BAB 7

Kromatografi Gas

Tipe Kromatografi Gas

Ada tiga tipe kromatografi gas, berdasarkan jenis fasa diamnya:

1. Gas-Cair
   - Fasa diam cair yang teradsorb pada permukaan padat
   - Merupakan tipe yang umum
2. Gas-padat
   - Fasa diam: berupa zat padat.
3. Gas- Fasa Terikat
   - Fasa diam adalah suatu material organik yang terikat dengan suatu permukaan padat

Prinsip Kerja

- Sample (solute) dilarutkan dalam suatu pelarut
- Sample and solvent diuapkan
- Uap solvent dan solute dibawa melewati kolom oleh suatu gas yang inert (fasa gerak)
  - Note: fasa gerak tidak boleh berinteraksi dengan komponen yang akan dipisahkan

Prinsip Kerja

- Pelarut juga melewati kolom,
- Pemisahan terjadi karena ada interaksi antara solut dengan fasa diam
- Sample terdeteksi oleh detektor.

  (e.g. thermal conductivity, flame ionization, thermionic or electron capture detectors)

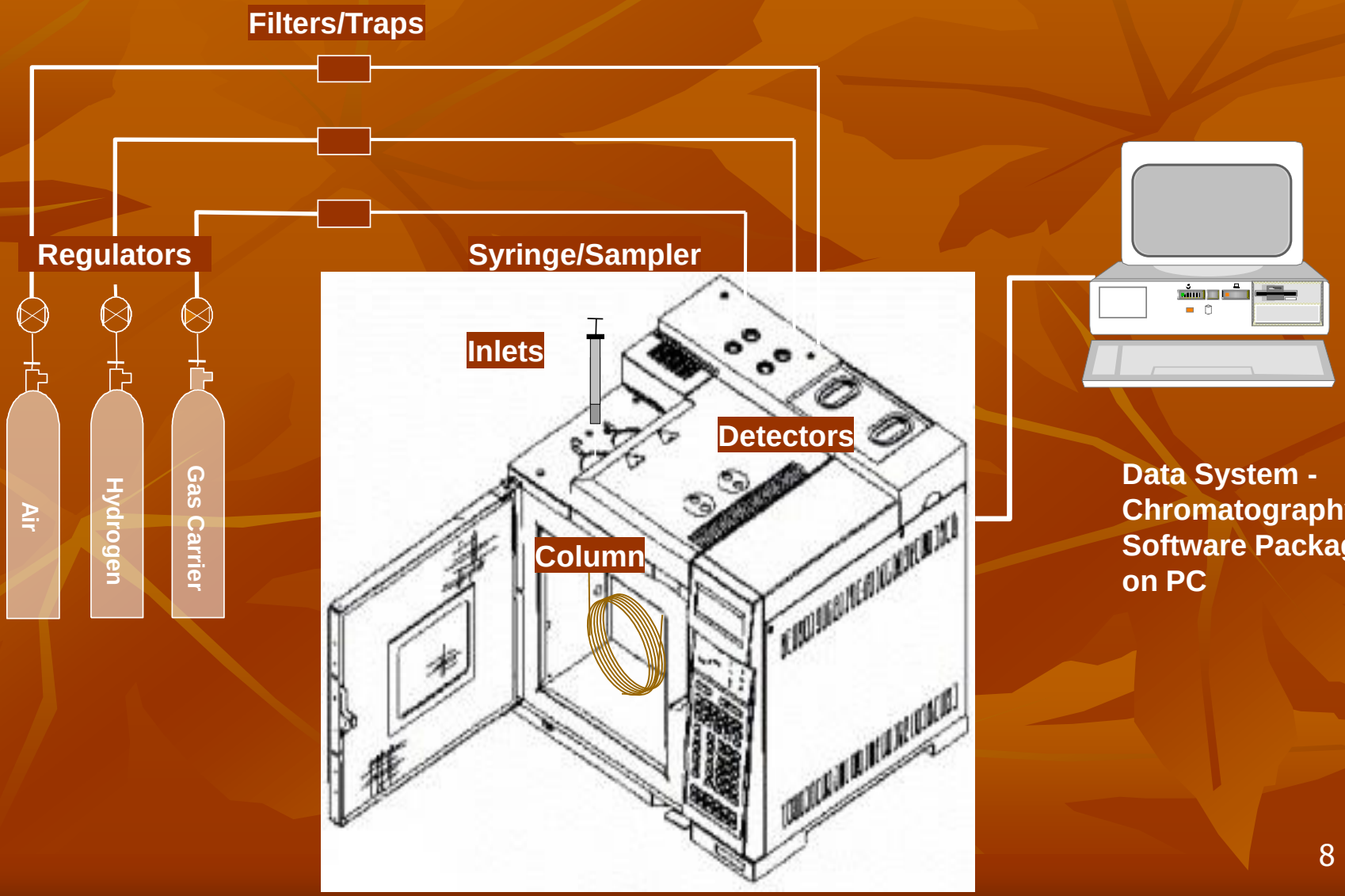
Komponen Dasar

1. Gas Pembawa (fasa gerak)
   - He, Ar, N_2 and H_2
2. Sistem Injeksi Sampel
3. Kolom Kromatografi
