TRAJAN

TECHNICAL ARTICLE

# Organochlorine pesticides USEPA 8081A method

## Introduction

With the widespread use of pesticides, especially over the last 40 years, pesticide analysis is one of the most universal methods used in environmental laboratories around the world. Their persistence in the environment, and in some cases, their non-specific mode of action, has led to bans in many countries. This persistence has also resulted in the continuing need for monitoring of this class of compounds.

## The analysis

The volatile nature of chlorinated pesticides naturally leads to gas chromatographic analysis. However, resolution requirements and breakdown performance criteria, especially for sample extracts containing high-boiling contaminants, are usually quite stringent. The USEPA has targeted 20 common chlorinated pesticides. Together with two internal standards this leads to a requirement to resolve 22 compounds (Figure 1). Because of the screening nature of most environmental methods, there is always pressure in a lab to reduce analysis time and hence increase sample throughput.

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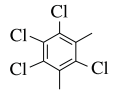
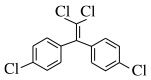
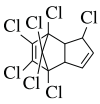
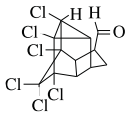
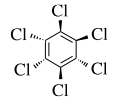
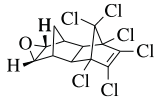
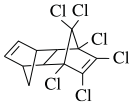
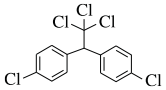
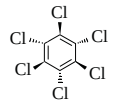
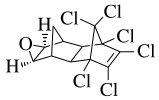
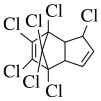
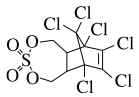
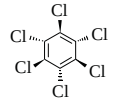
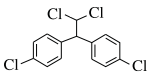
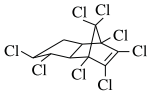
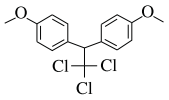
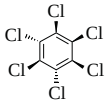
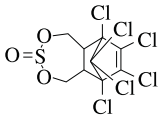
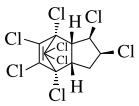
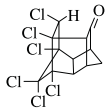
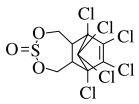
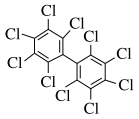
|  2,4,5,6-tetrachloro-meta-xylene (surrogate) |  p,p'-DDE |  Heptachlor |  Endrin Aldehyde |
|  Alpha BHC |  Dieldrin |  Aldrin |  p,p'-DDT |
|  Beta BHC |  Endrin |  Heptachlor epoxide |  Endosulfan Sulfate |
|  Gamma BHC |  p,p'-DDD |  Gamma Chlordane |  Methoxychlor |
|  Delta BHC |  Endosulfan B |  Alpha Chlordane |  Endrine Ketone |
|  Endosulfan A |  Decachlorobiphenyl Surrogate | | |

*Figure 1. Organochlorine pesticide structures*

## Choice of capillary column

There is a wide choice of capillary columns for the analysis of pesticides. It is common practice in labs around the world to split the sample after GC injection between two different capillary columns. These columns are usually of differing polarity and must show different retention times of analytes, preferably with some peak switching. It is common to quantify pesticide response on a non-polar column such as the 5% phenyl BPX5 column or the 100% methyl SolGel-1ms™ column. The latter column, although custom designed as a low-bleed MS column, can be used successfully with all GC detectors. The second column used is one of a range of columns of varying polarity. The range also includes the 35% or 50% phenyl columns (BPX35 and BPX50, respectively). Using any of the columns described above, it is possible to analyze the 22 targeted compounds with excellent baseline resolution in under 22 minutes. This allows for greater throughput of samples.

