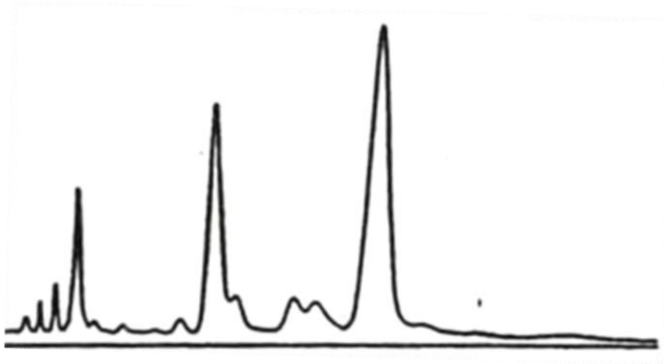
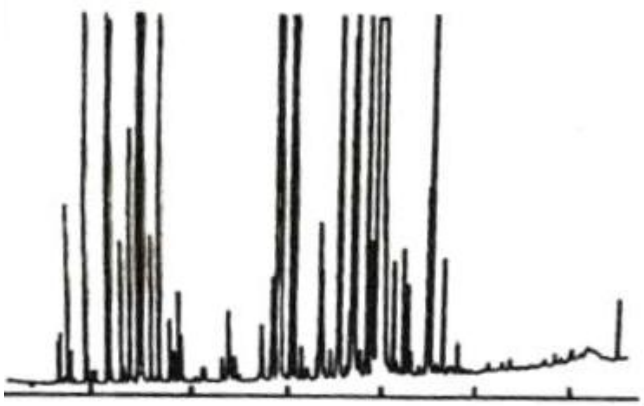
COLUMNS IN GAS CHROMATOGRAPHY

Packed column



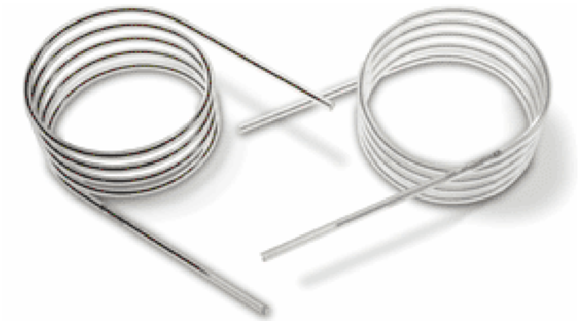
Capillary column



Separation of mint essential oil: Carbowax 20M

W. Jennings, J. Chromatogr. Sci. 17, 637 (1979)

PACKED COLUMNS



$$h_{min} = A + B / u + C\,u$$

LENGTH: **0.6 - 10 m**

INNER DIAMETER: **2.0-5.0 mm**

MATERIALS: **glass, steel, copper, nickel**

STATIONARY PHASE:

a) A<u>D</u>SORBENTS

b) A<u>B</u>SORBENTS

- inert support (Chromosorb, Carbopack, Tenax, Porapak, …)
- polymeric liquid phase (% stationary phase on support)

CAPILLARY COLUMNS

M.J.E. GOLAY

LENGTH: **5 - 150 m**

INNER DIAMETER: **0.1 – 0.75mm**

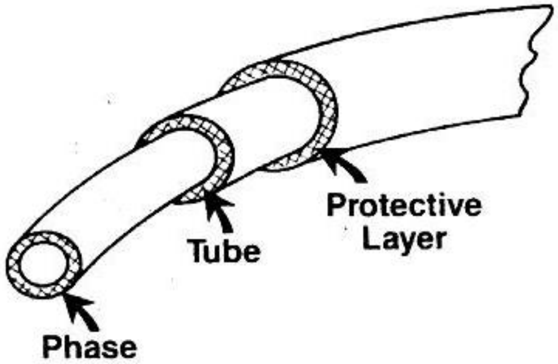
$$h_{min} = B / u + C u$$

FILM THICKNESS OF STATIONARY PHASE: **0.1 – 7μm**

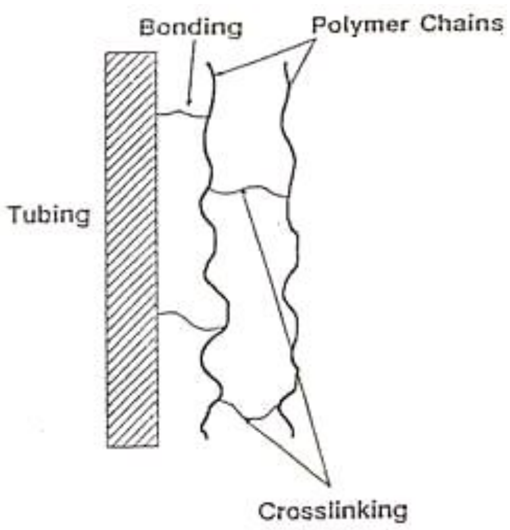
MATERIALS:

