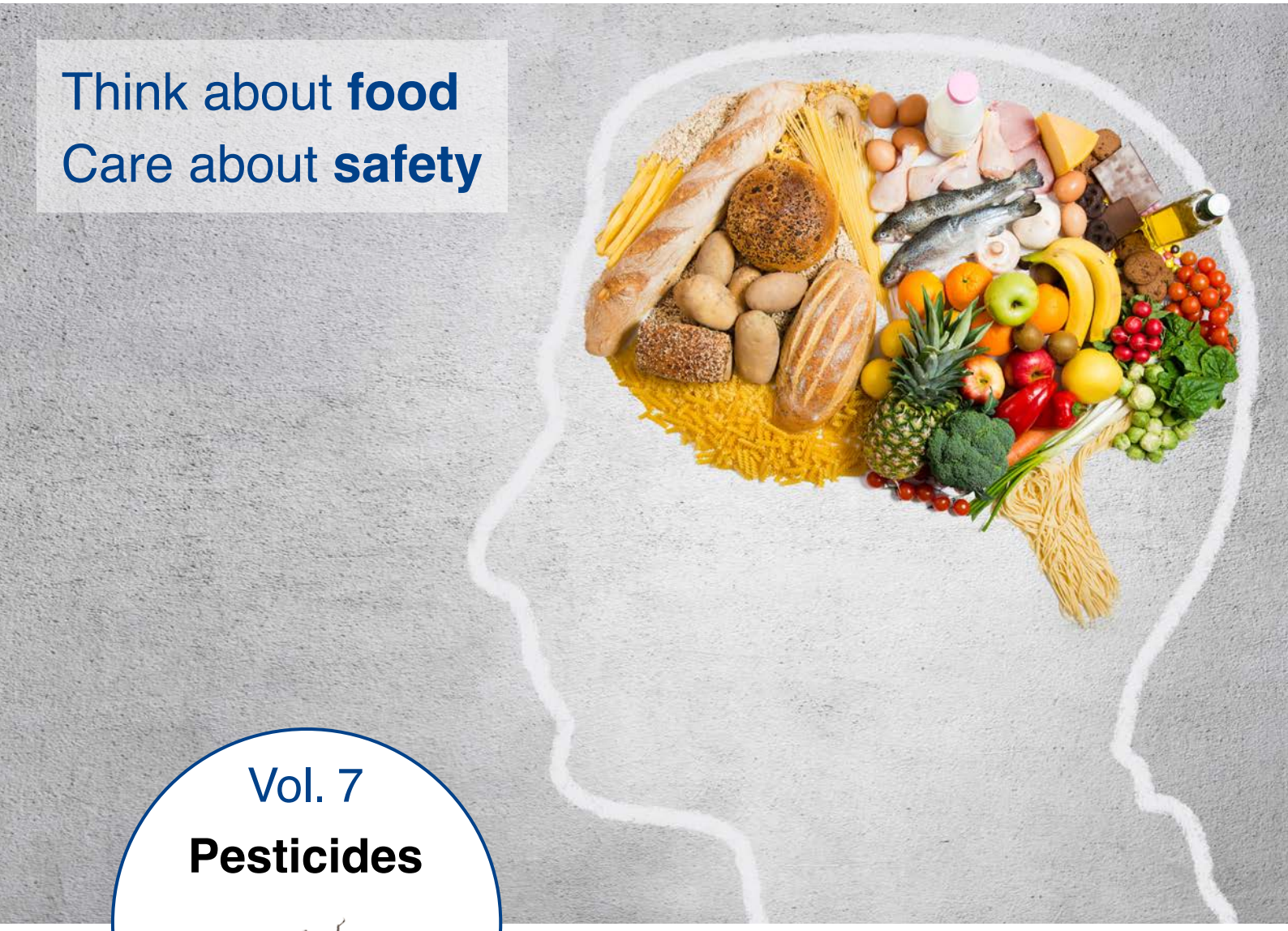
# CHROMATOGRAPHY

Think about **food**
Care about **safety**



Vol. 7

**Pesticides**

MACHEREY-NAGEL
www.mn-net.com

ADIS INTERNATIONAL

MN Since 1911

# Focus on pesticides

The global production and trading of food and feed products makes monitoring and control difficult.

