TYPES OF COLUMNS AND STATIONARY PHASES IN GAS CHROMATOGRAPHY

Packed columns - ***historically the first columns***

- glass, metallic, with metallic surface
- easier production, high robustness
- lower efficiency – peak capacity, higher LODs
- not suitable for temperature and pressure programming

Capillary columns - ***newer types created thanks to the production of polymers***

- made of fused silica coated with polyimide
- more demanding production, less robustness
- high efficiency – peak capacity, lower LODs
- suitable for temperature and pressure programming

Packed columns

Typical dimensions

Length: 0.6 - 10 m

Inner diameter: 2 - 5 mm

Material: glass, steel, copper, nickel

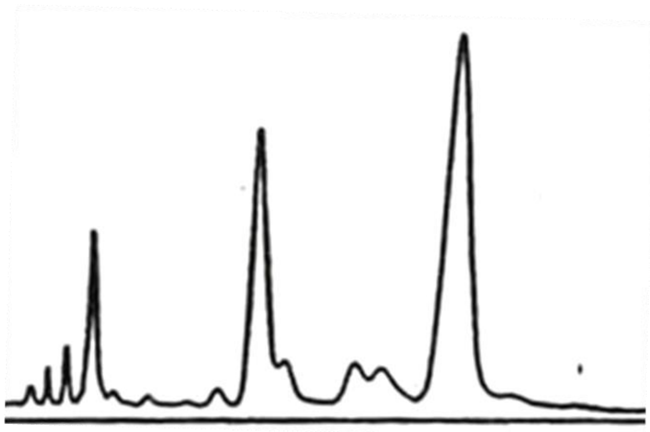
Stationary phases (SP):

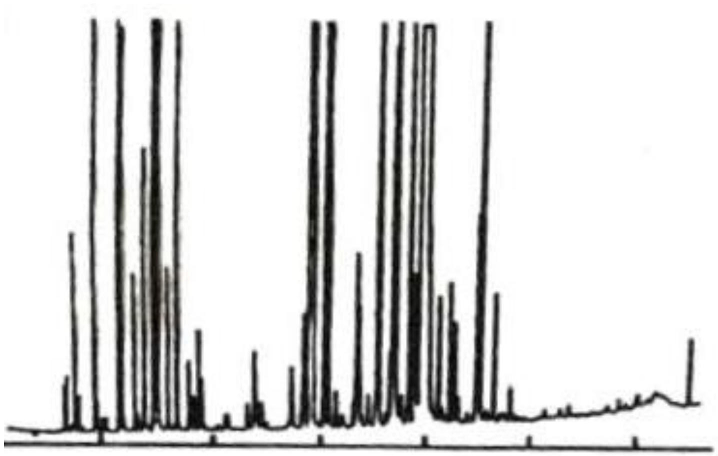
- ADSORBENT – direct interaction
- ABSORBENT on support
  - inert support (Chromosorb, Carbopack, Tenax, Porapak etc.)
  - polymeric liquid phase (def. % SP coated on support)

