Analysis of trace residues of explosive materials following the guidelines set out in USEPA method 8330B and DIN EN ISO 22478

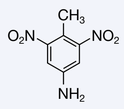
H. R. Wollseifen, T. Kretschmer, H. Riering,
MACHEREY-NAGEL GmbH & Co. KG, Düren, Germany
Contact hwollseifen@mn-net.com

INTRODUCTION

Nitroaromatics, nitramines, nitrate esters and peroxides represent the four major categories of explosive compounds in soil and ground water. Explosives are spread throughout the world because of their use in warfare, mining industries and civil constructions. Due to their toxicity, carcinogenicity and mutagenicity these compounds are considered a risk for public health and for the environment. Therefore the interest in highly sensitive analysis for explosives and propellants has increased. The most important guidelines for analysis of explosive materials are described in US Environmental Protection Agency (USEPA) method 8330B [1] and DIN EN ISO 22478 method [2]. These methods provide a solid phase extraction method and high performance liquid chromatographic conditions for 19 compounds (USEPA) and 20 compounds (DIN) with UV detection – in total for 22 different target compounds. In the first part of this work we present a methodology for sample preparation of water analysis which includes a solid phase extraction (SPE) method. The second part of this work points out the best high performance liquid chromatographic conditions on core-shell columns for 22 explosive compounds.

Nitrotoluenes
e.g., 2-nitrotoluene

Nitramines
e.g., 4-Amino-2,6-dinitrotoluene



Nitrate esters
e.g., ethylene glycol dinitrate

SOLID PHASE EXTRACTION METHOD

according to DIN EN ISO 22478 and EPA 8330B:

Conditioning
3 mL methanol, 3 mL acetonitrile,
10 mL water

Sample application
1000 mL water sample (with 5 g NaCl),
flow rate 1000 mL/h

Washing
10 mL water, 10 min drying with N_2

Elution
2 mL methanol + acetonitrile
(50 + 50, v + v)
2 mL methanol + acetonitrile
(50 + 50, v + v)

Solvent changing
0.5 mL water as keeper
reduce volume to 0.8 mL under N_2 flow
fill up to 1.0 mL with methanol + water
(50 + 50, v + v)

developed on CHROMABOND® HR-X PP columns (3 mL, 200 mg, 85 µm):

Conditioning
3 mL methanol, 3 mL acetonitrile,
10 mL water

Sample application
1000 mL water sample (with 5 g NaCl),
flow rate 1000 mL/h

Washing
10 mL water

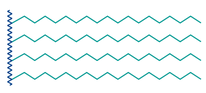
Elution
3 mL methanol + acetonitrile
(50 + 50, v + v)

Solvent changing
no use of keeper
reduce volume to 0.5 mL under N_2 flow
fill up to 1.0 mL with methanol + water
(40 + 60, v + v)

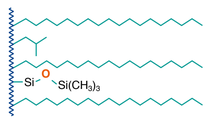
CHROMATOGRAPHIC METHOD

Column combinations for multidimensional chromatography

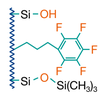
NUCLEOSHELL® RP 18
octadecyl, multi-endcapping,
particle size 2.7 µm, 100 mm x 2 mm ID



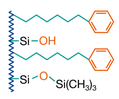
NUCLEOSHELL® RP 18plus
octadecyl (monomeric),
multi-endcapping,
particle size 2.7 µm,
50 mm x 2 mm ID



NUCLEOSHELL® PFP
pentafluorophenyl,
multi-endcapping,
particle size 2.7 µm,
50 mm x 2 mm ID



NUCLEOSHELL® Phenyl-Hexyl
phenyl-hexyl, multi-endcapping,
particle size 2.7 µm,
50 mm x 2 mm ID



HPLC system: Shimadzu UHPLC System Nexera X2

Columns:	see column combinations for multidimensional chromatography
Temperature:	40 °C
Injection:	25 µL (1 µg/mL for each compound)
Pump A	
Flow rate:	0.27 mL/min
Eluent:	A) water; B) methanol 15–80 % B in 40 min (5 min), 80–15 % B in 10 min (10 min)
Pump B	
Flow rate:	0.03 mL/min
Eluent:	25 mmol/L ammonium acetate buffer in water (pH 4.0 with acetic acid)
Detection:	UV: 210 nm, 230 nm, 254 nm, 360 nm

REFERENCES

[1] Method 8330B, Nitroaromatics, Nitramines, and Nitrate Esters by High Performance Liquid Chromatography (HPLC)

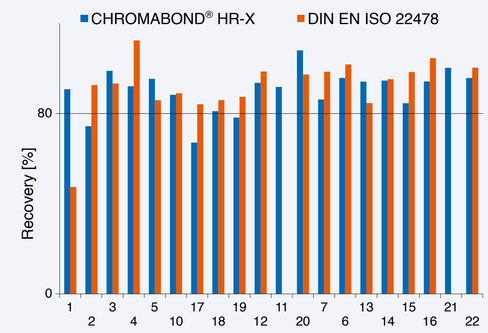
[2] Water quality – Determination of certain explosives and related compounds – Method using high-performance liquid chromatography (HPLC) with UV detection (ISO 22478:2006), German version EN ISO 22478:2006