Only analysis of food and raw materials for the production of food can ensure safe and edible food. Food safety is an essential part of our quality of life.

**MN shows examples for food analysis that will help you with your work and make our food safer!**

## Vol. 7: **Pesticides in food**

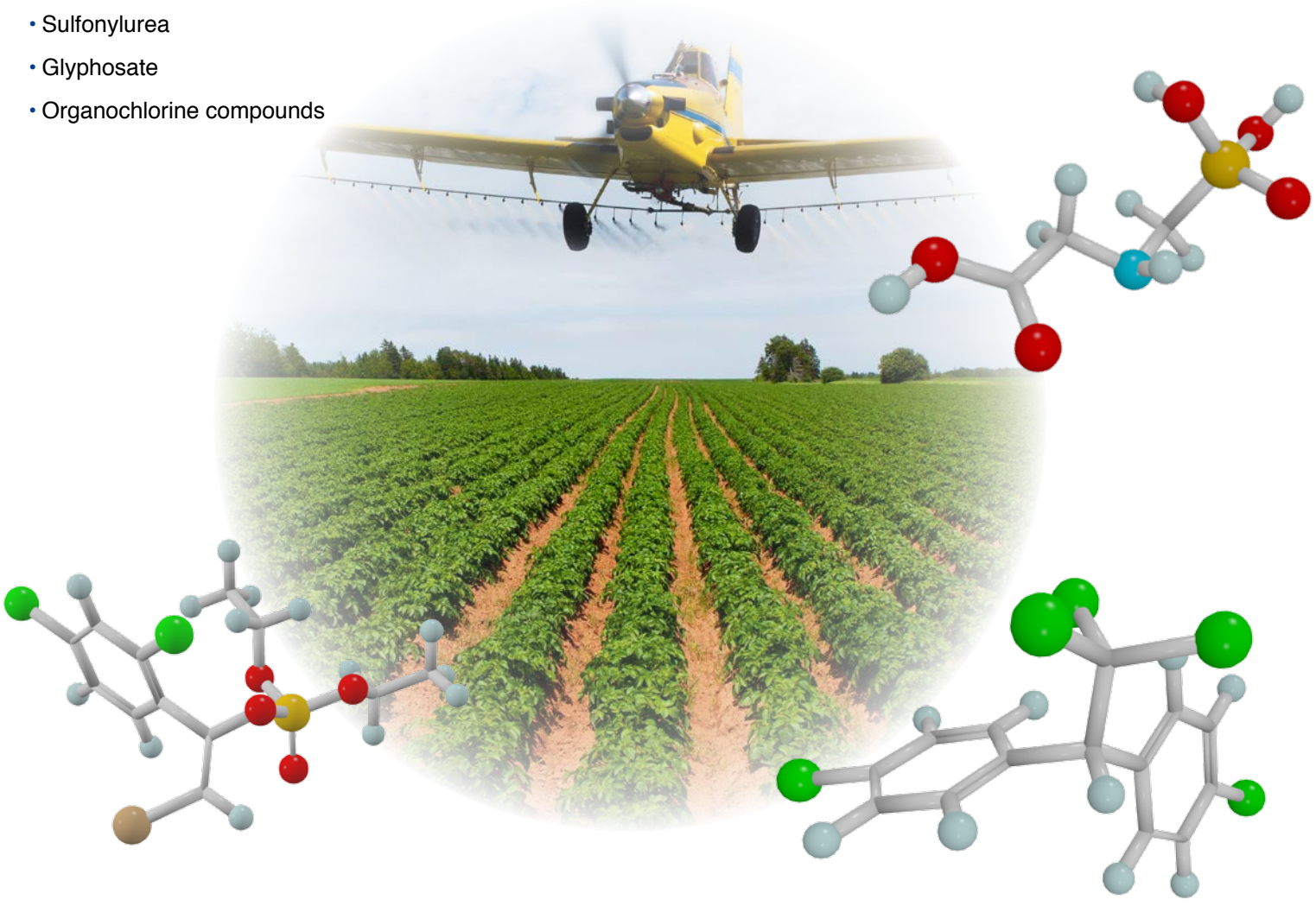
Pesticides are chemical agents used for prevention and control of various pests. Pesticides can be classified in herbicides (to control weeds), insecticides (to control insects), fungicides (to control molds and fungi) and rodenticides (to control rodents) [EPA – US Environmental Protection Agency – http://www.epa.gov/pesticides/food/].

