MACHEREY-NAGEL
Chromatography application note

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

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Abstract

This application note presents a method for the solid phase extraction of explosives from water in lower µg/L range using CHROMABOND® HR-X for sample clean up and analyte concentration. A significantly better recovery is achieved in the solid phase extraction of the explosive analyte tetryl. After eluent exchange, the eluates from SPE are finally analyzed by HPLC-UV on several core-shell columns. By combining differently modified phases it is possible to fulfill the criteria of DIN EN ISO 22478 und EPA 8330B for the 22 explosive materials prescribed. In the process, particularly suitable selectivity of two modifications will be brought together in one method proposal, making mass spectrometric detection possible as well as UV detection.

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 procedure and high performance liquid chromatographic conditions for 19 compounds (USEPA) and 20 compounds (DIN) with UV detection – in total for 22 different target compounds.

Compounds of interest

Nitrotoluenes	Nitramines	Nitrate esters
e.g., 2-nitrotoluene	e.g., 4-amino-2,6-dinitrotoluene	e.g., ethylene glycol dinitrate

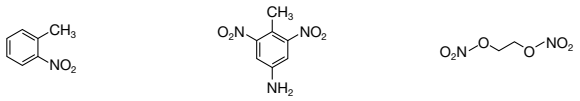

Figure 1: Overview of categories of explosive compounds.

Sample preparation: Solid phase extraction

Column type: CHROMABOND® HR-X polypropylene columns (85 µm), 3 mL, 200 mg, (REF 730931)

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

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

Washing: 10 mL water

Elution: 3 mL hexane – ethyl acetate – glacial acetic acid (75:25:1, v/v/v) in a screw neck vials N 13 (REF 702923)

Eluent exchange

Eluates from SPE are evaporated to 0.5 mL at 40 °C under a stream of nitrogen and then filled up to 1.0 mL with methanol/water mixture (40 + 60; v + v) for the subsequent analysis.

Screw neck vials N 9 (REF 702293)
N 9 PP screw cap with septum silicone white / PTFE red (REF 702107)

Subsequent analysis: HPLC-UV

Chromatographic conditions:

Column combinations for multidimensional chromatography:

First Column:
EC 100/2 NUCLEOSHELL® RP 18, 2.7 µm, (REF 763134.20)

Second Column A:
EC 50/2 NUCLEOSHELL® RP 18plus, 2.7 µm, (REF 763232.20)

Second Column B:
EC 50/2 NUCLEOSHELL® PFP, 2.7 µm, (REF 763532.20)

Second Column C:
EC 50/2 NUCLEOSHELL® Phenyl-Hexyl, 2.7 µm, (REF 763732.20)

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
Temperature: 40 °C
Injection volume: 25 µL

Detection: UV: 210 nm, 230 nm, 254 nm, 360 nm

Analysis of trace residues of explosive materials

Chromatograms

Separation on NUCLEOSHELL® RP 18 x RP 18plus

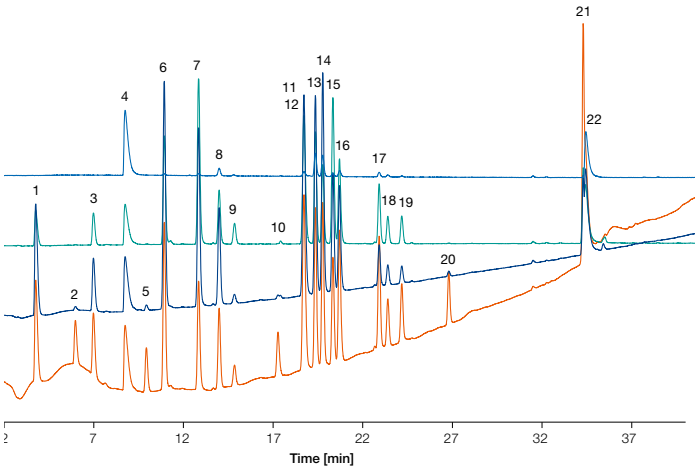

Figure 2: Chromatograms of aqueous standard solution of explosives from water, separation on NUCLEOSHELL® RP 18 x NUCLEOSHELL® RP 18plus; red: UV at 210 nm; dark blue: UV at 230 nm; green: UV at 254 nm; blue: UV at 360 nm (for peak numbers see table 1).