Metal: thermostability, strong interactions with analytes
Silica coated with aluminium: thermostability,
poor adhesion, thermal expansion
Silica coated with polyimide: **max. temp up to 400°C,**
protecting against moisture and chemicals

CAPILLARY COLUMNS - types



WCOT — PLOT — SCOT



WCOT (Wall-Coated Open Tubular column)
- liquid polymer on inner wall of capillary

SCOT (Support-Coated Open Tubular column)
- liquid polymer embedded on support attached to inner wall of capillary

PLOT (Porous-Layer Open Tubular column)
- adsorbent attached on capillary by chemical bond (Al_2O_3), sep. mech.: *adsorption, gas-solid,* ↑ *retention*

CAPILLARY COLUMNS - parameters

1) TEMPERATURE RANGE

Phase stability: degradation = higher noise = lower sensitivity, less lifetime $\Rightarrow$ *bonded cross-linked phases*

Stability of base material – polyimide 360 – 400°C

Temperature column limit:

- low: column losses its chromatographic abilities (not separating)
- high: *isothermal* – unlimited time
programmed – limited to 10 – 15 min

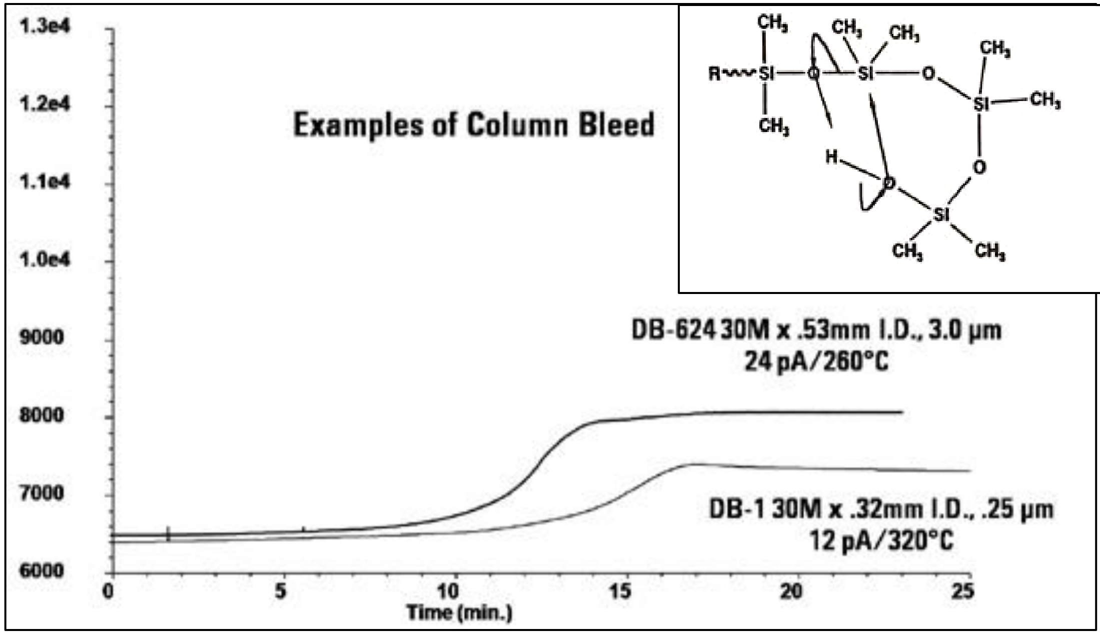
Overheating = damage of st.ph., loss of efficiency and retention