Most commonly used are

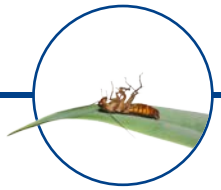
- Organophosphates
- Carbamates
- Pyrethroids
- Sulfonylurea
- Glyphosate
- Organochlorine compounds

Since pesticides can be harmful to health of humans, animals or the environment, they need to be monitored and very responsibly used [EPA – US Environmental Protection Agency – http://www.epa.gov/pesticides/health/human.htm].

Among other authorities, the US Environmental Protection Agency (EPA) sets limits on how much of a pesticide can be used on food during the growing and processing, and how much is allowed to remain in the food [EPA – US Environmental Protection Agency – http://www.epa.gov/pesticides/safety/applicators/restrict.htm].

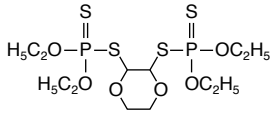


# Compounds of interest

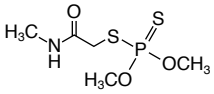


## Chemical structures of selected pesticides

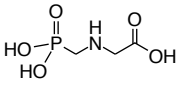
Dioxathion



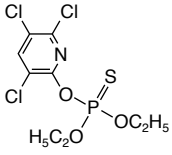
Dimethoate



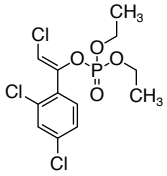
Glyphosate



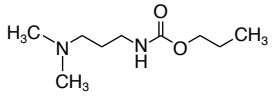
Chlorpyriphos



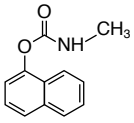
Chlorfenvinphos



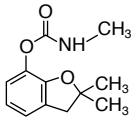
Propamocarb



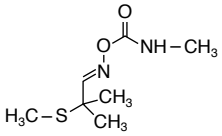
Carbaryl



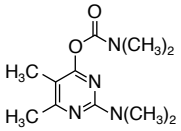
Carbofuran



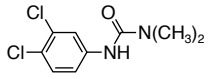
Aldicarb



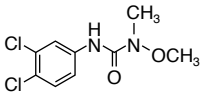
Pirimicarb



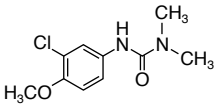
Diuron



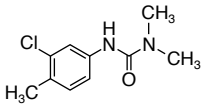
Linuron



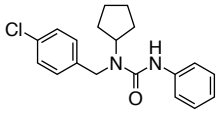
Metoxuron



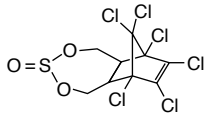
Chlortoluron



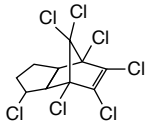
Pencycuron



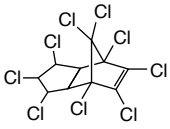
Endosulfan



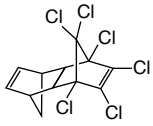
Heptachlor



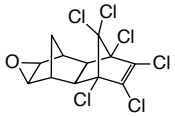
Nonachlor



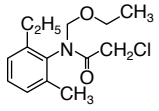
Aldrin



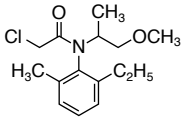
Endrin



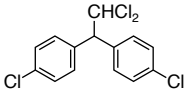
Actochlor



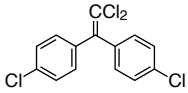
Metholachlor



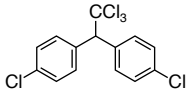
4,4'-DDD



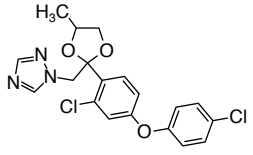
4,4'-DDE



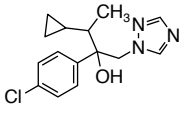
4,4'-DDT



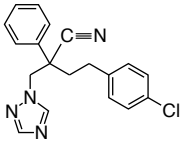
Difenoconazol



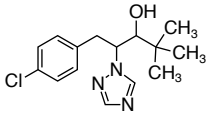
Cyproconazol



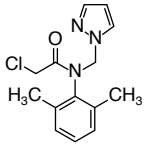
Fenbuconazole



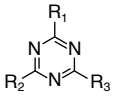
Paclobutrazol



Metazachlor



Triazines