## BPX5

### 5% phenyl (equiv) polysilphenylene-siloxane

USEPA 8081 organochlorine pesticide mix analyzed on the BPX5 column (Figure 2), shows an excellent separation of the components in less than 24 minutes. DDT (peak 18) and Methoxychlor (peak 20) show no on-column breakdown indicating the high degree of inertness of BPX5. Also note the exceptional bleed profile at 300°C.

| BPX5 replaces | |
|---|---|
| DB-5 | HP5-TA |
| DB-5MS | SPB-5 |
| DB-5.625 | MDN-5S |
| XTI-5 | CP-Sil 8CB |
| Rtx-5ms | Rtx-5Sil MS |
| Ultra-2 | AT-5 |
| HP-5 | CP-Sil 8CB |
| HP-5MS | MS |

| Column part number | 054101 | | |
|---|---|---|---|
| Phase | BPX5 | Carrier gas | He, 10.5 psi |
| Column | 30 m x 0.25 mm x 0.25 µm | Carrier gas flow | 1.0 mL/min |
| Sample | 100 ppm in dichloromethane | Constant flow | On |
| Initial temperature | 110°C, 1 min | Average linear velocity | 36 cm/sec at 110°C |
| Rate 1 | 25°C/min to 150°C | Injection mode | Split (50:1) |
| Rate 2 | 12°C/min to 260°C | Injection volume | 1 mL |
| Rate 3 | 15°C/min to 310°C | Injection temperature | 250°C |
| Final temperature | 310°C, 6 min | Autosampler | No |
| Detector | MS | Liner type | 4 mm ID Single taper liner |