   - Contains stationary phase
   - Many configurations

Komponen Dasar

4. Oven
   - Isothermal or temperature programmed
5. Detector
   - FID, TC, ECD, MS, etc.
6. Pencatat
   - Chromatography software (strip chart and integrator package)

Example GC System



Sample Injector

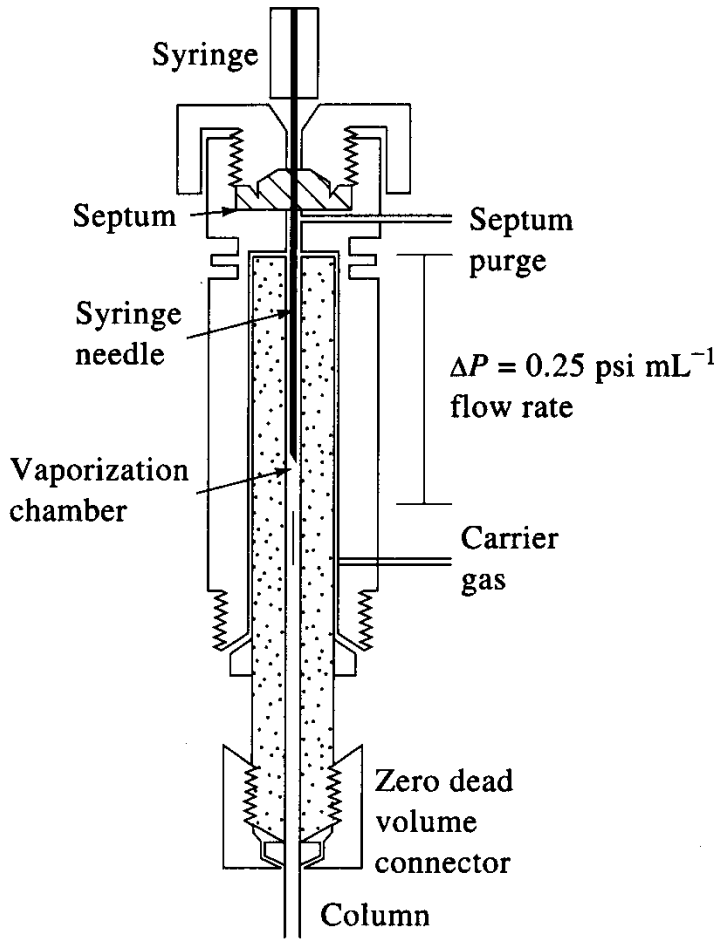


Figure 27-3 Cross-sectional view of a microflash vaporizer direct injector.

- Purpose: to introduce sample as "plug" at the head of the column
  - Effects band broadening
- Injector typically 50 °C hotter than oven
- Sample is "flash evaporated" and expands into gas expansion chamber
- Injection volumes are small
  - Capillary columns ~ 1 µL
  - Packed columns 1-20 µL

Detektor

- Sangat banyak jenis detektor, pemilihan detektor dapat didasarkan pada analit yang akan dipisahkan dan sensitifitasnya.
- Characteristics dari detektor yang ideal yaitu:
  - Sensitivity – wide range (~10^7)
  - Stabil
  - Mempunyai range suhu yang panjang (sampai 400 °C)
  - Merespon dalam waktu yang singkat
  - Tidak merusak sampel

