Environmental Applications

Analysis of Explosives

by Liquid Chromatography

Reliable analysis of explosives is largely dependent on the selectivity and sensitivity of the analytical column. C18 columns are commonly used as primary columns; however, reliable results are difficult to obtain for several critical compounds. Alternative phases were evaluated and the Ultra II Aromax and Ultra C8 columns were determined to provide better separations for the routine analysis of explosives.

Introduction

Recently, there has been increased interest in highly sensitive explosives analyses for forensic applications, due to the increased emphasis on homeland security. Explosives methods have long been employed by environmental labs focused on soil and groundwater quality in areas where munitions are disposed of through combustion. Target compounds include nitroaromatics, nitramines, and nitrate esters, which present health concerns due to their carcinogenic, mutagenic, and toxic effects. Testing can be performed by gas chromatography (GC), liquid chromatography (LC), or other methods, but LC has several advantages for routine analysis including, ease-of-use, sensitivity, and reliability for thermally unstable compounds.

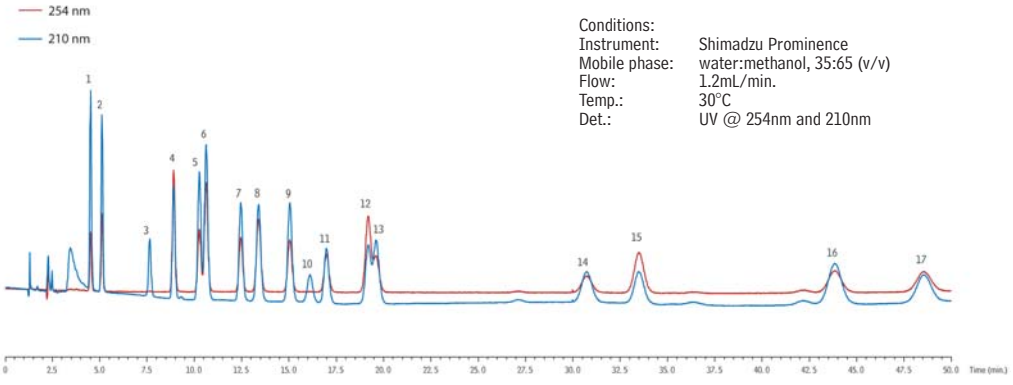
Analysis of explosives by LC often follows EPA Method 8330B, an update of the original method, which now incorporates mass spectrometry (MS) as an alternative to ultraviolet (UV) detection. An advantage of MS is that it requires only one column, so it is faster as no confirmation analysis is required. MS is also more sensitive than UV; however, when evaluating columns for LC/MS, it is important that the column resolve all critical pairs that may have isobaric interferences. In contrast, UV is less expensive and generally is more readily available in most labs, so both detection techniques are commonly used.

Typically, when analyzing by UV, a C18 primary column with a cyano- or phenyl-based confirmation column is used. However, several compounds can be problematic on these phases, including 2,6-dinitrotoluene and 2,4-dinitrotoluene which may coelute or show poor response with UV detection. Gradients can be used to achieve separation, but this is more time-consuming than using an isocratic method. Tetryl is another difficult explosive compound. It is susceptible to heat degradation and false positives can result from matrix interference causing a retention time shift for 3,5-dinitroaniline (which elutes near tetryl on a C18 column). By using columns with different selectivities, analysts can more accurately identify the compounds of interest. Here we evaluated several alternative LC column phases to determine which phase produced optimal separations for commonly analyzed explosive compounds.

Figure 1 Ultra II Aromax columns separate all 17 target compounds and can be used alone (MS) or with a confirmation column (UV).

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

Sample:	Nitroaromatics and Nitramine Explosives by HPLC, EPA 8330B (cat.# 33204)
Inj.:	10µL
Conc.:	10µg/mL each component
Sample diluent:	methanol
Column:	Ultra II Aromax
Cat.#:	9607575
Dimensions:	250mm x 4.6mm
Particle size:	5µm
Pore size:	100Å
Conditions:	
Instrument:	Shimadzu Prominence
Mobile phase:	water:methanol, 35:65 (v/v)
Flow:	1.2mL/min.
Temp.:	30°C
Det.:	UV @ 254nm and 210nm



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Procedure

Several columns were evaluated for selectivity and retention of the target explosives compounds listed in EPA Method 8330B. Each column was first evaluated for application as a primary UV or stand-alone MS column; secondarily, remaining columns were evaluated for orthogonal characteristics for use as a confirmation column. Orthogonal characteristics included elution order changes and retention time shifts.