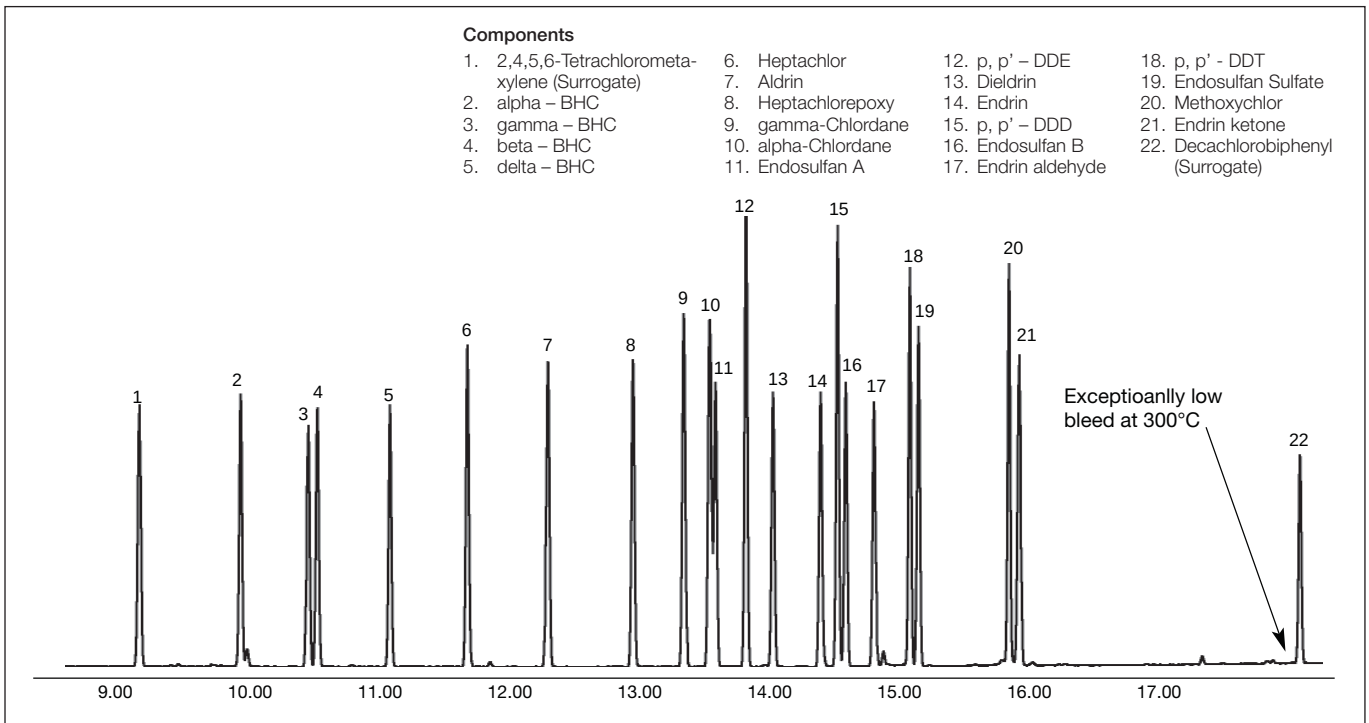



*Figure 2. USEPA 8081 organochlorine pesticide*

## The advantage of high maximum temperature columns

The composition of sample extracts in an environmental lab can be extremely variable. From relatively clean water samples to extremely complex 'dirty' soil samples. It is extremely useful to use a capillary column with a high maximum operating temperature. The column can then be 'baked out' following deposition of semi and non-volatile residue material on the front end of the column. Once peak shape deteriorates, it is common practice to condition the column at the upper maximum temperature of the column for at least 60 minutes to remove this residue. If this fails to re-establish good chromatography then the front 0.5 meter of the column can be cut and discarded. The second advantage of a column with a high maximum operating temperature is lower bleed at the upper method temperature. Thus, for example, if the upper maximum temperature of the column is 370°C, the bleed level at 300°C will be lower compared with a column with an upper maximum level of 320°C. This leads to better sensitivity for the higher maximum temperature column.

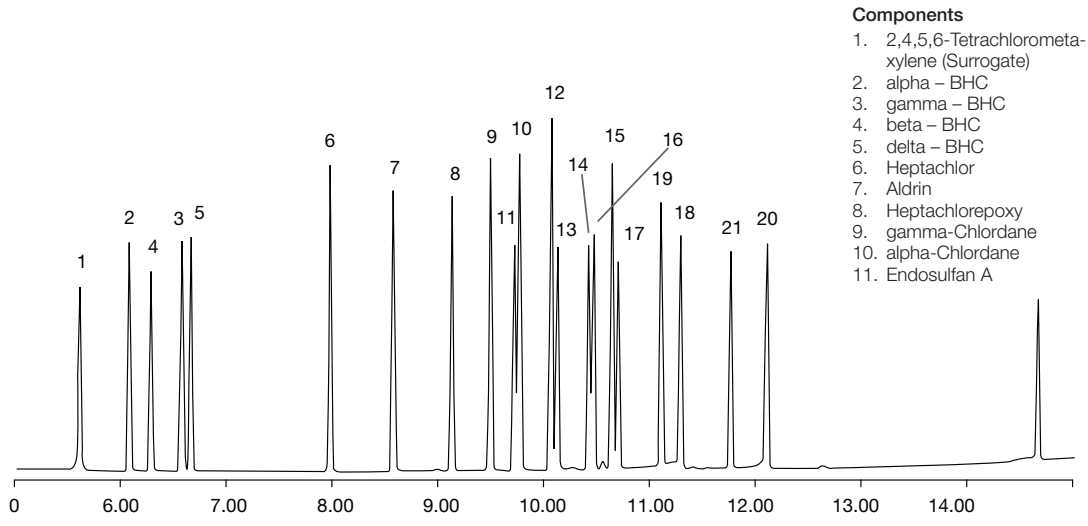
Thermal stability of our stationary phases is excellent because of advanced polymer technology. For example, up to 360°C for BPX5, BPX35, BPX50 and up to 380°C for a SolGel-1ms column. The very low bleed level at the maximum operating temperatures of these columns is particularly advantageous to the chromatographer.

## SolGel-1ms

Figure 3 shows the USEPA 8081 pesticide mix analyzed using a SolGel-1ms column. Note the bleed profile at 300°C and separation of the components with no coelution's in less than 15 minutes, allowing multiple samples to be run in the laboratory. Again, SolGel-1ms, like BPX5, BPX35 and BPX50 shows superior inertness with no-column breakdown of the susceptible DDT and Methoxychlor. Also note, 4 different elution orders making SolGel-1ms an exceptional conformational column to that of BPX5.