Detektor Konduktivitas Termal

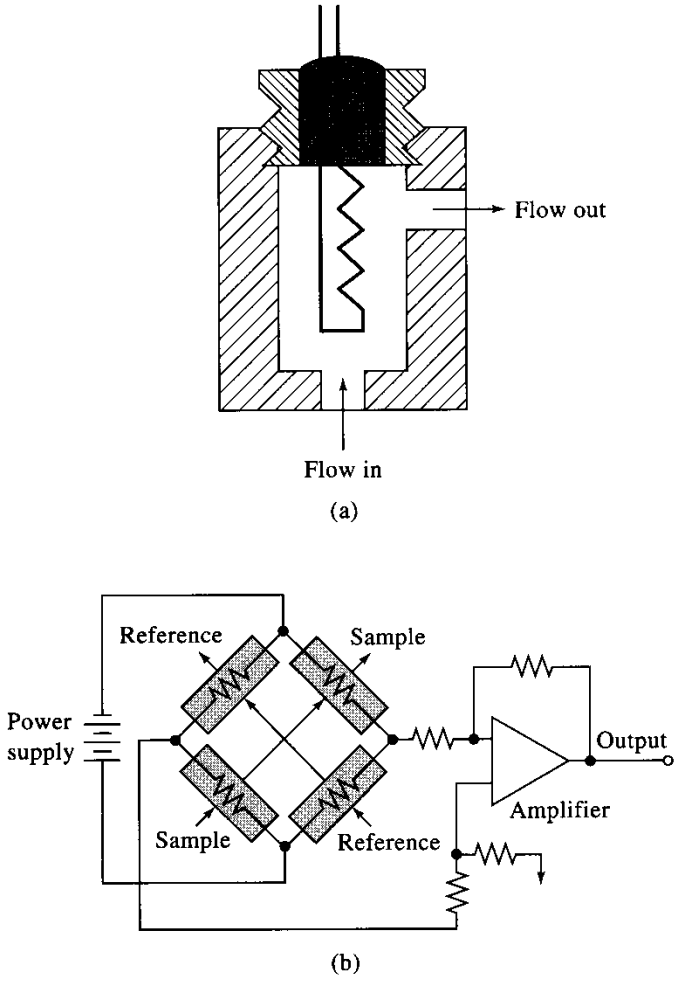
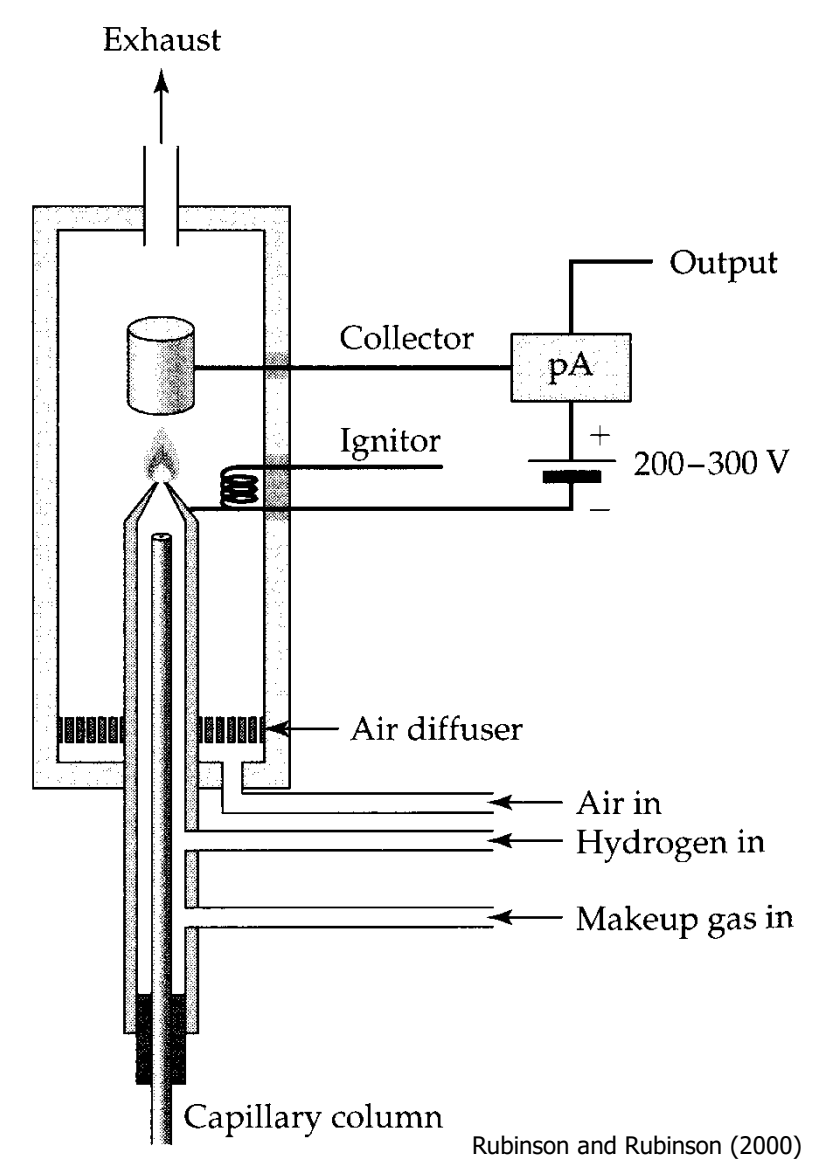