| Compound | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| Atrazine | Cl | $NH\text{-}C_2H_5$ | $NH\text{-}CH(CH_3)_2$ |
| Simazine | Cl | $NH\text{-}C_2H_5$ | $NH\text{-}C_2H_5$ |
| Terbuthylazine | Cl | $NH\text{-}C_2H_5$ | $NH\text{-}C(CH_3)_3$ |
| Terbutryn | $S\text{-}CH_3$ | $NH\text{-}C_2H_5$ | $NH\text{-}C(CH_3)_3$ |

# Typical samples, preparation

## Pesticides from natural water

***MN Appl. No. 305520***

*Column type:*
CHROMABOND® HR-X, 3 mL, 60 mg
REF 730936

*Column conditioning:*
5 mL methanol, then 5 mL ultrapure water

*Sample aspiration:*
50 mL water sample is passed through the column by vacuum

*Washing:* 5 mL ultrapure water with 5 % methanol

*Drying:*
with gentle nitrogen stream, 15 min
(storage before elution step at 4 °C is possible for 1 month)

*Elution:*
2 x 3 mL methanol; then 1 x 3 mL methanol – ethyl acetate (75:25, v/v)

*Evaporation:*
to dryness after addition of 10 µL internal standard

*Reconstitution:*
in 1 mL of the initial HPLC eluent

*Compounds investigated:*
acetochlor; alachlor; atrazine; azoxystrobin; carbaryl; carbofuran; 3-hydroxycarbofuran; chlorfenvinphos; chlorpyriphos; chlortoluron; 1-(3,4-dichlorophenyl)-3-methyl urea (DCPMU, metabolite of diuron); desethylatrazine (DEA, metabolite of atrazine); desethylterbuthylazine (DET, metabolite of terbuthylazine); desisopropylatrazine (DIA, metabolite of atrazine); dimethoate; dimetomorph; diuron; hexazinone; 1-(4-isopropylphenyl)-3-methyl urea (IPPMU, metabolite of isoproturon); 1-(4-isopropyl phenyl) urea (IPPU, metabolite of isoproturon); isoproturon; linuron; metazachlor; methomyl; metolachlor; metoxuron; pyrimicarb; simazine; terbuthylazine; thiodicarb

We recommend using the **CHROMABOND® vacuum manifold for 12 columns** REF 730150

## Pesticide residues from fruit and vegetables using the QuEChERS procedure

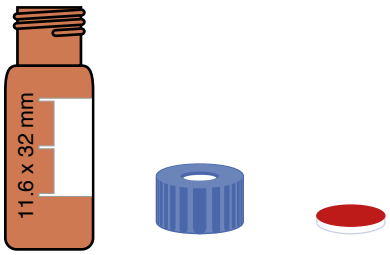
***MN Appl. No. 305190***

*Column type:*
CHROMABOND® QuEChERS Mix I, REF 730970
CHROMABOND® QuEChERS Mix III, REF 730972

*Sample pretreatment:*
The food sample is homogenized in a 50 mL centrifuge tube (REF 730223) with 8 mL acetonitrile and then cleaned up with pre-weighed mixes of salts and adsorbents in a 15 mL centrifuge tube.

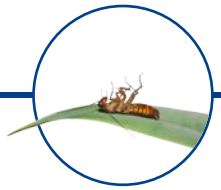
*Procedure for complex food samples:*
The sample is extracted with Mix I, then 1 mL supernantant is transferred to the centrifuge tube with Mix III (samples with low fat content). It is shaken, centrifuged and analyzed by HPLC.