Separation on NUCLEOSHELL® RP 18 x Phenyl-Hexyl

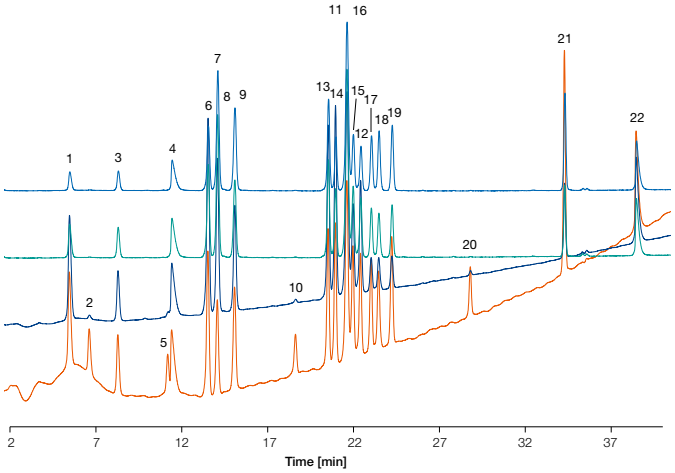

Figure 3: Chromatograms of aqueous standard solution of explosives from water, separation on NUCLEOSHELL® RP 18 x NUCLEOSHELL® Phenyl-Hexyl; red: UV at 210 nm; dark blue: UV at 230 nm; green: UV at 254 nm; blue: UV at 360 nm (for peak numbers see table 1).

Separation on NUCLEOSHELL® RP 18 x PFP

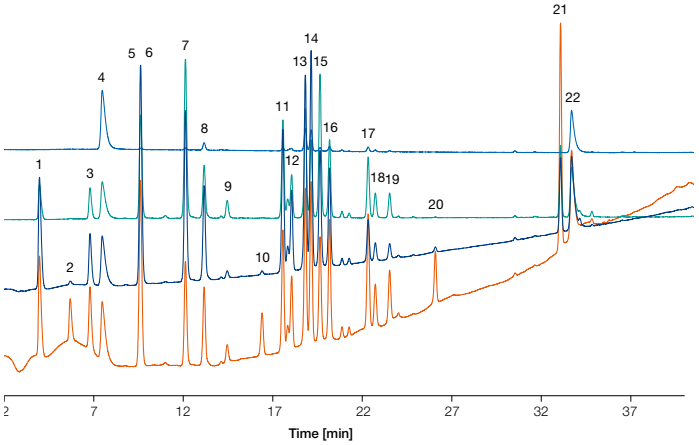

Figure 4: Chromatograms of aqueous standard solution of explosives from water, separation on NUCLEOSHELL® RP 18 x NUCLEOSHELL® PFP; red: UV at 210 nm; dark blue: UV at 230 nm; green: UV at 254 nm; blue: UV at 360 nm (for peak numbers see table 1).

Recovery rate

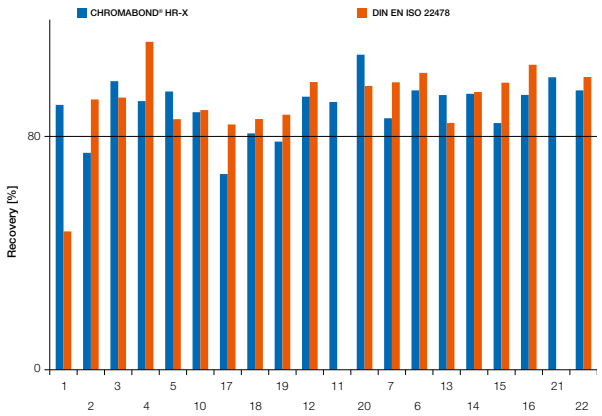

Figure 5: Comparison between the recovery rates of explosives from water using CHROMABOND® HR-X for solid phase extraction and the values described in DIN EN ISO 22478 (for analytes see table 1).