Figure 27-7 Schematic of (a) a thermal conductivity detector cell, and (b) an arrangement of two sample detector cells and two reference detector cells. *(From J. V. Hinshaw, LC-GC, 1990, 8, 298. With permission.)*

- Detection Principle: analyte gases have different thermal conductivities than carrier gases
- A platinum, gold or tungsten wire (or a thermister) is placed in the exit gas stream from the column
- A constant voltage is applied to heat the wire
- Temperature/Resistance of the wire is proportional to the thermal conductivity of the surrounding gas
- Double detector system: one detector in carrier gas and one in the carrier + analyte
  - Cancels out resistance due to carrier gas giving signal only for analyte

Detektor Ionisasi Nyala



Rubinson and Rubinson (2000)

- Organic analytes are pyrolyzed in an air/H_2 flame
- Ions are produced in the plasma around the flame
  - proportional to number of carbons present
- Positive voltage is applied to collector; negative to the flame body
- Ions migrate to collector producing a current (signal)

Detektor GC yang lain:

- Mass Spectrometer
  - GC-MS “hyphenated” system
  - Used for identification purposes
- Atomic Emission Detector
  - GC-AED
- Sulfur Chemiluminescence Detector (SCD)
- Fourier-Transform Infrared (FTIR)
  - Used with polar molecules