* typical SP: modif. polysiloxanes, polyethylene glycols

Transition from packed columns to capillaries

packed column $\Rightarrow\Rightarrow$ capillary column





Separation of peppermint essential oil - Carbowax 20M

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

Capillary columns

Typical dimensions

Length: **5 - 150 m**

Inner diameter: **0.1 – 0.75 mm**

SP film thockness: **0.1 - 7 μm**

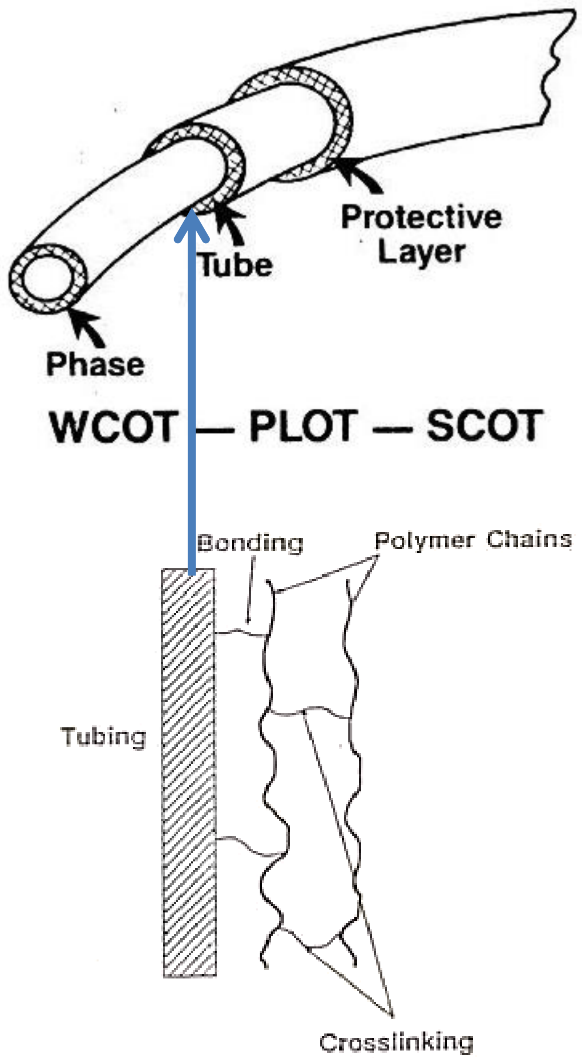
Material:

metal: thermal stability, strong interactions with analytes

silica coated by aluminum: thermal stability, poor adhesion, thermal expansion

silica coated by polyimide: max. temperature up to 400 °C, polyimide - flexible, protects against moisture

Types of capillary columns



WCOT (Wall-Coated Open Tubular) **column**
- liquid polymer coated (chemically bonded) 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 to inner wall of capillary by chemical bond (Al_2O_3)

sep. mech.: *adsorption, gas-solid ch.,*

↑ *retention*

Parameters of capillary columns I

1) Applicable temperature range

SP stability – (gradual) SP degradation = higher noise = higher LOD and shorter lifetime
⇒ application of bonded cross-linked SP

Stability of building material – polyimide max. 360 - 400 ° C

Temperature limits:
low: column losses its chromatographic abilities (not separating)
high: *a) isothermal* – unlimited time
b) programmed – limited e.g. to 10 – 15 min

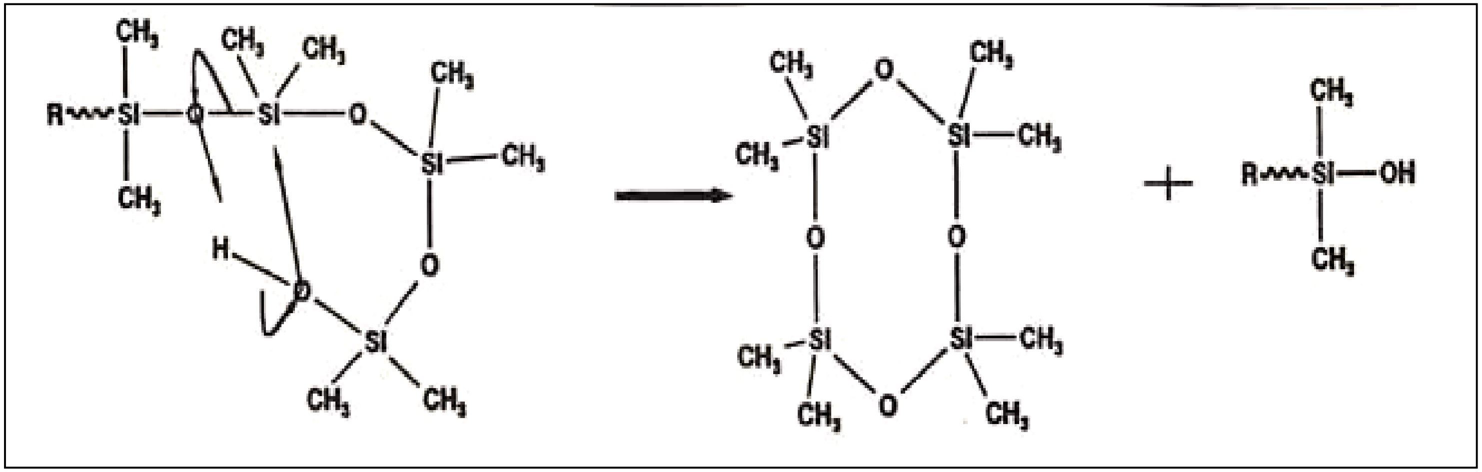
Large single or repeated slight exceedances
⇒ SP degradation, loss of efficacy and retention