Mixed standards containing all 17 target explosives were prepared in methanol. A simple isocratic elution using methanol and water was used in order to follow the method closely and to eliminate the need to re-equilibrate the columns prior to each analysis (as required when using a gradient elution). Column dimension were consistent with method recommendations of 250mm x 4.6mm, 5µm. Column temperature variations were eliminated by using a column heater set at 30°C. All peak identities were confirmed by comparison to individual standards for each compound.

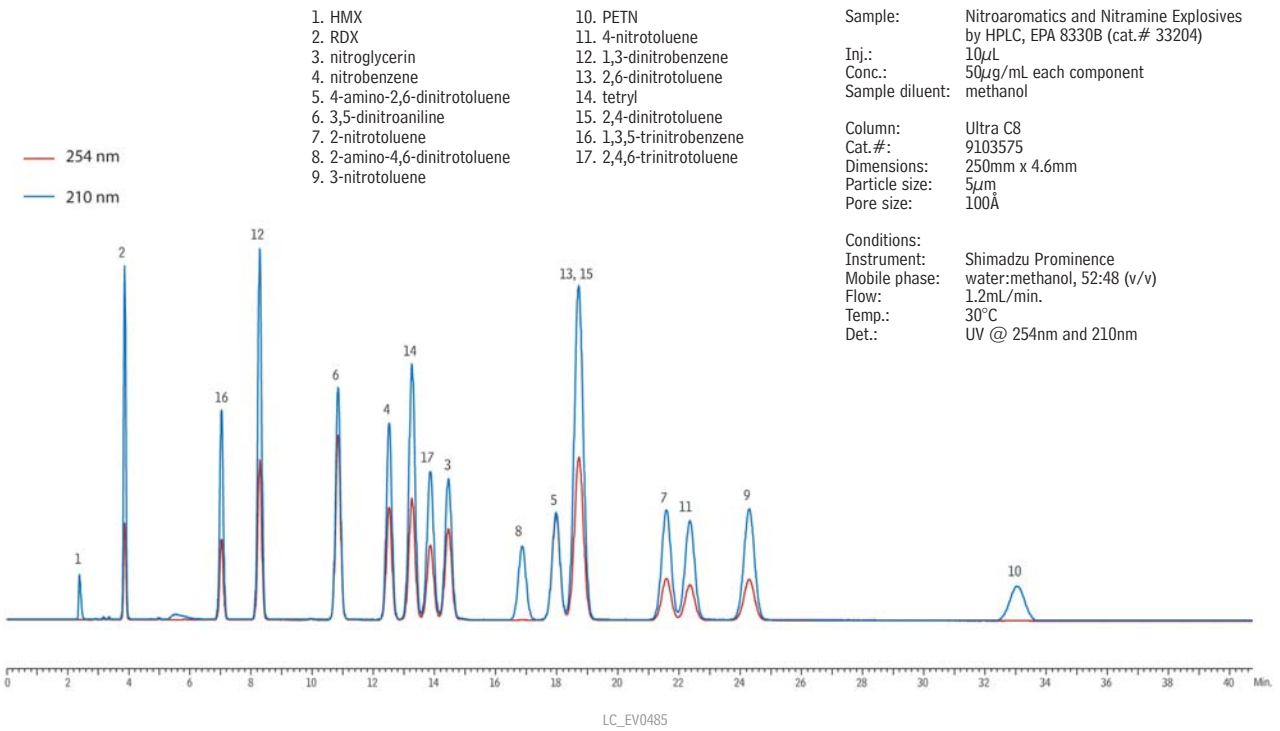
Results

The Ultra II Aromax column provided the best separation of all columns tested (Figure 1). The unique selectivity of this column allows for the separation of all 17 analytes with no coelutions. All compounds that are typically problematic were well-resolved and positively identified. Since all compounds were resolved on the Ultra II Aromax column, it is recommended for both UV and MS methodology. Further, because the mobile phase has a higher organic content (65% methanol) than is typically used, it has the added benefit of improving MS sensitivity by allowing better desolvation at the mass spectrometer interface. For labs running UV methods, the Ultra C8 column provided several elution order changes and retention time shifts relative to the Ultra II Aromax column, making it an ideal confirmation column for UV analyses (Figure 2). Only a single coelution is seen on the Ultra C8 column, which is fully separated on the Ultra II Aromax column.