RESULTS

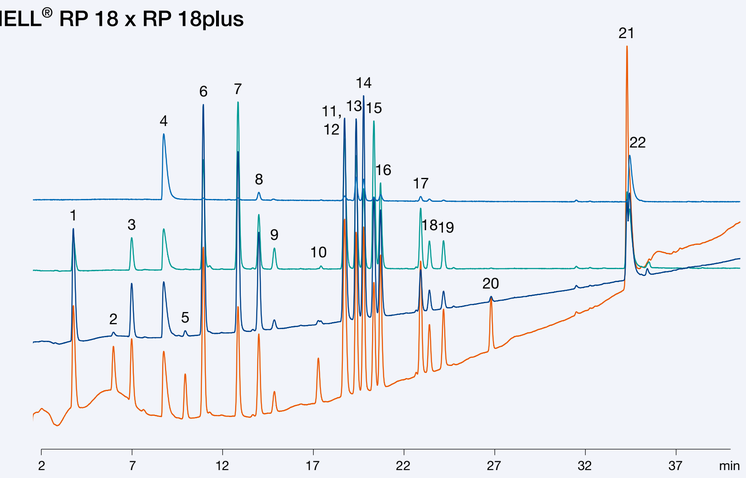
Compounds investigated

Peak	Explosive
1	Methyl-2,4,6-trinitrophenylnitramine (Tetryl)
2	Diethylene glycol dinitrate (DEGN)
3	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
4	2,4,6-Trinitrophenol (TNP)
5	Ethyleneglycol dinitrate (EGDN)
6	1,3,5-Trinitrobenzene (1,3,5-TNB)
7	1,3-Dinitrobenzene (1,3-DNB)
8	3,5-Dinitroaniline
9	Nitrobenzene
10	Nitroglycerin (NG)
11	2,4,6-Trinitrotoluene
12	Octahydro- 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
13	2-Amino-4,6-dinitrotoluene
14	4-Amino-2,6-dinitrotoluene
15	2,4-Dinitrotoluene
16	2,6-Dinitrotoluene
17	2-Nitrotoluene
18	4-Nitrotoluene
19	3-Nitrotoluene
20	Pentaerythritol tetranitrate (PETN)
21	Diphenylamine (DPA)
22	2,2',4,4',6,6'-Hexanitrodiphenylamine (Hexyl, HND)

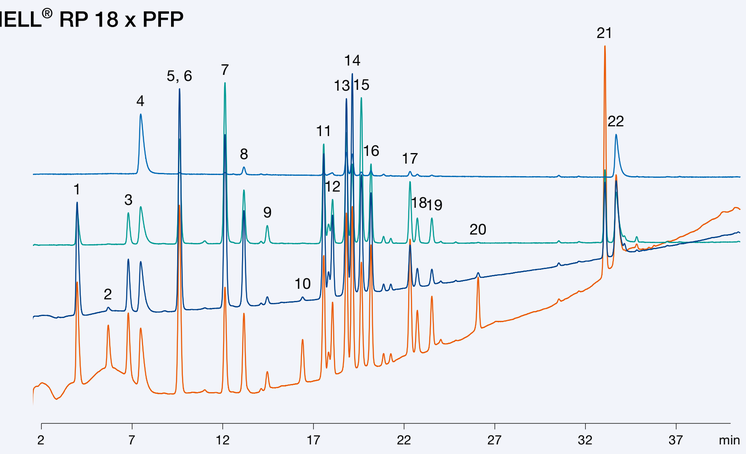
SPE recoveries



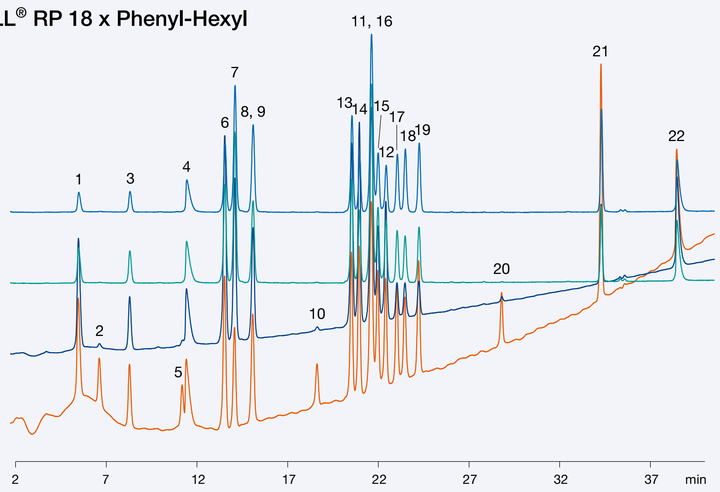
Separation on NUCLEOSHELL® RP 18 x RP 18plus



Separation on NUCLEOSHELL® RP 18 x PFP



Separation on NUCLEOSHELL® RP 18 x Phenyl-Hexyl



CONCLUSION

The results of this work show that the solid phase extraction of explosives with CHROMABOND® HR-X is very well suited. In particular, a significantly better recovery is achieved in the solid phase extraction of the explosive analyte tetryl.

The chromatographic results illustrate that each of the column combinations has advantages in the separation of different classes of explosives due to the combined selectivities. Especially, a separation of the 19 analytes described by USEPA 8330B in a single run is made possible by the combination of the columns NUCLEOSHELL® RP 18 and PFP.

If the respective explosives categories are supplemented by other analytes such as degradation products, the results shown are good starting conditions for further optimizations.

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www.tuv.com
ID 9000008338

MACHEREY-NAGEL GmbH & Co. KG
Valencienner Str. 11
52355 Düren · Germany

DE Tel.: +49 24 21 969-0 info@mn-net.com
CH Tel.: +41 62 388 55 00 sales-ch@mn-net.com
FR Tel.: +33 388 68 22 68 sales-fr@mn-net.com
US Tel.: +1 888 321 62 24 sales-us@mn-net.com