*Compounds investigated:*
aldicarb sulfone; aldicarb; desmethyl-pirimicarb; desmethyl-formamido-pirimicarb; carbofuran; paclobutrazol; terbutryn; pencycuron; dioxathion; fenpyroximate; oxamyl; pymetrozin; propamocarb; dimethoate; carbendazim; metalaxyl; methoxyfenozide; tebufenozide; fenoxycarb; pyraclostrobin; difenoconazol; propargite; spinosad; methiocarb sulfoxide; thiophanate-m; dimethomorph I; fludioxonil; fenbuconazol; famoxadone; prosulfocarb; dimethomorph II; cyproconazol I; cyproconazol II; hydroxycarbofuran




Transfer into a sample vial, e.g., 1.5 mL screw neck vials N 9, amber, flat bottom, label and scale, wide opening, REF 702284 and ready assembled screw closures N 9, blue, center hole with septum silicone / PTFE, REF 702287.1

## For other applications see *www.mn-net.com/apps*



## Fungicides carbendazime and thiabendazole from fruit juice

### Solid phase extraction

*MN Appl. No. 304740*

*Sample pretreatment:*
see ***www.mn-net.com/apps***

*Column type:*
CHROMABOND® HR-XC, 3 mL, 200 mg
REF 730952

*Column conditioning:* 5 mL methanol, then 5 mL 2 % $NH_3$
(Do not let run the column dry!)

*Sample aspiration:* The prepared sample is passed through the column by vacuum.

*Washing:*
impurities are removed with the following washing mixtures:
a) 2 mL 2 % $NH_3$
b) 2 mL 30 % methanol – 5 % $NH_3$
c) 2 mL 0.1 mol/L HCl
d) 2 mL methanol

*Drying:*
with nitrogen or air

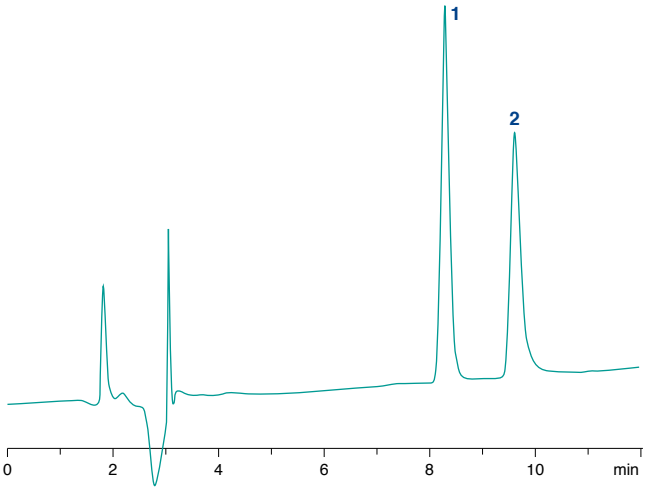
*Elution:*
4 mL methanol / 5 % $NH_3$

It is recommended to filter the prepared sample through disposable filters **CHROMAFIL® Xtra PET-45/25**
REF 729220

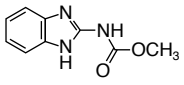
### HPLC analysis

*MN Appl. No. 122200*

*Column:* EC 125/4 NUCLEODUR® $C_{18}$ Gravity, 5 µm
REF 760100.40




**Peaks**
1. Carbendazime
2. Thiabendazole





## Detailed conditions are available online at *www.mn-net.com/apps*

MN suggests using guard columns to protect your main column and significantly increase column life.

The **Column Protection System** (REF 718966)
is suitable for all analytical HPLC columns with 1/16" fittings!