### Conditions

| Column part number | 054795 | | |
|---|---|---|---|
| Phase | SolGel-1ms | Constant flow | On |
| Column | 30 m x 0.25 mm x 0.25 µm | Average linear velocity | 35 cm/sec at 110°C |
| Sample | 100 ppm in dichloromethane | Injection mode | Splitless |
| Initial temperature | 100°C, 1 min | Purge on time | 0.5 min |
| Rate 1 | 25°C/min to 150°C | Vent flow | 60 mL/min |
| Rate 2 | 12°C/min to 260°C | Injection volume | 1 µL |
| Rate 3 | 15°C/min to 300°C | Injection temperature | 250°C |
| Final temperature | 300°C, 5 min | Autosampler | No |
| Detector | MS | Liner type | 4 mm ID Single taper liner |
| Carrier gas | He, 31.6 psi | Full scan/SIM | Full scan 40-500 |
| Carrier gas flow | 1.7 mL/min | | |




**Components**

1. 2,4,5,6-Tetrachlorometa-xylene (Surrogate)
2. alpha – BHC
3. gamma – BHC
4. beta – BHC
5. delta – BHC
6. Heptachlor
7. Aldrin
8. Heptachlorepoxy
9. gamma-Chlordane
10. alpha-Chlordane
11. Endosulfan A
12. p, p' – DDE
13. Dieldrin
14. Endrin
15. p, p' – DDD
16. Endosulfan B
17. Endrin aldehyde
18. p, p' - DDT
19. Endosulfan Sulfate
20. Methoxychlor
21. Endrin ketone
22. Decachlorobiphenyl (Surrogate)

*Figure 3. SolGel-1ms column*

## BPX35

### 35% phenyl (equiv) polysilphenylene-siloxane

Figure 3 shows the 8081 USEPA pesticide mix analyzed on a BPX35 column. Note the excellent peak shape, separation and the high degree of inertness with respect to DDT and Methoxychlor components. Also note the different order of elution of the components. BPX35 has two differences in the order of elution making it a perfect confirmation column for BPX5. It also has a very low bleed profile at 300°C.

| BPX35 replaces | |
|---|---|
| DB-35 | HP-35MS |
| DB-35MS | SPB-35 |
| Rtx-35ms | MDN-35 |
| HP-35 | AT-35 |

### Conditions

| Column part number | 054701 | | |
|---|---|---|---|
| Phase | BPX35 | Average linear velocity | 36 cm/sec at 40°C |
| Column | 30 m x 0.25 mm x 0.25 µm | Injection mode | Splitless |
| Initial temperature | 40°C, 1 min | Purge on time | 1 min |
| Rate 1 | 30°C/min to 190°C, 3 min | Purge on (split) vent | 60 mL/min |
| Rate 2 | 10°C/min to 300°C, 5 min | Injection volume | 1 µL |
| Detector | MS | Injection temperature | 250°C |
| Carrier gas | He at 10.0 psi | Autosampler | No |
| Carrier gas flow | 1.3 mL/min | Liner type | 4 mm ID Double taper liner |
| Constant flow | On | | |