GC Columns

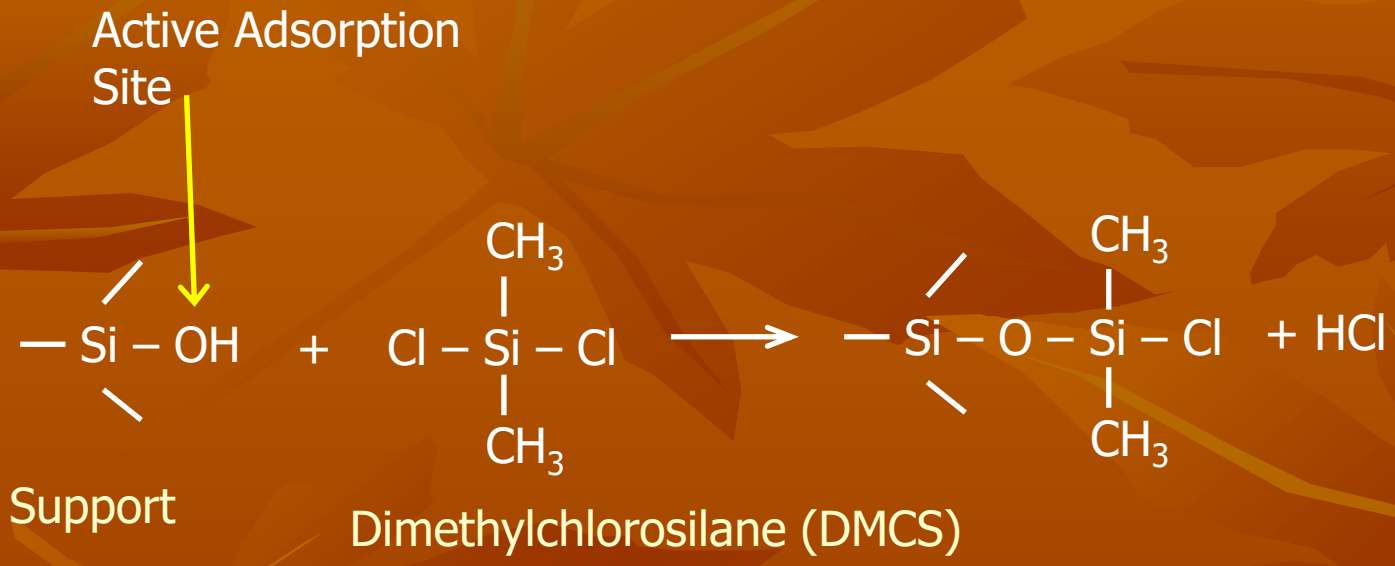
There are two basic types of GC columns

1. Packed Columns
   - Used in early gas-liquid chromatography
   - Typically made of glass, Teflon and aluminum
   - Length typically 2-3 m; ID ~3 mm
   - Filled with a material called a "solid support"; the material which holds the stationary phase
   - Solid supports have
     - Large surface areas (>1 m^2/g)
     - Good strength characteristics
     - Inert (w.r.t. the solutes)
     - Uniformly wetted
   - Most Common Solid Support Material – Diatomaceous Earth

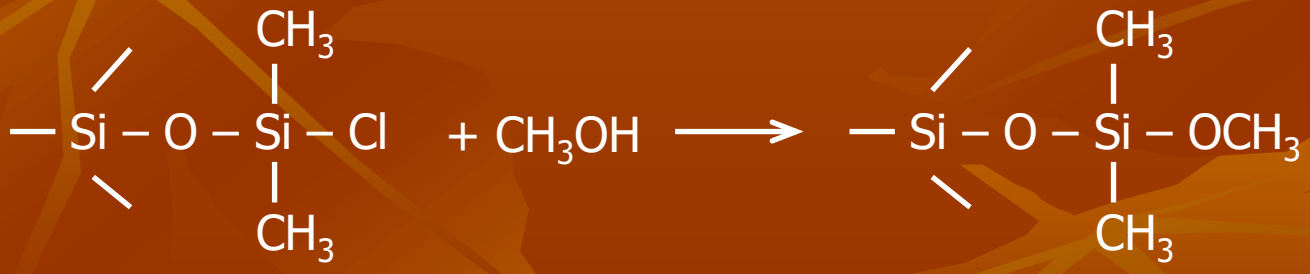
GC Columns

2. Open Tubular (or Capillary) Columns
   - Now made mostly of fused silica
     - Permits bending into coils for easy handling
   - Have small IDs (0.1-1 mm) and long lengths (15-100 m)
   - Uses same stationary phases as packed columns
   - Stationary phase is coated on the inside of the column
     - Wall-coated tubular (WCOT)
     - Support-coated tubular (SCOT)

Silanization of Solid Support Material



Silanization Reaction



Wash with methanol

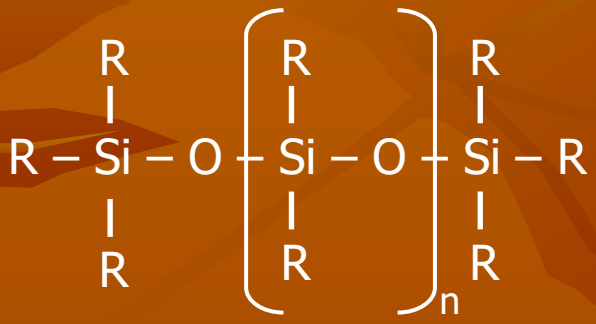
Fasa Diam pada GC

- Sifat:
  1. Low volatility
  2. Thermal Stability
  3. Chemical inertness
  4. Solvent characteristics that optimize *k'* and α
- Pemilihan fasa diam sering didasarkan karena polaritasnya
- solute dan fasa diamharus mempunyai polaritas yang sama "Like dissolves like"

Jenis-jenis Fasa Diam

Stationary Phase	Common Name	Polarity	Common Applications
Cycloparaffin	Squalane	Non-polar	Hydrocarbons
Polydimethyl siloxane	OV-1, SE-30	Non-polar	General purpose non-polar phase; hydrocarbons; polynuclear aromatics; drugs; steroids; PCB's
Poly(phenylmethyldimethyl) siloxane (10% phenyl)	OV-3, SE-52	Slightly Polar	Fatty acid methyl esters; alkaloids; drugs; halogenated compounds
Polyethylene glycol	Carbowax	Polar	Free acids; alcohols; ethers; essential oils; glycols
Poly(phenylmethyldimethyl) siloxane (50% phenyl)	OV-17	Moderately Polar	Drugs; steriods; pesticides; glycols

Struktur Fasa Diam



Polydimethyl siloxane

- Polydimethyl siloxane (all R = CH_4) is a common "backbone" for creating different stationary phases
- Replacing methyl groups with other groups changes its polarity and separation capabilities
  - Phenyl – C_6H_5
  - Cyanopropyl – C_3H_3CN
  - Trifluropropyl - $C_3H_6CF_3$