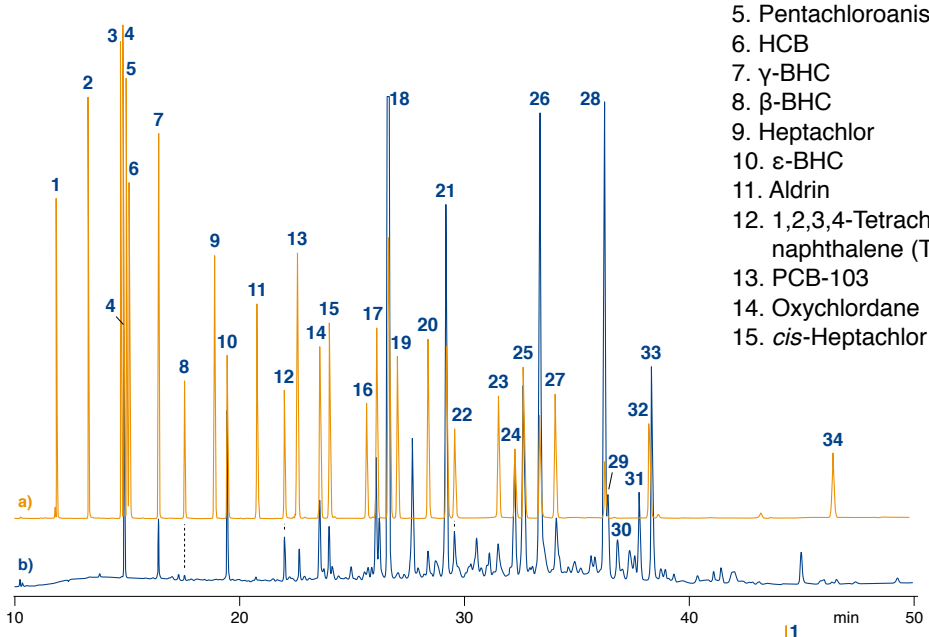
## Subsequent analysis: GC

### Pesticides from cod liver oil

***MN Appl. No. 213270***

R. Looser, K. Ballschmiter, J. Chromatogr. A 836, 271–284 (1999)

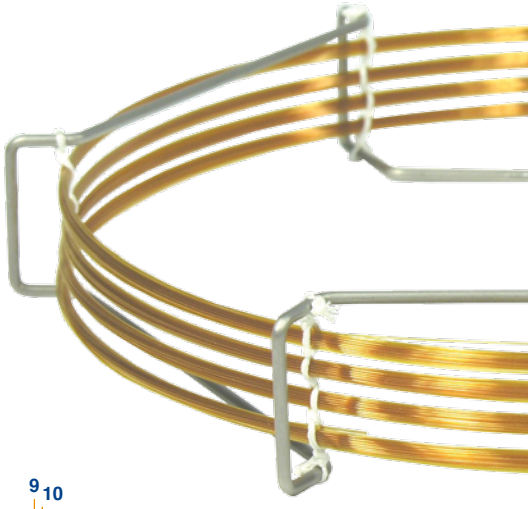
*Column:* OPTIMA® δ-3, 60 m x 0.25 mm ID, 0.25 µm film, REF 726420.60




**Peaks:**

1. Pentachlorobenzene
2. 2,4,6-Tribromoanisole
3. Tetrachloro-1,4-dimethoxy-benzene
4. α-BHC
5. Pentachloroanisole
6. HCB
7. γ-BHC
8. β-BHC
9. Heptachlor
10. ε-BHC
11. Aldrin
12. 1,2,3,4-Tetrachloro-naphthalene (TCN)
13. PCB-103
14. Oxychlordane
15. *cis*-Heptachlor epoxide
16. 2,4'-DDE
17. *trans*-Chlordane
18. *cis*-Chlordane / *trans*-Nonachlor
19. Endosulfan I
20. 4,4'-DDE
21. Dieldrin
22. 2,4'-DDD
23. Endrin
24. 2,4'-DDT
25. *cis*-Nonachlor
26. 4,4'-DDD
27. Endosulfan II
28. 4,4'-DDT
29. Parlar 41
30. Parlar 40
31. Parlar 44
32. Endosulfan sulphate
33. Parlar 50
34. Mirex

It is recommended to filter the prepared sample through disposable filters CHROMAFIL® PTFE-45/25 REF 729205



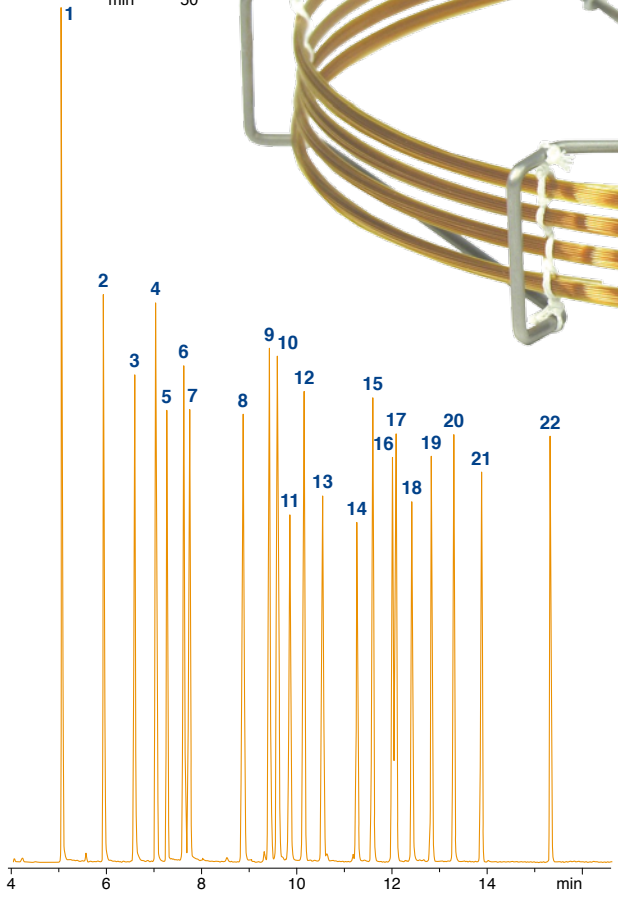
### Organochlorine pesticides (EPA 8081)