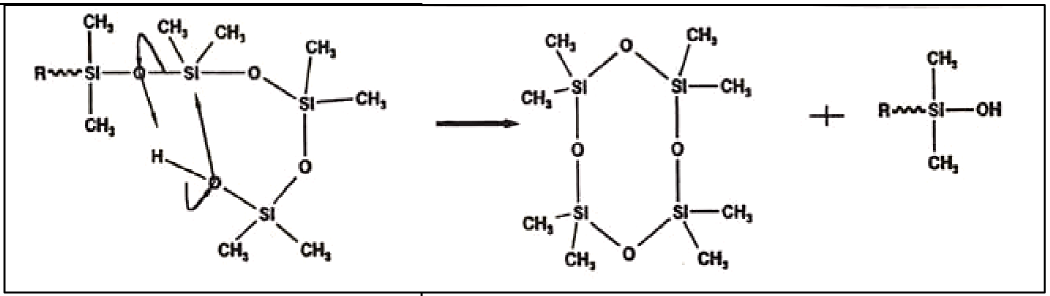
CAPILLARY COLUMNS - parameters

Column bleeding:

Degradation of polymer chains in the Si-O bond
- formation of volatile fragments.

- increasing with temperature, oxygen content
- various sensitivity of detectors (NPD – cyanopropyl, not problem for FID)





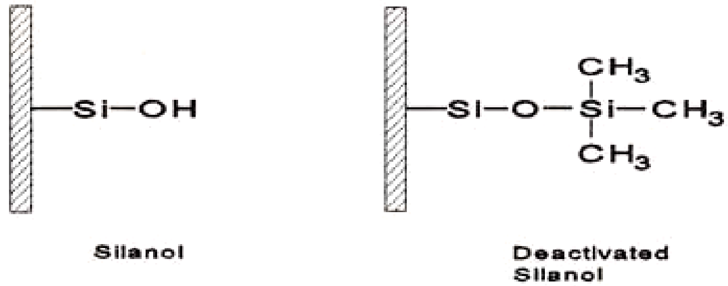
CAPILLARY COLUMNS - parameters

2) ACTIVITY / INERTNESS COLUMNS

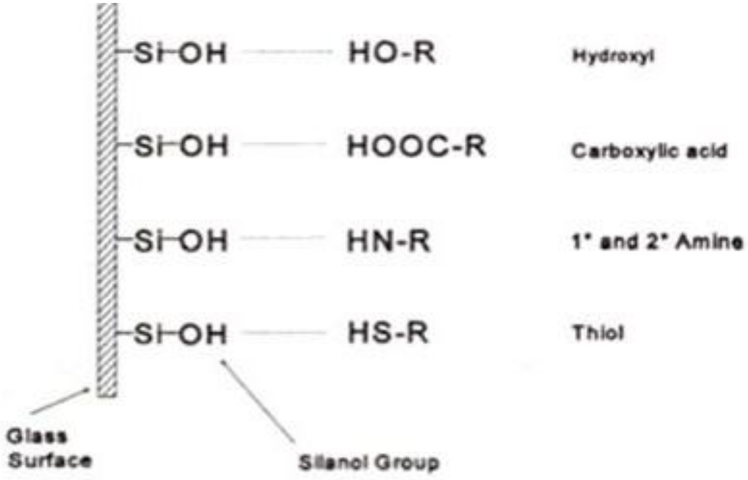
affecting peak symmetry = wider peaks

peak tailing = lower sensitivity

Deactivation of base material:



Interactions of silanols:

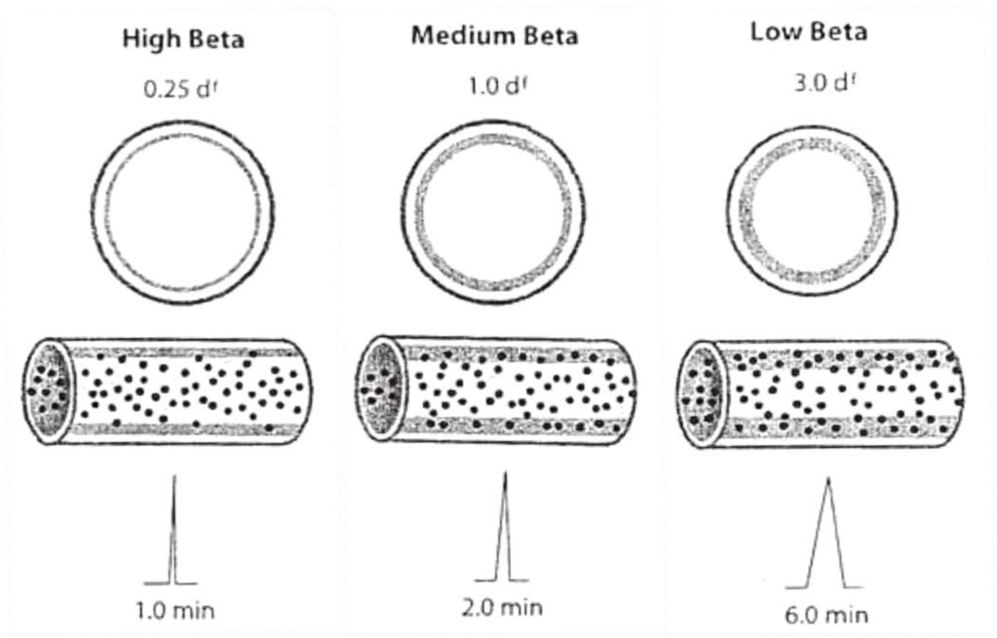


CAPILLARY COLUMNS - parameters

3) COLUMN CAPACITY

affecting peak symmetry = wider peaks

peak tailing = lower sensitivity



↑ solubility in st.ph.
⇒ ↑ capacity

↑ i.d., d_f
⇒ ↑ capacity

CAPILLARY COLUMNS - parameters

4) STATIONARY PHASE - POLARITY

given by an amount and polarity of each functional group
like dissolves like (higher capacity)

Nonpolar phase: separation based on vapour pressure (volatility)
- greater temperature range
- higher resistance, lower bleed

Polar phase: separation is affected by specific interaction

Medium polar phase: separation efficiency changing with temperature

↓ *temperature* ⇒ *as a nonpolar phase*

↑ *temperature* ⇒ *as a polar phase*

CAPILLARY COLUMNS - parameters

5) STATIONARY PHASE – interaction analyte / stationary ph.

DISPERSIVE INTERACTIONS:

- *universal, primary separation mechanism of all compounds*
- *intermolecular attraction: analyte / stationary phase (polarizability)*
- *compounds with lower vapour pressure – stronger retention*

DIPOLE INTERACTIONS: cyanopropyl, PEG

- *stationary phase and analytes with dipole moment* (*unevenly distributed charge: heteroatom, halogen, -OH, = bond, esters, ...*)

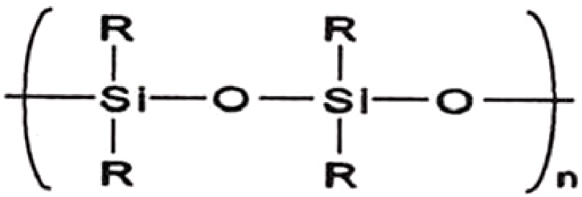
INTERACTIONS WITH HYDROGEN BOND: cyanopropyl, PEG

- *strong bond:* -OH, -NH group
- *weak bond: esters, ethers, ketones*
- *none bond: hydrocarbons, halogens*

CAPILLARY COLUMNS - parameters

6a) STATIONARY PHASE – types

POLYSILOXANES (SILICONES):

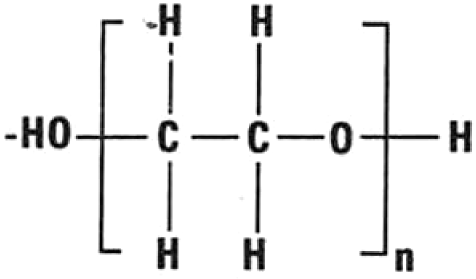


- very resistant, various functional groups

  5% phenyl methyl polysiloxane (= 95% methyl)

  approx. 1% of silicone backbone carries a vinyl group for cross-linking

POLYETHYLENE GLYCOLS:

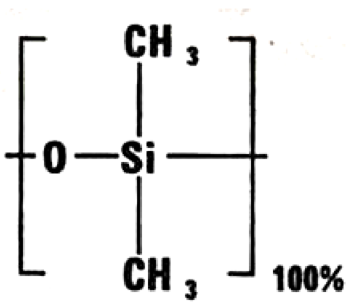


- extremely sensitive to oxygen
- lower temperature applicability

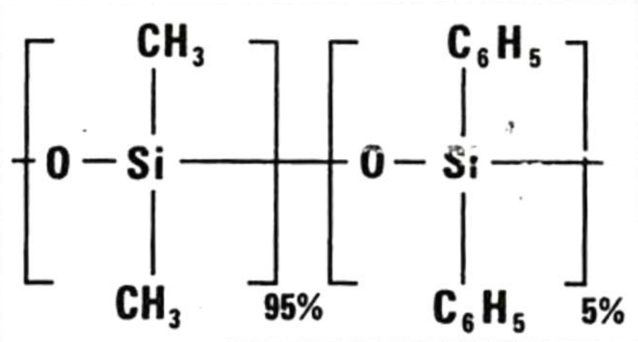
CAPILLARY COLUMNS - parameters

6b) STATIONARY PHASE – types

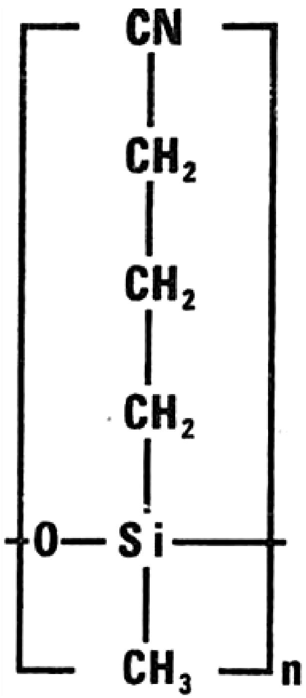
POLYSILOXANES (SILICONES):



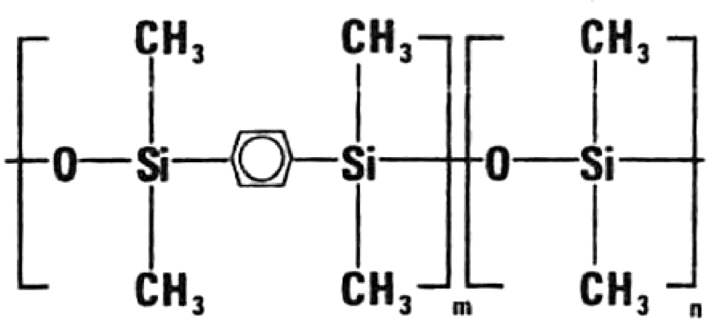
Dimethylpolysiloxane



Diphenyldimethylpolysiloxane

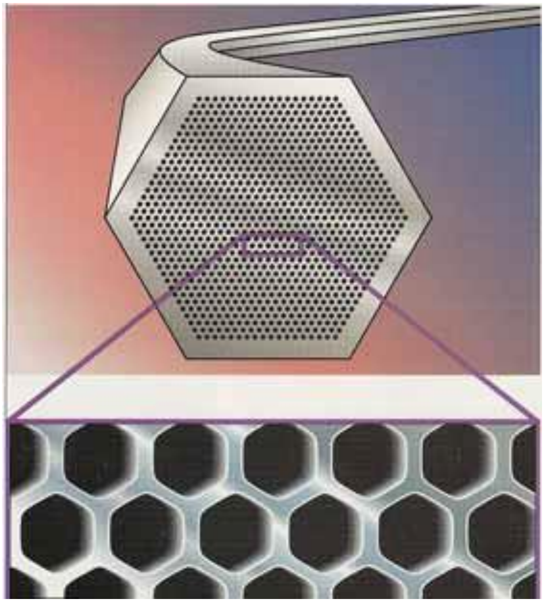


Cyanopropylmethylpolysiloxane



Poly(dimethylsiloxy)poly(1,4-bis(dimethylsiloxy)phenylenesiloxane

MULTI-CAPILLARY COLUMNS



Alltech Bulletin 328, (1995)