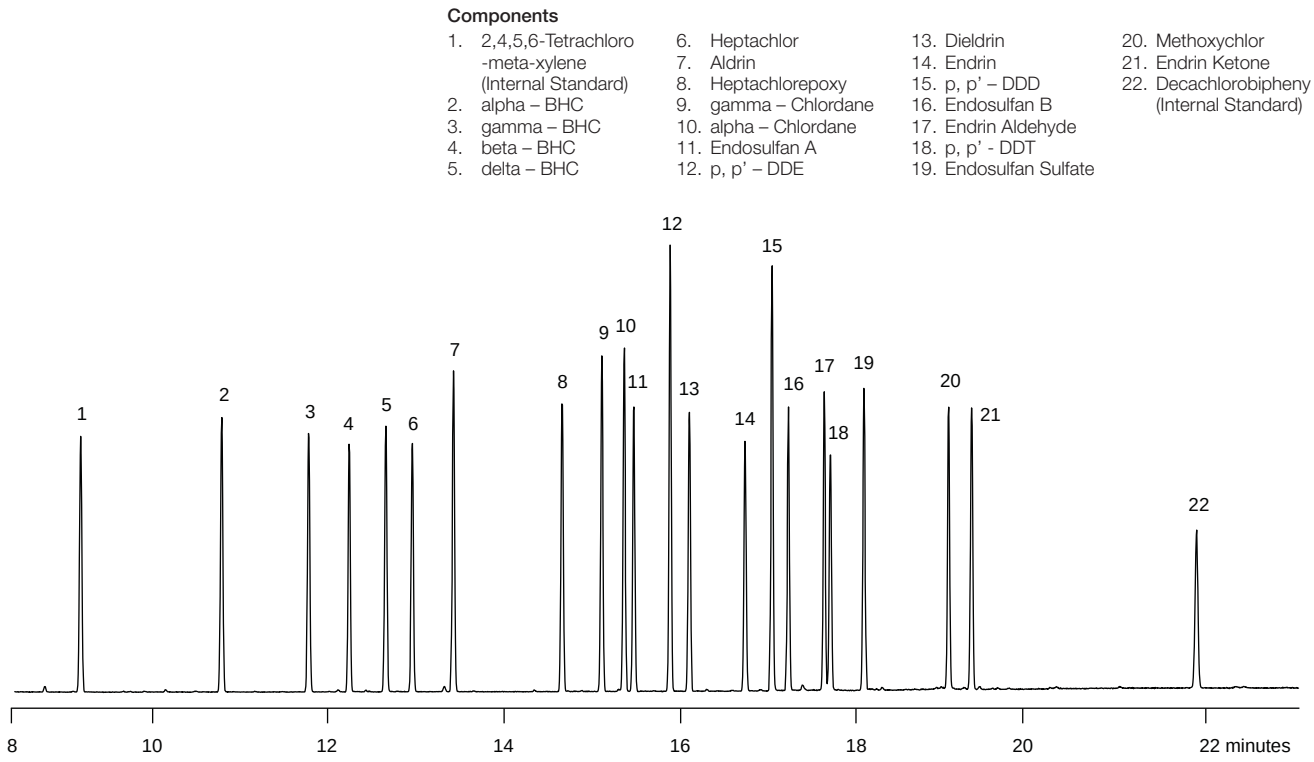



*Figure 3. USEPA 8081 organochlorine pesticide*

## BPX50

### 50% phenyl (equiv) polysilphenylene-siloxane

In Figure 4, the USEPA 8081 pesticide mix is analyzed on a BPX50 column. Note the excellent bleed profile at 300°C and separation of the components in less than 22 minutes allowing multiple samples to be run in the laboratory. Again BPX50, like BPX5, SolGel-1ms and BPX35, shows superior inertness with no on-column breakdown of the susceptible DDT and Methoxychlor.

| BPX50 replaces | |
|---|---|
| OV-17 | Rtx-50 |
| SP-2250 | SPB-50 |
| DB-17 | HP-50+ |
| DB-17MS | AT-50 |
| DB-17ht | 007-17 |

### Conditions

| Column part number | 054751 | | |
|---|---|---|---|
| Phase | BPX50 | Column flow | 1.3 mL/min |
| Column | 30 m x 0.25 mm x 0.25 µm | Pressure | 14.1 psi |
| Initial temperature | 40°C, 1 min | Injection mode | Splitless |
| Rate 1 | 30°C/min to 190°C, 3 min | Purge on time | 0.5 min |
| Rate 2 | 10°C/min to 300°C, 5 min | Purge on (split) vent | 60 mL/min |
| Detector | FID, 310°C | Injection volume | 1 µL |
| Carrier gas | He | Injector temperature | 240°C |
| Constant flow | On | Liner type | Single taper |
| Average linear velocity | 30 cm/sec at 40°C | | |