***MN Appl. No. 213630***

*Column:* OPTIMA® 17 MS, 30 m x 0.25 mm ID, 0.25 µm film, REF 726162.30

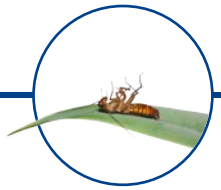
**Peaks:**

1. 2,4,5,6-Tetrachloro-*m*-xylene
2. α-BHC
3. γ-BHC (Lindane)
4. Heptachlor
5. β-BHC
6. Aldrin
7. δ-BHC
8. Heptachlor epoxide
9. γ-Chlordane
10. α-Chlordane
11. Endosulfan I
12. 4,4'-DDE
13. Dieldrin
14. Endrin
15. 4,4'-DDD
16. Endosulfan II
17. 4,4'-DDT
18. Endrin aldehyde
19. Endosulfan sulfate
20. Methoxychlor
21. Endrin ketone
22. Decachlorobiphenyl




**Detailed conditions are available on-line at *www.mn-net.com/apps***

# Product information



## Ordering information

| Step | Product | Pack of | REF |
|---|---|---|---|
| **SPE 1** | CHROMABOND® HR-X, 3 mL, 60 mg | 30 | 730936 |
| | CHROMABOND® vacuum manifold for 12 columns | 1 | 730150 |
| **SPE 2 (QuEChERS)** | CHROMABOND® QuEChERS Mix I (citrate extraction mix) | 50 | 730970 |
| | CHROMABOND® QuEChERS Mix III (Diamino clean-up mix) | 50 | 730972 |
| **SPE 3** | CHROMABOND® HR-XC, 3 mL, 200 mg | 30 | 730952 |
| | CHROMABOND® vacuum manifold for 12 columns | 1 | 730150 |
| **Filtration** | Disposable filters CHROMAFIL® Xtra PET-45/25 | 100 | 729220 |
| | Disposable filters CHROMAFIL® Xtra PTFE-45/25 | 100 | 729205 |
| **Vials and caps** | 1.5 mL screw neck vials N 9, amber, label and scale | 100 | 702284 |
| | Ready assembled screw closures N 9, blue, center hole with septum Silicone white / PTFE red | 100 | 702287.1 |
| **HPLC** | | | |
| Column | EC 125/4 NUCLEODUR® $C_{18}$ Gravity, 5 µm | 1 | 760100.40 |
| Guard column | EC 4/3 NUCLEODUR® $C_{18}$ Gravity, 5 µm | 3 | 761903.30 |
| Guard column holder | Column Protection System | 1 | 718966 |
| **GC 1** | | | |
| Column | OPTIMA® δ-3, 60 m x 0.25 mm ID, 0.25 µm film | 1 | 726420.60 |
| **GC 2** | | | |
| Column | OPTIMA® 17 MS, 30 m x 0.25 mm ID, 0.25 µm film | 1 | 726162.30 |

## Visit us at *www.mn-net.com/chroma* to get more helpful information

### Selection tools for

Vials and caps

Syringe filters

### Troubleshooting guides

GC and HPLC

### Detailed product information

…and much more

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Melamine

Vol. 2
Vitamins

Vol. 3
Antibiotics

Vol. 4
Acrylamide

Vol. 5
Sugars
Sweeteners

Vol. 6
Mycotoxins

Vol. 7
Pesticides

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