Conclusion

Reliable analysis of explosives is largely dependent on the selectivity and sensitivity of the analytical column. The Ultra II Aromax column separates all 17 target analytes in EPA Method 8330B and is compatible with a high organic content mobile phase, which improves performance with MS detectors. If analysis by UV is desired, the Ultra C8 column provides several elution order changes and retention time shifts, making it an excellent confirmation column. The selectivities of the Ultra II Aromax and Ultra C8 columns allow definitive analyte identifications, even for difficult compounds, making them excellent choices for the routine analysis of explosives in both environmental and forensic applications.

Figure 2 The alternate selectivity of the Ultra C8 column makes it an ideal confirmation column for UV detection.



Recommended HPLC Columns

Ultra II Aromax Columns (USP L11)

Physical Characteristics:

particle size: 3µm or 5µm, spherical
pore size: 100Å
carbon load: 17%
endcap: fully endcapped
pH range: 2.5 to 7.5
temperature limit: 80°C

Chromatographic Properties:

Ultra II Aromax is a unique reversed phase material that exhibits superior retention and selectivity for aromatic and/or unsaturated compounds, compared to conventional alkyl and phenyl phases. This column is a great alternative to our Biphenyl phase when increased retention is required. A very suitable choice for analysis of steroids, tetracyclines, drug metabolites, and other compounds that contain some degree of unsaturation.

Length	1.0mm ID cat.#	2.1mm ID cat.#	3.0mm ID cat.#	3.2mm ID cat.#	4.6mm ID cat.#
2.2µm Columns					
30mm			9607833		
50mm			9607853		
100mm			9607813		
3µm Columns					
30mm	9607331	9607332	—	9607333	9607335
50mm	9607351	9607352	—	9607353	9607355
100mm	9607311	9607312	—	9607313	9607315
150mm	9607361	9607362	—	9607363	9607365
5µm Columns					
30mm	9607531	9607532	—	9607533	9607535
50mm	9607551	9607552	—	9607553	9607555
100mm	9607511	9607512	—	9607513	9607515
150mm	9607561	9607562	—	9607563	9607565
200mm	9607521	9607522	—	9607523	9607525
250mm	9607571	9607572	—	9607573	9607575

Ultra C8 Columns (USP L7)
Excellent for a wide range of analyses

Physical Characteristics:

particle size: 3µm or 5µm, spherical
pore size: 100Å
carbon load: 12%
endcap: fully endcapped
pH range: 2.5 to 7.5
temperature limit: 80°C

Chromatographic Properties:

A retentive, high-purity, base-deactivated reversed phase packing that exhibits excellent peak shape for a wide range of compounds. Less retention for neutral, hydrophobic compounds, compared to the Ultra C18 column.

Length	1.0mm ID cat.#	2.1mm ID cat.#	3.2mm ID cat.#	4.0mm ID cat.#	4.6mm ID cat.#
3µm Columns					
30mm	9103331	9103332	9103333	—	9103335
50mm	9103351	9103352	9103353	—	9103355
100mm	9103311	9103312	9103313	—	9103315
5µm Columns					
30mm	9103531	9103532	9103533	—	9103535
50mm	9103551	9103552	9103553	—	9103555
100mm	9103511	9103512	9103513	9103514	9103515
150mm	9103561	9103562	9103563	9103564	9103565
200mm	9103521	9103522	9103523	—	9103525
250mm	9103571	9103572	9103573	—	9103575

To order a 2.1mm, 3.2mm, or 4.6mm ID column with a Trident Integral Inlet Fitting, add "-700" to the catalog number for the column.

Example: 100mm x 4.6mm ID Ultra C18 column with Trident Integral Inlet Fitting: 9174315-700
Nominal additional charge.

Visit www.restek.com for guard cartridges for these columns.

Recommended Analytical Reference Materials

To ensure the highest quality explosives standards, Restek chemists carefully purify or synthesize all of the compounds listed in EPA Method 8330.