919 capillaries in a glass column - **1 m**

1 capillary: i.d. **40 µm**, d_f= **0,2 µm (SE-30, SE-54, Carbowax-20M, …)**

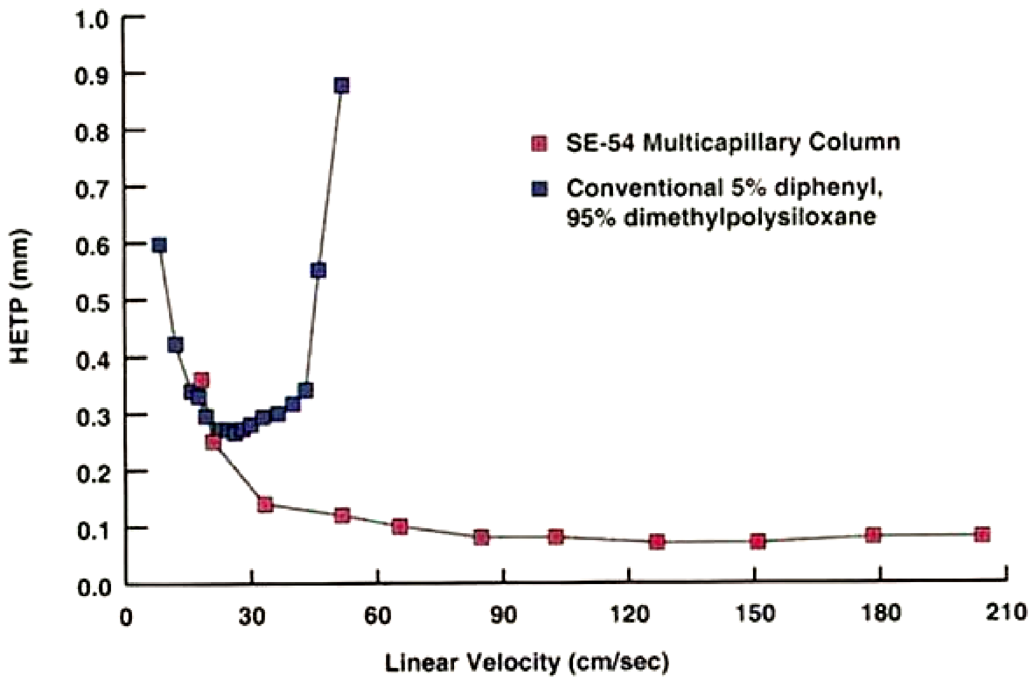
To maintain the same length and geometry the capillaries are twisted; at both ends is deactivated standard capillary tube (0.53 mm)

MULTI-CAPILLARY COLUMNS - properties

Operating temperatures: 20 – 200°C
Flow rates: 20 – 210 mL/min

FAST ANALYSIS without loss of efficiency in wide range of flow rates

van Deemter curves



MULTI-CAPILLARY COLUMNS - properties

Efficiency

COLUMN	n for 1 m	n for entire column
Packed	1316	2632
Multicapillary	13664	13664
Capillary	3774	113220

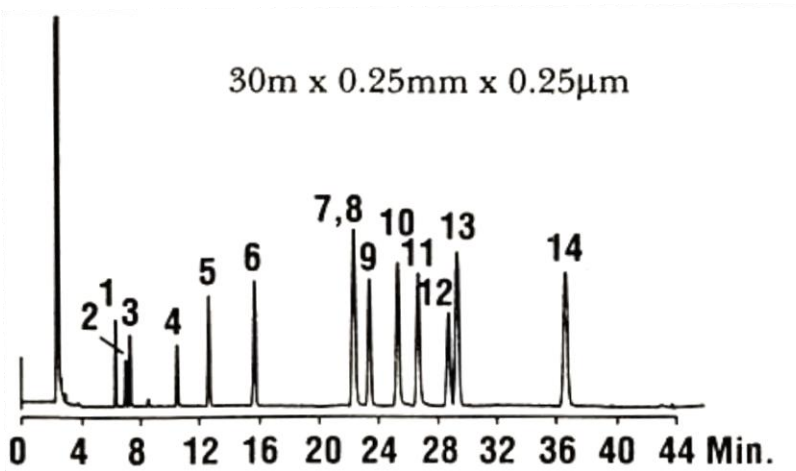
Capacity: capillary < multicapillary < packed column

Resolution: capillary > multicapillary > packed column

APPLICATION:
replacement of packed columns for very rapid screening

MULTI-CAPILLARY COLUMNS - applications

Common capillary



1. α-BHC
2. Lindane
3. β-BHC
4. Heptachlor
5. Aldrin
6. Heptachlor epoxide
7. p,p'-DDE
8. Dieldrin
9. o,p'-DDD
10. Endrin
11. o,p'-DDT
12. p,p'-DDD
13. β-Endosulfan
14. p,p-DDT

Multi-capillary