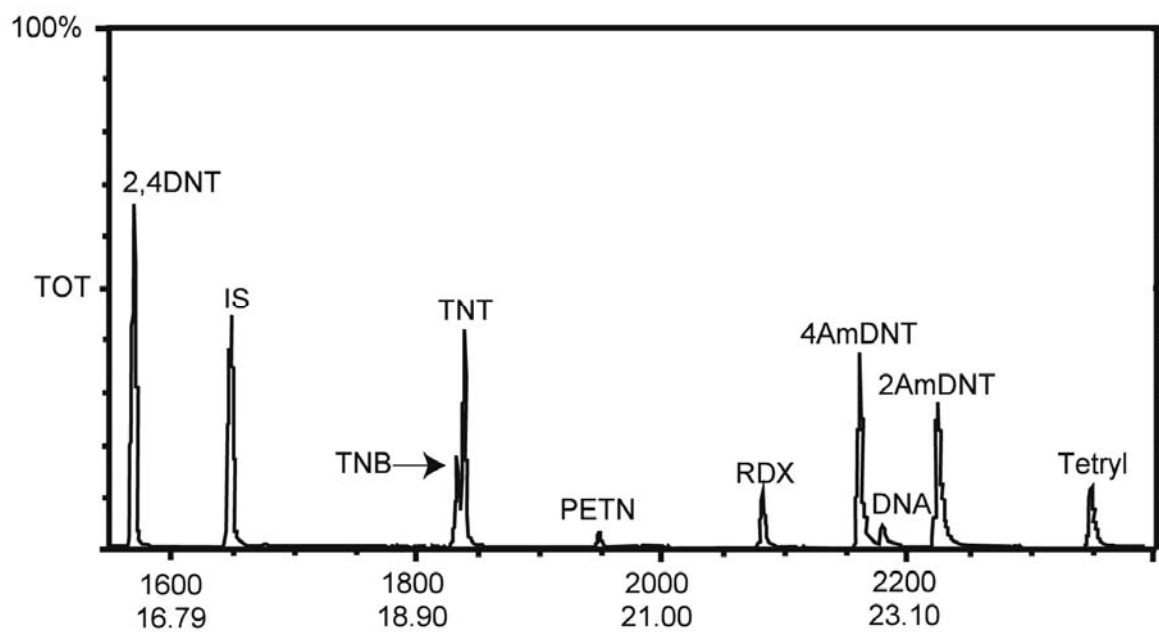
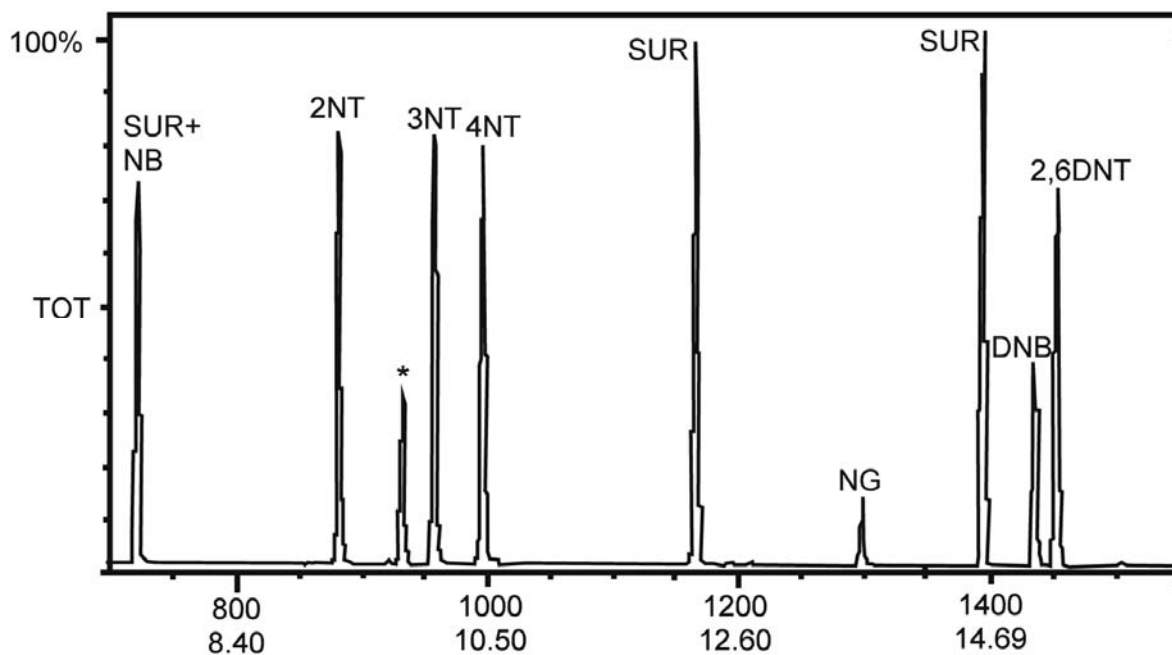
Programmed Temperature Vaporizing Injector (PTV) Splitless Injection, Full Scan Mass Spectrometry

