

Abstract

In modern days, a new breed of energetic (explosive) materials is emerging. Traditional aromatic nitrates are still in use, but there is dire need of analytical techniques for energetic materials in the chemical class of peroxides, azo etc. This presentation will demonstrate the use of a modern HPLC system with traditional detector (DAD) and also coupled with mass spectrometry for the analysis of above-mentioned various classes of energetic materials.

Introduction

This method is intended for the trace analysis of explosives and propellant residues by high performance liquid chromatography (HPLC) using a dual-wavelength UV detector. The following RCRA (resource conservation and recovery act) compounds in a water, soil, or sediment matrix have been determined by this method:

Analyte	Abbreviation	CAS number
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	2691-41-0
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4
1,3,5-Trinitrobenzene	1,3,5-TNB	99-35-4
1,3-Dinitrobenzene	1,3-DNB	99-65-0
2,4,6-trinitrophenyl-N-methylnitramine	Tetryl	479-45-8
Nitrobenzene	NB	98-95-3
2,4,6-Trinitrotoluene	2,4,6-TNT	118-96-7
4-Amino-2,6-dinitrotoluene	4-Am-DNT	19406-51-0
2-Amino-2,6-dinitrotoluene	2-Am-DNT	35572-78-2
2,4-Dinitrotoluene	2,4-DNT	121-14-2
2,6-Dinitrotoluene	2,6-DNT	606-20-2
2-Nitrotoluene	2-NT	88-72-2
3-Nitrotoluene	3-NT	99-08-1
4-Nitrotoluene	4-NT	99-99-0
Nitroglycerin	NG	55-63-0
Pentaerythritol tetranitrate	PETN	78-11-5
3,5-Dinitroaniline	3,5-DNA	618-87-1

Instrumentation

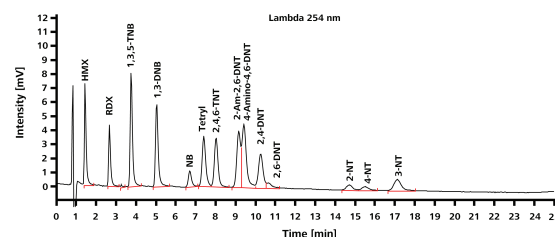
- 850 Professional IC
- 858 Professional Sample Processor
- 844 UV/VIS Compact IC



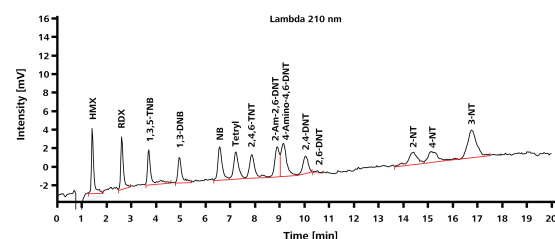
Reference herein to any specific commercial products or nonprofit organization, process, or service by trade name, trademark, manufacturer, or other-wise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government and shall not be used for advertising or product endorsement purposes.

Diode array detector chromatogram

a) Wavelength: 254 nm



b) Wavelength: 210 nm



Discussion

Chemical warfare and energetic compounds can be analyzed using traditional HPLC instrumentation. We have tried to analyze these chemical agents on a PEEK-based inert instrumentation in order to minimize corrosion problems or other interferences from stainless steel instrumentation.

Aqueous samples of low concentration are extracted by a salting-out extraction procedure with acetonitrile and sodium chloride. The small volume of acetonitrile that remains undissolved above the salt water is drawn off and transferred to a smaller volumetric flask. It is back-extracted by vigorous stirring with a specific volume of salt water. After equilibration, the phases are allowed to separate and the small volume of acetonitrile residing in the narrow neck of the volumetric flask is removed using a Pasteur pipet. The concentrated extract is mixed either 1:1 or 1:3 with reagent water (depending on the separations chosen). An aliquot is separated on a primary reversed-phase column (either C-18 or C-8 column), determined at 254 nm and 210 nm, and target analytes tentatively identified on the primary column are confirmed on a second reversed-phase column that provides a different order of analyte elution (CN or phenylhexyl).

Aqueous samples of higher concentration can be diluted either 1:1 v/v or 1:3 v/v (depending on the selected separation) with methanol or acetonitrile, filtered, separated on a primary reversed-phase column, determined at 254 and 210 nm, and confirmed on a reversed-phase confirmation column. If HMX is an important target analyte, methanol is preferred.

Interferences

- Solvents, reagents, glassware, and other sample processing hardware may produce artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary.
- 2,4-DNT and 2,6-DNT elute at similar retention times on C-18 columns using the specified separation conditions (retention time difference of 0.2 minutes). A large concentration of one isomer (generally 2,4-DNT) may mask the response of the other isomer. If it is not apparent that both isomers are present (or are not detected), an isomeric mixture should be reported.
- Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. All aqueous samples expected to contain tetryl should be diluted with acetonitrile prior to filtration and acidified to pH<3. All samples expected to contain tetryl should not be exposed to temperatures above room temperature.
- Degradation products of tetryl appear as a shoulder on the 2,4,6-TNT peak using the C18 separation. Peak heights rather than peak areas should be used when tetryl is present in concentrations that are significant relative to the concentration of 2,4,6-TNT.

Conclusion

Currently, application for LC-MS/MS is under development at US EPA region 6 laboratory because traditional LC-UV/DAD is inferior in sensitivity and selectivity to LC-MS or LC-MS/MS. Agilent Technologies already developed application for explosives using LC-TOFMS.

Acknowledgements

The authors acknowledge the support of Mr. David Neligh, Mr. Rick McMillin and Dr. Melvin Ritter from the USEPA Region 6 as well as the help of Dr. Sheher Mohsin from Agilent Technologies.

References

- (1) Determination of concentration of nitroaromatics and nitroamines by high-performance liquid chromatography (HPLC), EPA Method 8330, Methods manual for detection of PEP compounds. US Environmental Protection Agency.
- (2) HPLC analysis of explosive constituents in soil samples, Agilent Technologies, publication 5901-7626E, www.agilent.com/chem
- (3) Reversed-Phase separation, 15 explosives from soil extract, Agilent Technologies, publication 5988-6342EN, www.agilent.com/chem
- (4) Qualitative and quantitative analysis of explosives and related compounds using polar and nonpolar HPLC columns, Agilent Technologies, Publication 5988-6345EN, www.agilent.com/chem
- (5) X. Zhao and J. Yinon, Characterization and origin identification of 2,4,6-trinitrotoluene through its byproduct by liquid chromatography-atmospheric pressure chemical ionisation mass spectrometry (2002), J. Chromat. A **946**, 125-132.
- (6) C. Sanchez, H. Carlson, A. Colmsjo, C. Crescenzi and R. Battle, Determination of nitroaromatic compounds in air samples at femtogram level using C18 membrane sampling and on-line extraction with LC-MS (2003), Anal. Chem. **75**, 4639-4645.