Parameters of capillary columns II

Evaluation of stability and degree of SP degradation

- we monitor the so-called column bleed or bleeding of column, which is due to the degradation of SP to volatile fragments that are released from the column

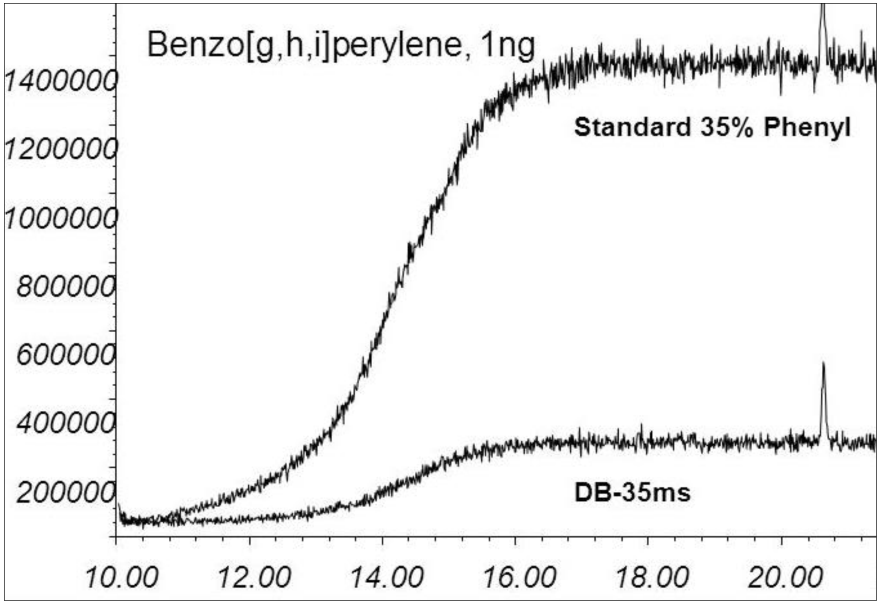
For polydimethylsiloxane phases are typically formed tri- and tetra- cyclo- dimethyl-siloxanes (*m/z = 207 a 281*)



Parameters of capillary columns III

Evaluation of stability and degree of SP degradation

Column bleed (-ing) is typically manifested by increased baseline of GC/MS chromatogram



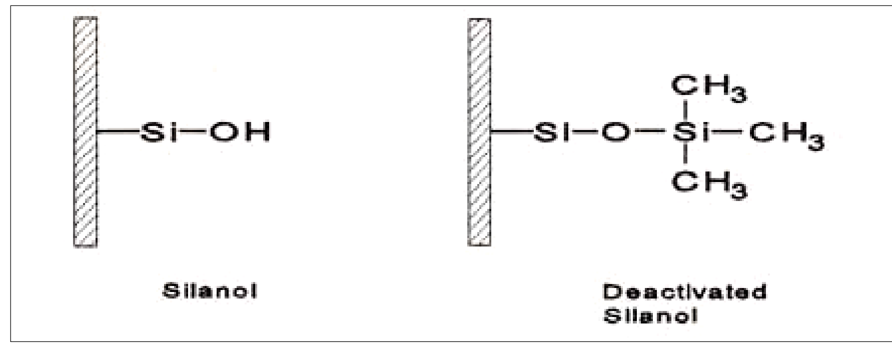
Column bleed (-ing) increases with temperature and oxygen content - detectors are differently sensitive to this phenomenon (NPD x cyanopropyl, does not matter for FID, problematic for MS)