- Injector must be capable of rapidly heating at 100-100 $^{\circ}$ C/minute
- Injector temperature of 60 $^{\circ}$ C
- Program injector at 200 $^{\circ}$ C per minute to 250 $^{\circ}$ C
- Hold in splitless mode for 1.0 minute
- Initial GC oven temperature of 45 $^{\circ}$ C for 3.3 minutes
- Program oven temperature at 7 $^{\circ}$ C per minute to 210 $^{\circ}$ C, then 20 $^{\circ}$ C per minute to 250 $^{\circ}$ C

Cold On-Column Injection, Full Scan Mass Spectrometry

- Injector temperature at 50 $^{\circ}$ C
- Program the injector at 150 $^{\circ}$ C per minute to 220 $^{\circ}$ C
- Hold in splitless mode for 2.0 minutes
- Initial GC oven temperature of 50 $^{\circ}$ C for 3 minutes
- Program oven temperature at 7 $^{\circ}$ C per minute to 210 $^{\circ}$ C, then 20 $^{\circ}$ C per minute to 250 $^{\circ}$ C

Chromatogram of Explosives and Related Compounds



Total ion chromatogram of 16 explosives and related compounds using a J&W DBS-5 column. Concentration: 5 ng each analyte with surrogate and IS except for DNA which is 1 ng. Results will be different for other analytical columns

Notes

Surrogate standards (nitrobenzene-*d*₅; 1,3,5-trimethyl-2-nitro-benzene; and 1,2,4-trimethyl-5-nitro-benzene) are added to all calibration standards, samples, LFBs, LFM, FDs, and LRBs

Internal Standard Stock - Prepare a stock standard of the internal standard, 3,4-dinitrotoluene (CAS# 610-39-9), at approximately 2.0 mg/mL in ethyl acetate. Store at 0° C or less.

Surrogate Standard Stock Solutions - Prepare or purchase individual stock standards of the following surrogate analytes: 1,3,5-trimethyl-2-nitrobenzene commonly known as 2-nitromesitylene [CAS# 603-71-4], 1,2,4-trimethyl-5-nitrobenzene commonly known as 2-nitropseudocumene [CAS# 610-91-3], and nitrobenzene-*d*₅ [CAS# 4165-60-0]. Standards of 2-nitromesitylene and 2-nitropseudocumene should be prepared in methanol at concentrations of 1-2 mg/mL. Nitrobenzene-*d*₅ should be prepared in methylene chloride at a concentration of 1-2 mg/mL. Store at 0° C or less. During method development, these solutions were stable for at least 1 year.

Analyte Stock Standard Solutions -- It is recommended that individual solutions of analytes, or mixtures of analytes, be purchased from commercial suppliers. All work done during development of this method was done with commercial mixtures. RDX, Tetryl and TNT are explosives and require special handling to be used safely. They are not readily available as neat materials.

Stock Standard Solutions of explosives are frequently provided in acetonitrile. The acetonitrile will be sufficiently diluted in preparation of calibration standards and spiking solutions

Stock standards of method analytes that are not explosive may be prepared from neat materials. Typical concentrations of stock standards that can be used conveniently are 1-10 mg/mL

#See UCT "Vacuum Extraction Manifold" for complete details on availability and operation

*For complete details on Method 529, September 2002, the analyst is referred to: J.W.Munch, "Determination Of Explosives And Related Compounds In Drinking Water By Solid Phase Extraction And Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS)", National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268

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