8330 Internal Standard

3,4-dinitrotoluene
1,000µg/mL in methanol, 1mL/ampul
cat. # 31452 (ea.)

8330 Surrogate

1,2-dinitrobenzene
1,000µg/mL in methanol, 1mL/ampul
cat. # 31453 (ea.)

Nitroaromatics and Nitramine Explosives by HPLC, EPA 8330B* (17 components)

2-amino-4,6-dinitrotoluene
4-amino-2,6-dinitrotoluene
3,5-dinitroaniline
1,3-dinitrobenzene
2,4-dinitrotoluene
2,6-dinitrotoluene
HMX
nitrobenzene
nitroglycerin
2-nitrotoluene
3-nitrotoluene
4-nitrotoluene
PETN
RDX
tetryl
1,3,5-trinitrobenzene
2,4,6-trinitrotoluene
1,000µg/mL each in acetonitrile, 1mL/ampul
cat. # 33204 (ea.)

Nitroaromatics and Nitramine Explosives by HPLC* (14 components)

1,3-dinitrobenzene
2-amino-4,6-dinitrotoluene
4-amino-2,6-dinitrotoluene
2,4-dinitrotoluene
2,6-dinitrotoluene
HMX
nitrobenzene
2-nitrotoluene
3-nitrotoluene
4-nitrotoluene
RDX
tetryl
1,3,5-trinitrobenzene
2,4,6-trinitrotoluene
1,000µg/mL each in acetonitrile, 1mL/ampul
cat. # 33905 (ea.)

8330 Calibration Mix #1* (7 components)

1,3-dinitrobenzene
2,4-dinitrotoluene
HMX
nitrobenzene
RDX
1,3,5-trinitrobenzene
2,4,6-trinitrotoluene
1,000µg/mL each in acetonitrile, 1mL/ampul
cat. # 31450 (ea.)

8330 Calibration Mix #2* (7 components)

2-amino-4,6-dinitrotoluene
4-amino-2,6-dinitrotoluene
2,6-dinitrotoluene
2-nitrotoluene
3-nitrotoluene
4-nitrotoluene
tetryl
1,000µg/mL each in acetonitrile, 1mL/ampul
cat. # 31451 (ea.)

8330 Nitroaromatics Kit (1,000µg/mL)

31450: 8330 Calibration Mix #1
31451: 8330 Calibration Mix #2
31452: 8330 Internal Standard Mix
31453: 8330 Surrogate Mix

kit

Contains 1mL each of these mixtures.
cat. # 31454 (kit)

Single-Component Explosives Solutions

Volume is 1mL/ampul. Concentration is µg/mL.

Compound	Solvent	Conc.	cat.# (ea.)
2-amino-4,6-dinitrotoluene	ACN	1,000	31670
4-amino-2,6-dinitrotoluene	ACN	1,000	31671
ammonium picrate*	ACN	2,000	31890
3,5-dinitroaniline	ACN	1,000	31661
1,2-dinitrobenzene	M	1,000	31453
1,3-dinitrobenzene	ACN	1,000	31662
2,4-dinitrotoluene	ACN	1,000	31663
2,6-dinitrotoluene	ACN	1,000	31664
3,4-dinitrotoluene	EA	2,000	33901
3,4-dinitrotoluene	M	1,000	31452
EGDN*	M	1,000	31601
HMX*	ACN	1,000	31665
nitrobenzene	ACN	1,000	31657
nitroglycerin*	M	1,000	31498
nitroguanidine*	M	1,000	31602
2-nitrotoluene	ACN	1,000	31659
3-nitrotoluene	ACN	1,000	31660
4-nitrotoluene	ACN	1,000	31658
PETN (pentaerythritol tetranitrate)*	M	1,000	31600
picric acid*	M	1,000	31499
propylene glycol dinitrate (PGDN)	M	1,000	31821
RDX*	ACN	1,000	31666
tetryl*	ACN	1,000	31667
1,3,5-trinitrobenzene*	ACN	1,000	31668
2,4,6-trinitrotoluene*	ACN	1,000	31669

ACN=acetonitrile
M = methanol

*Meet all DOT requirements. Available only to customers or distributors inside the 48 contiguous United States; items may not be resold for export.