LOD/LOQ

Peak No.	Run Phenyl-Hexyl at 60 °C	Analyte	LOD (UV) in µg/L	LOQ (UV) in µg/L
1	A1	*N*-methyl-*N*-2,4,6-tetranitroaniline	0.03	0.10
2	A2	Diethylene glycol dinitrate	0.04	0.13
3	A3	Hexahydro-1,3,5-trinitro-1,3,5-triazine	0.02	0.09
4	A4	2,4,6-Trinitrophenol	0.03	0.11
5	A5	Ethylene glycol dinitrate	0.03	0.12
6	B1	1,3-Dinitrobenzene	0.03	0.11
7	B2	1,3,5-Trinitrobenzene	0.01	0.05
8	A6	Nitroglycerin	0.06	0.22
9	B3	2-Amino-4,6-dinitrotoluene	0.02	0.09
10	B4	4-Amino-2,6-dinitrotoluene	0.04	0.13
11	B5	2,4-Dinitrotoluene	0.04	0.15
12	A7	4-Nitrotoluene	0.04	0.13
13	B6	2,6-Dinitrotoluene	0.06	0.22

Analysis of trace residues of explosive materials

Peak No.	Run Phenyl-Hexyl at 60 °C	Analyte	LOD (UV) in µg/L	LOQ (UV) in µg/L
14	A8	3-Nitrotoluene	0.03	0.10
15	A9	2-Nitrotoluene	0.03	0.10
16	A10	2,4,6-Trinitrotoluene	0.01	0.05
17	A11	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	0.02	0.06
18	A12	Pentaerythritol tetranitrate	0.04	0.16
19	B7	Diphenylamine	0.02	0.06
20	B8	2,2´,4,4´,6,6´-Hexanitrodiphenylamine	0.08	0.27

Table 1: Limit of quantification (LOQ) and limit of detection (LOD), the concentration that provides a signal-to-noise ratio (S/N) of > 3 was considered as LOD and S/N > 10 was considered as LOQ.

Conclusion

The results of this work show that CHROMABOND® HR-X is very well suited for the solid phase extraction of explosives. 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 have advantages in the separation of different classes of explosives due to the combined selectivities. The hydrophobic interactions of the octadecyl modification with the analytes are significant for the separation of the explosive materials observed. The PFP modification improves the separation of the explosives by polar interactions (H bonds), dipole-dipole interactions, π–π interactions, and hydrophobic interactions.

The chromatographic separation of explosives is also influenced by column temperature. For RP 18 modification 40 °C leads to the best chromatographic separation. Higher temperatures like 60 °C are more suited for Phenyl-Hexyl modification.

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 shown results are good starting conditions for further optimizations.

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.

Additional information

The following applications regarding “Analysis of trace residues of explosive materials” and further applications can be found on our online application database at *www.mn-net.com/apps*:

SPE: MN Appl. No. 305920
HPLC: MN Appl. No. 127210

Product information

The following MACHEREY-NAGEL products have been used in this application note:

REF 730931, CHROMABOND® HR-X, 3 mL, 200 mg
REF 763134.20, EC 100/2 NUCLEOSHELL® RP 18, 2.7 µm
REF 763232.20, EC 50/2 NUCLEOSHELL® RP 18plus, 2.7 µm
REF 763532.20, EC 50/2 NUCLEOSHELL® PFP, 2.7 µm
REF 763732.20, EC 50/2 NUCLEOSHELL® Phenyl-Hexyl, 2.7 µm
REF 702293 Screw neck vials N 9, 1.5 mL
REF 702107 N 9 PP Screw cap, yellow, center hole, silicone white / PTFE red
REF 702923 Screw neck vials N 13, 4 mL