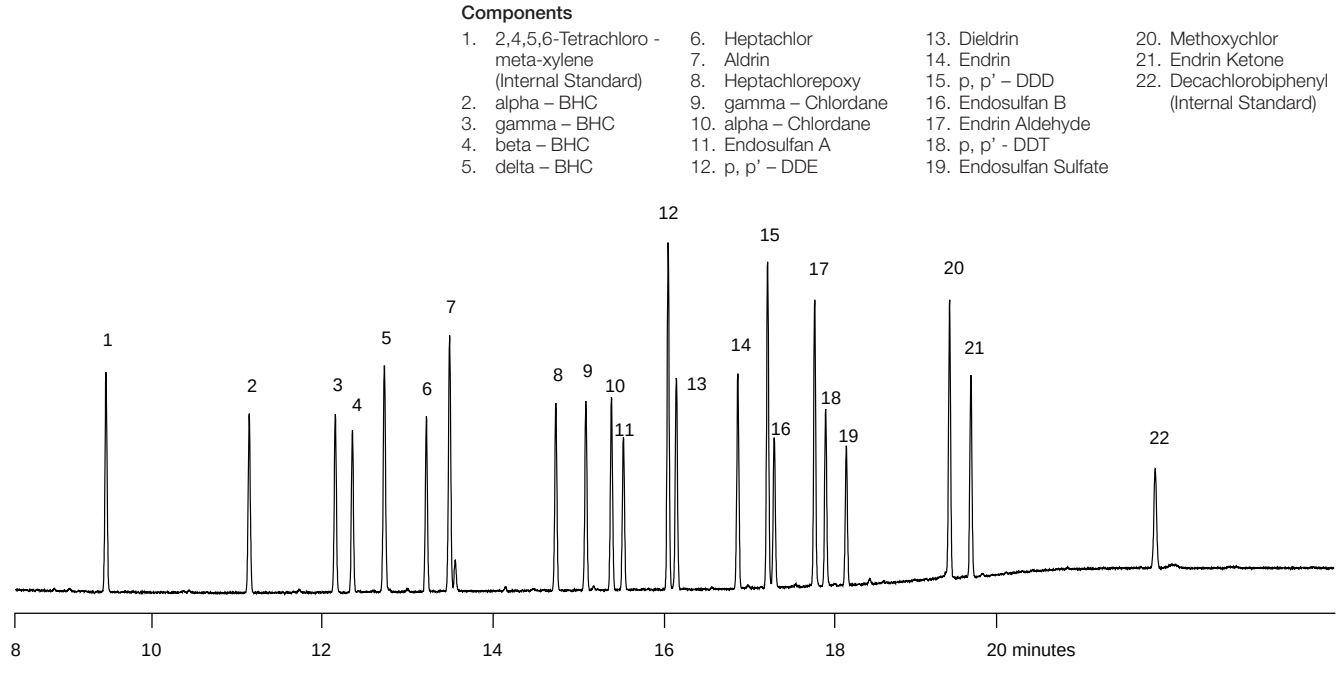



*Figure 4. USEPA 8081 organochlorine pesticide*

## The chromatography

The BPX5, SolGel-1ms, BPX35 and BPX50 phases show excellent inertness and do not have problems such as on column breakdown of methoxychlor and DDT. Indeed these four columns are exceptional for the analysis of the 22 chlorinated pesticides in the USEPA methods 8081 and 608. With at least two changes in the elution order of each column to that of BPX5, SolGel-1ms, BPX35 and BPX50 columns are excellent confirmation columns for this type of analysis.

## Information and support

Visit www.trajanscimed.com or contact techsupport@trajanscimed.com

*Specifications are subject to change without notice.*