Parameters of capillary columns IV

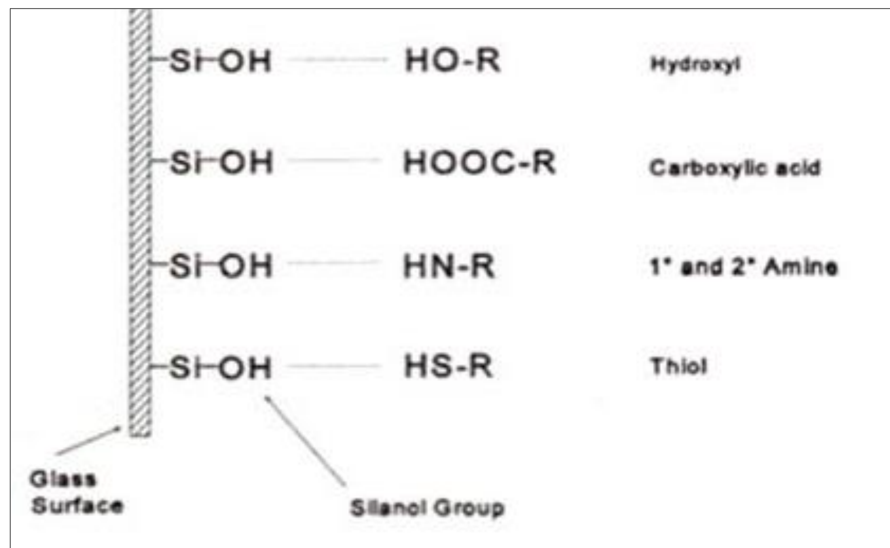
2) ACTIVITY / INERTNESS

Effect on symmetry and peak width - wider (distorted) peaks ⇒ higher LOD

Deactivation of building material (fused silica walls)



Different interactions of silanols



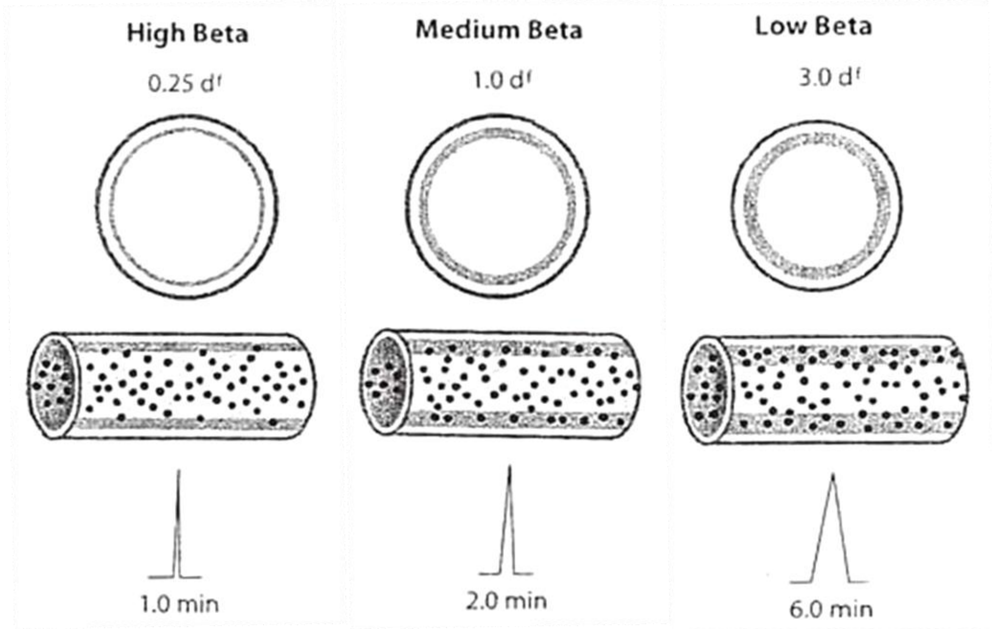
Parameters of capillary columns V

3) COLUMN CAPACITY

Effect on symmetry and peak width

- wider (distorted) peaks ⇒ higher LOD

$\uparrow$ solubility in SP, i.d., d_f $\Rightarrow \uparrow$ capacity



Parameters of capillary columns VI

4) SP POLARITY

Given by the amount and polarity of each functional group (similar dissolves similar ⇔ capacity range)