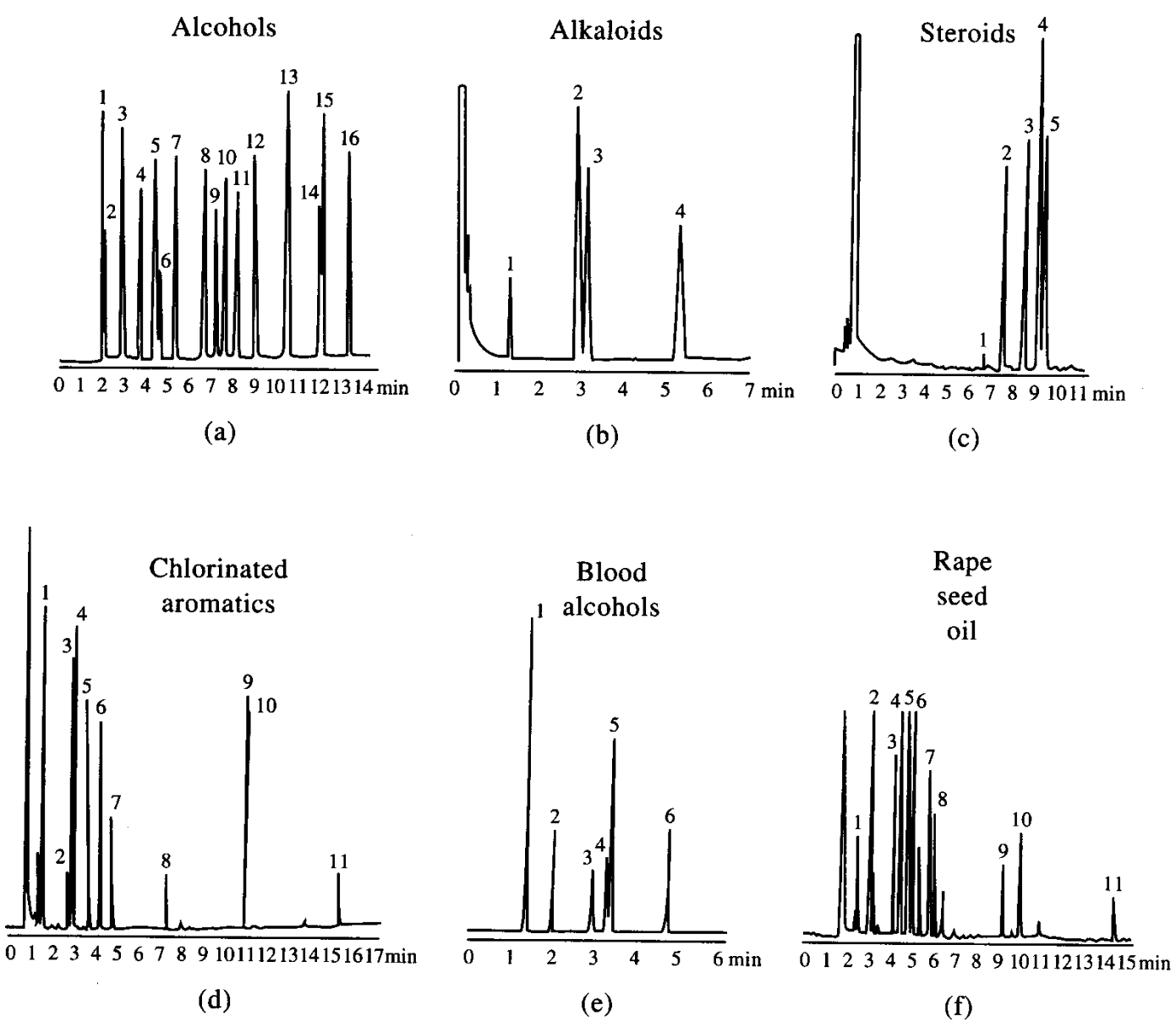


Figure 27-11 Typical chromatograms from open tubular columns coated with (a) polydimethyl siloxane; (b) 5 (phenylmethyldimethyl) siloxane; (c) 50 (phenylmethyldimethyl) siloxane; (d) 50% poly(trifluoropropyl-dimethyl) siloxane; (e) polyethylene glycol; (f) 50% poly(cyanopropyl-dimethyl) siloxane. *(Courtesy of J & W Scientific.)*