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

MEDIUM POLAR: **separation efficiency changing with temp.**
↓ temperature⇒ as a nonpolar phase
↑ temperature ⇒ as a polar phase

POLAR: **separation is based on by specific interactions**

Parameters of capillary columns VII

5) TYPES OF INTERACTIONS SP - ANALYTES

DISPERSION 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)

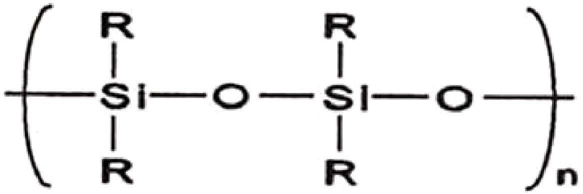
- **stationary phase and analytes with dipole moment (unevenly distributed charge: heteroatom, halogen, -OH, = bond, esters etc.)**

INTERACTIONS WITH HYDROGEN BOND (cyanopropyl, PEG)

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

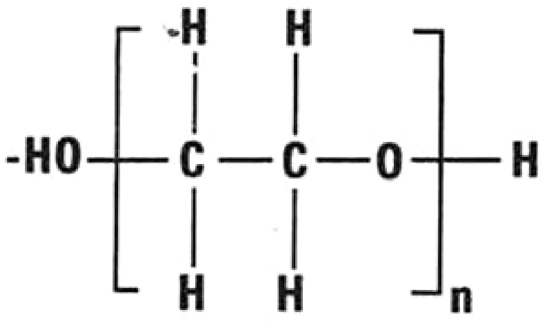
6) SF Chemical structures - I

POLYSILOXANES (SILICONES):



- very resistant, various functional groups
- *e.g. 5% phenyl methyl polysiloxane (R= 5% of phenyl and 95% of methyl)*
- approx. 1% of silicone backbone carries a vinyl group for cross-linking

POLYETHYLENE GLYCOLS:

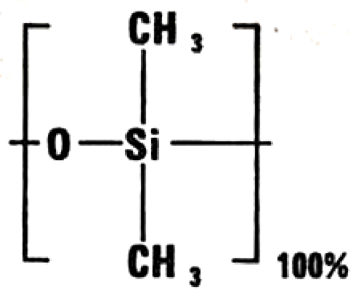


- extremely sensitive to oxygen
- lower temperature applicability

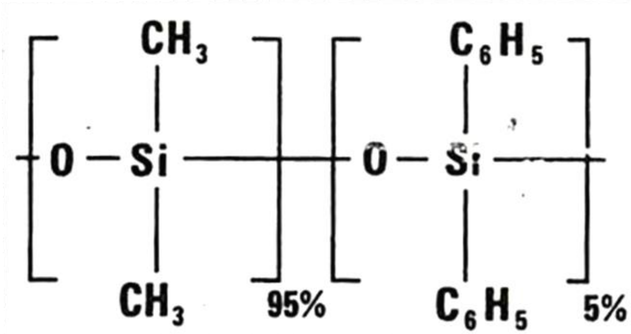
Parameters of capillary columns IX

6) SF CHEMICAL STRUCTURES - II

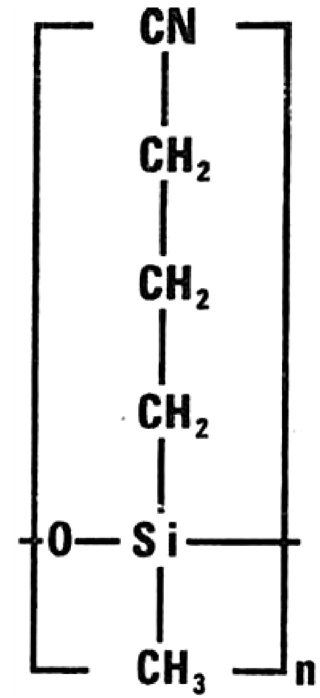
POLYSILOXANES (SILICONES):



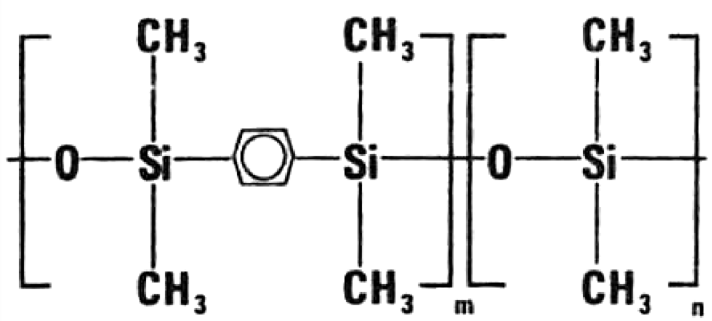
Polydimethylsiloxane



Polydiphenyldimethylsiloxane

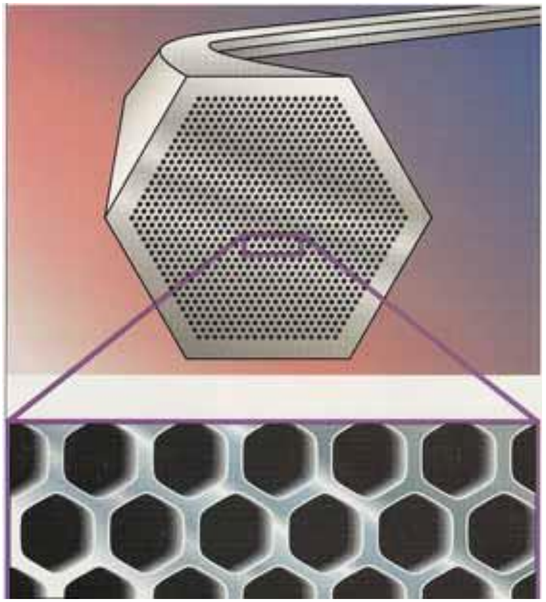


Polykyanopropylmethylsiloxane



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

MULTI-CAPILLARY COLUMNS I



Alltech Bulletin 328, (1995)

919 capillaries in a glass column - 1 m
1 capillary: i.d. 40 μm, df = 0,2 μm (SE-30, SE-54, Carbowax-20M etc.)

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

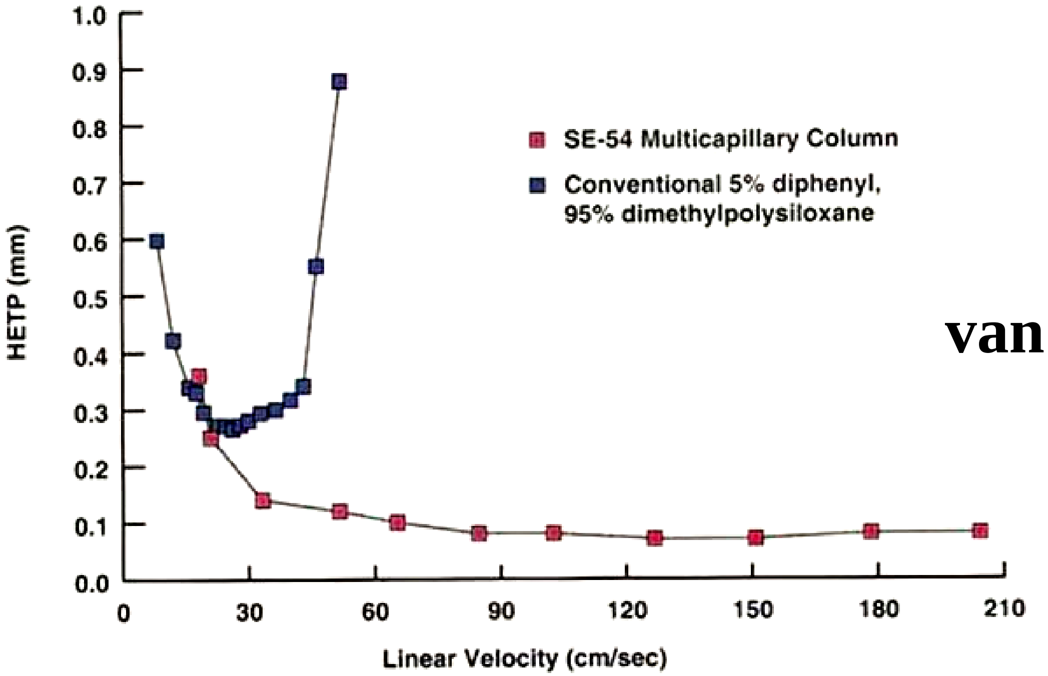
MULTI-CAPILLARY COLUMNS II

Operating temperatures: 20 – 200 °C

Flow rates: 20 – 210 ml/min

FAST ANALYSES - without loss of efficiency

in wide range of flow rates



van Deemter curves

MULTI-CAPILLARY COLUMNS III

Efficiency

COLUMN	**n for 1 m**	**n for entire column**
Packed	1316	2632 (2 m)
Multicapillary	13664	13664 (1 m)
Capillary	3774	113220 (30 m)

Capacity: capillary <multicapillary <packed column

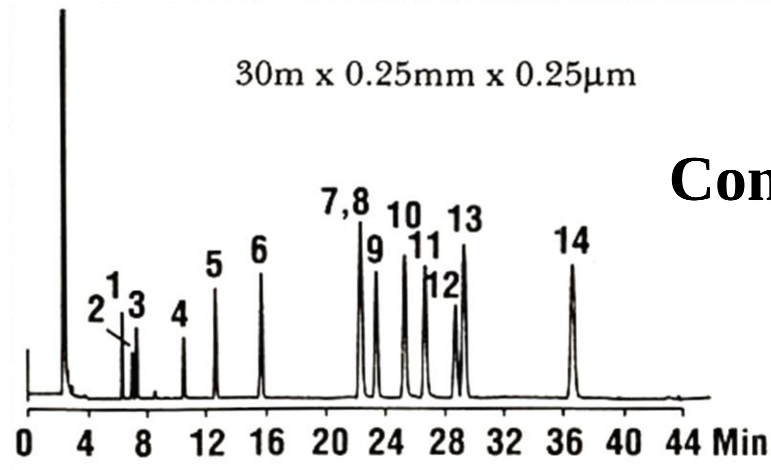
Resolution: capillary >multicapillary >packed column

APPLICATION:

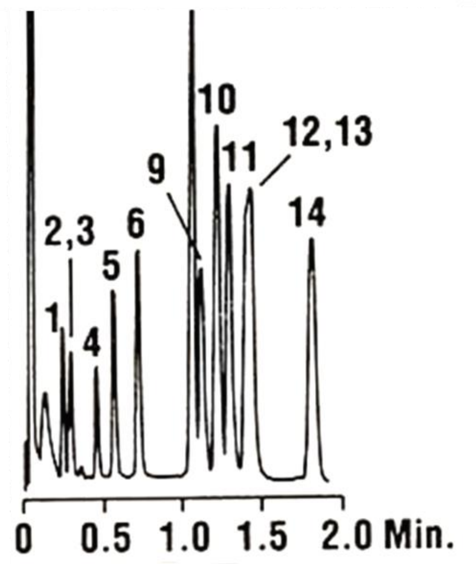
replacement of packed columns for very rapid screening
Available for analytes with boiling point temp. higher than pentane with d_f 0.2 μm only.

MULTI-CAPILLARY COLUMNS IV

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



Common capillary



Multi-capillary